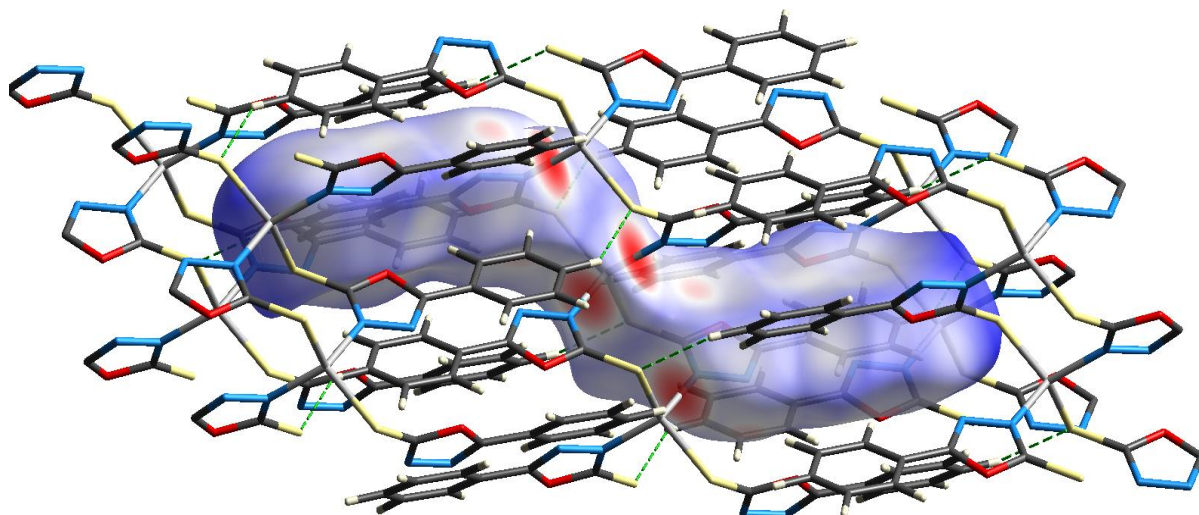**O'ZBEKISTON RESPUBLIKASI**
OLIY TA'LIM, FAN VA INNOVATSIYALAR VAZIRLIGI
TOSHKENT DAVLAT STOMATOLOGIYA INSTITUTI

M.A.PIRIMOVA

Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} VA VO_2^{+} METALLARNING 1,3,4-OKSADIAZOL HOSILALARI BILAN GOMO- VA GETEROMETALLI KOMPLEKS BIRIKMALARI SINTEZI VA TADQIQOTI

MONOGRAFIYA

TOSHKENT – 2025 y

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Monografiyada Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} va VO_2^+ metallarning 1,3,4-oksadiazol hosilalari bilan gomo- va geterometalli kompleks birikmalarini sintezi va tuzilishini o'rganishga oid bo'lgan tajriba va laboratoriya tadqiqotlari natijalari keltirilgan. Geterometalli kompleks birikmalarning biologik ta'sir doirasi gomometalli kompleks birikmalarnikiga qaraganda bir qator faolliklarga ega: dissotsiyalanish darajasi yuqori, yuqori antioksidantlik faollikga ega, dissotsiyalanganda donor markazlarining ko'p bo'lishi sababli turli biokimyoviy jarayonlarda ishtirok etadi, korroziya jarayonida anaerob bakteriyalarning devoriga elektrofil ta'sir etib korroziyalanish jarayonini oldini oladini olishi yoritib berilgan.

Monografiya materiallari bakalavrlar, magistrlar, ilmiy-tadqiqot institutlari ilmiy xodimlari va universitet o'qituvchilari uchun foydali bo'lishi mumkin.

MUNDARIJA

KIRISH

Ushbu monografiyada Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} tuzlarining VO_2^+ hamda 1,3,4-oksadiazol hosilalari bilan gomo- va geterometalli kompleks birikmalarini sintez qilish, komplekslar sintezida qo'llanilgan geterohalqali ligandlarning elektron tuzilishi, energetik va geometrik parametrlari hamda reaksion qobiliyatini zamonaviy kvant-kimyoviy usullar yordamida hisoblash, olingan koordinatsion birikmalarning tarkibi, tuzilishi va xossalarini zamonaviy fizik-kimyoviy usullar yordamida tahlil qilish; gomo- va geterometalli kompleks birikmalar tarkibi, tuzilishi va xossalari orasidagi bog'liqlikni aniqlash; yangi sintez qilingan moddalarning korroziyaga qarshi ingibitorlik va *in vitro* sharoitida antioksidantlik faolliklarini baholash kabi vazifalar amalga oshirilgan.

Tadqiqotlarimizda birinchi marta Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ionlarining VO_2^+ va 1,3,4-oksadiazol hosilalari asosidagi gomo- va geterometalli kompleks birikmalarini sintez qilishning optimal sharoitlari ishlab chiqilgan bo'lib, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ionlarining VO_2^+ va 1,3,4-oksadiazol hosilalari (L^{1-3}) bilan jami 39 ta gomo- va geterometalli yangi kompleks birikmalari sintez qilingan. Ligandlarning tuzilishi kvant-kimyoviy usullar yordamida $L^{1,2}$ bidentat ligandlar ekanligi va komplekslarda tiol guruhining S atomi va oksadiazol halqasining N3 atomi orqali, L^3 ligandi esa karboksil guruhidagi O atomlari orqali metall ionlariga bidentat koordinasiyalanish ehtimolligi aniqlangan. $[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O$ kompleksning kristall tuzilishi ilk bor X-Ray ga asoslangan monokristall rentgen strukturaviy tahlil usuli yordamida aniqlangan.

Monografiyada rentgenstrukturaviy analiz usuli yordamida $[Zn(L^2)_2]_n$ kompleksning fazoviy tuzilishi, geometriyasi, ichki va molekulalararo vodorod bog'larning ta'siri natijasida, polimer tuzilishli kompleksning [Zn-S-C-N-Zn-S-C-N] sakkiz a'zoli "kreslo" hosil qilishi va kompleksning geometriyasi siqilgan tetraedrik shaklda ekanligi isbotlangan. $[Zn(L^2)_2]_n$ tarkibli kompleks birikmaning fazoviy tuzilishi va barcha kristallografik kattaliklari aniqlanib, Cambridge Crystallographic Data Center xalqaro ma'lumotlar bazasiga joylashtirilgan.

Ligandlarning termik barqarorligi **L³**-(2-karboksimetiltio-5-fenil-1,3,4-oksadiazol), **L²**-(5-fenil-1,3,4-oksadiazol-2(3H)-tion/tiol), **L¹**-(5-(4-piridil)-1,3,4-oksadiazol-2(3H)-tion/tiol) qatori bo'yicha ortishi hamda gomometalli kompleks birikmalarning termik barqarorligi geterometalli kompleks birikmalarnikidan yuqoriligi aniqlangan. Ligandlar va sintez qilingan kompleks birikmalarning termogrammalaridagi endo- va ekzoeffektlarning hosil bo'lish sabablari aniqlanib, termik destruksiya mahsulotlari identifikasiyalandi. Gomometalli kompleks birikmaning termik barqarorligi geterometalli kompleks birikmanikidan yuqoriligi aniqlandi va bu holat geterometalli komplekslarda d-orbitallarning qoplanishi natijasidagi HOMO-LUMO=Δ ayirmasining farqi gomometalli komplekslardagiga nisbatan kichik bo'lishi bilan izohlandi.

Gomo- va geterometalli kompleks birikmalarning barqarorligi taqqoslanganda gomometalli kompleks birikmalarning barqarorligi nisbatan yuqoriligi aniqlandi, bu geterometalli kompleks birikmalarning quyi gidratlanish energiyasiga ega bo'lishi hamda geterometalli kompleksning markaziy qismida zaryadlangan $[V_4O_{12}]^{4-}$ siklning mavjudligi bilan izohlandi. kompleks tarkibida $[V_4O_{12}]^{4-}$ ning mavjudligi Gibbs energiyasining kamayishiga olib keladi, bu esa erituvchida kompleksning gidratlanishini oshishi hisobiga bo'lishi ko'rsatildi

Monografiyada 1,3,4-oksadiazol hosilalari (L^{1-3}) hamda ular asosida sintez qilingan kompleks birikmalarning antioksidantlik faolligi *in vitro* usulida fitokimyoviy tekshiruv orqali baholangan bo'lib, L^1 asosida yangi sintez qilingan $[Cu_2V_4O_{12}(L^1)_4]\cdot2H_2O$, $[Zn_2V_4O_{12}(L^1)_4]\cdot2H_2O$, $[V_4O_{12}](L^1+H^+)_4$ komplekslarning antioksidantlik faolligi boshqalarga nisbatan yuqori ekanligi o'rganilgan. Gomo- va geterometalli kompleks birikmalarning antioksidantlik faolligi o'zaro solishtirilganda, geterometalli kompleks birikmalarning faolligi yuqoriligi kuzatildi. Bu geterometalli kompleks birikmalar tarkibidagi elektronodonor vazifasini bajarishi mumkin bo'lgan metall atomlarining ko'pligi orqali izohlangan.

L^3 asosidagi $[Cu(L^3)_2(H_2O)_2]$, $[Zn(L^3)_2(H_2O)_2]$ larning anaerob bakterial biokorroziyaga qarshi ingibitorlik xossasi o'rganildi, kompleks birikma

tarkibidagi -N=C-O- guruhi bakteriya hujayrasining nukleofil markazi bilan ta'sirlashib xujayra devorini yemirishi sababli, litotrof bakteriyalardan korrozion himoya ta'siri 76-80% samaraga ega bo'lgan biokorroziya ingibitori ekanligi aniqlangan.

I BOB. 1,3,4-OKSADIAZOL HOSILALARI VA ULAR ASOSIDAGI KOMPLEKS BIRIKMALARNING OLINISHI, XOSSALARI

1.1-§. Oksadiazol hosilalarining sintezi, tuzilishi, fizik-kimyoviy va biologik xossalari

Besh a'zoli geterotsikllardan oksadiazolning tuzilishini ko'rib chiqamiz. Oksadiazollar tarkibidagi kislorod va azot atomlarining o'zaro joylashishiga qarab quyidagi oksadiazollar mavjud:
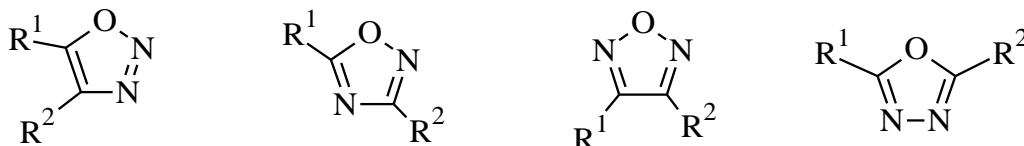
1,2,3-oksadiazol   1,2,4-oksadiazol   1,2,5-oksadiazol   1,3,4-oksadiazol

Xamma bu birikmalar (yoki uning hosilalari) laboratoriyada sintez qilingan hamda oksadiazol halqasi tutuvchi tabiiy birikmalar ma'lum emas. Diazol halqasiga kislorod atomining kiritilishi uning nukleofilligini kamaytiradi. Boshqa tomondan, oksobirikmalarga elektrofil reagentlar hujum qilganda siklni barqarorlashtiradi. Bunday sharoitlarda halqadagi o'rinbosarlar muhim rol o'ynaydi [1-3].

Ishda ligand sifatida 1,3,4-oksadiazol hosilalari tanlab olinganligi sababli, adabiyotlardan 1,3,4-oksadiazol hosilalarining olinishi, xossalari va ishlatilishi haqidagi ma'lumotlar tahlil qilindi.

1,3,4-Oksadiazol hosilalari biologik ta'siri ko'p qirrali bo'lganligi sababli muhim ahamiyatga ega. Xususan 1,3,4-oksadiazol halqasini o'z ichiga olgan birikmalar o'ziga xos shish va yallig'lanishga qarshi xususiyatlarga ega [1, 4, 5]. Shuningdek turli xil radikal almashingan oksadiazol hosilalari boshqa qiziqarli ta'sirga ega ekanligi aniqlandi, masalan, analgetik [4, 5], antimikrob [6, 7], silga qarshi [8, 9], tutqanoqqa qarshi [10- 13], OITS ga qarshi faollik [14], 1,3,4-

oksadiazollar yurak-qon tomir kasalligini davolovchi dorilar [15, 16], pestitsidlar, insektitsidlar [17], pufak fibrozini va prostata saratonini davolovchi [18-20] va boshqa faolliklari mavjud.
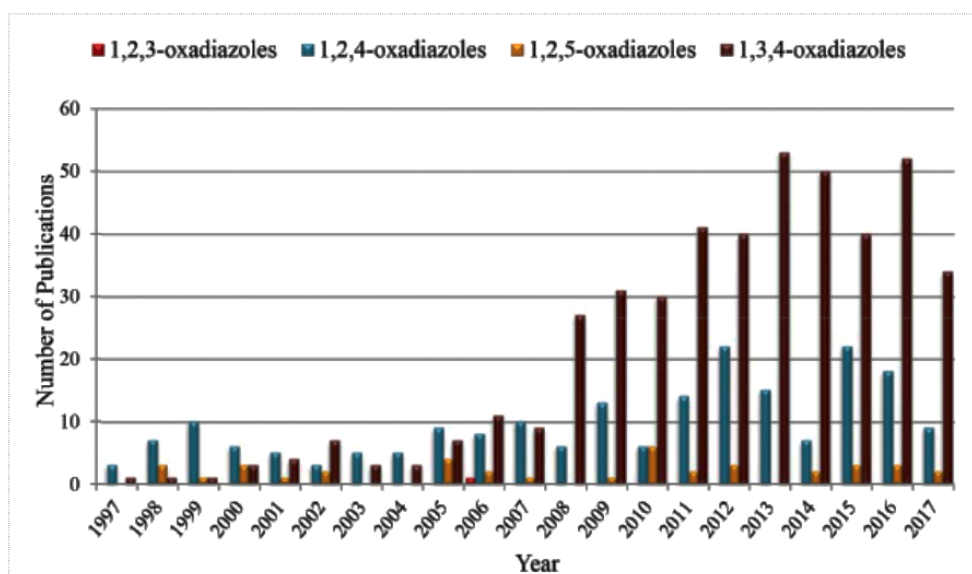
1-Rasm. 1997-2017 yillar oralig'ida oksadiazol hosilalari bo'yicha nashrlar

Diagramma ma'lumotlaridan (1-rasm) ko'rinib turibdiki, 1,3,4-oksadiazollarning hosilalari olimlar tomonidan eng istiqbolli yo'nalishlardan deb hisoblanadi.

1,3,4-Oksadiazol hosilalarini sintez qilishning umumiy tartiblari

1,3,4-Oksadiazollarni olishning eng qulay usuli [8, 9, 21, 22, 23] adabiyotlarda keltirilgan bo'lib, unda sintez uchun degidratlovchi qo'shimchalar ishtirokida gidrazin hosilalaridan suv, spirt, vodorod sulfid va boshqalarni ajratib olgan holda sikllash yo'li bilan olingan. Diatsillangan gidrazinni $POCl_3$, yoki $SOCl_2$, yoki H_2SO_4 bilan kuchli qizdirish natijasida 1,3,4-oksadiazol halqasi hosil bo'lgan (1-reaksiya).

$$RCONHNHCOR' \xrightarrow[- H_2O]{POCl_3, SOCl_2, H_2SO_4}$$
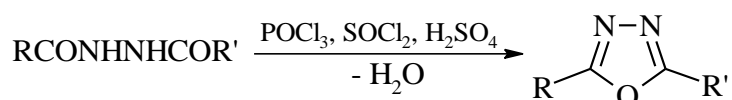
1-Reaksiya. Diatsillangan gidrazindan 1,3,4-oksadiazol olinishi

[10] Adabiyotda ultrabinafsha spektr natijalari oksadiazollarda benzolning aromatik tizimidagi o'xshash π bog'lanish tizimi borligini ko'rsatgan. 1,3,4-Oksadiazol halqasidagi uglerod atomi uchun kislotali muhitda protonlanishi va

halqaning ochilishi ma'lum bo'lmaganligi sababli, elektrofil almashinish reaksiyasiga kirishmasligi o'rganilgan. 2-Aril-1,3,4-oksadiazollari karbon kislota gidrazidlariga mo'l miqdordagi trietilortoformiat ta'sir ettirish yo'li bilan olingan (1-sxema).

$$RCONHNH_2 \xrightarrow{CH(OC_2H_5)_3} RCONHN=CHOC_2H_5 \xrightarrow{T^0} \underset{R \quad O \quad H}{\overset{N-N}{\bigcirc}}$$
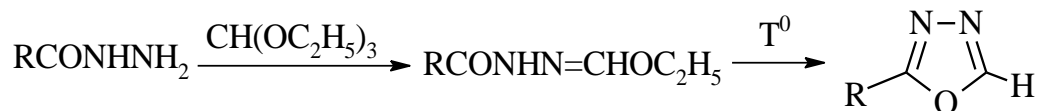
1-Sxema. 2-Aril-1,3,4-oksadiazollarni olinishi

[13, 14, 24] Ishda mualliflar 2-amino-1,3,4-oksadiazolni, tiosemikarboziddan PbO katalizatori ishtirokida vodorod sulfidni ajratib olish orqali sintez qilingan. Ushbu jarayonda 2-amino-1,3,4-oksadiazol bilan bir qatorda 3-merkapto-1,2,4-triazolning sezilarli miqdori hosil bo'lgan (2-reaksiya).

$$HCONHNHCSNH_2 \xrightarrow{PbO} \underset{H_2N \quad O}{\overset{N-N}{\bigcirc}}$$

2-Reaksiya. 2-Amino-1,3,4-oksadiazolni olinishi

2-Amino-1,3,4-oksadiazol sintez qilingan bo'lsada, uning nomlanishi haqida adabiyotlarda 1929 yilga kelib Shtoll va Ferenbax tomonidan ma'lumot berilgan. 1916 yilda Boygolt bazi α-ketokislotalarni semikarbazonlarini yod bilan oksidlab,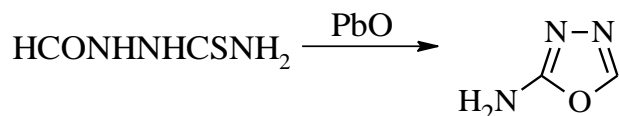 atsilsemikarbozid sintez qilish jarayonida o'zi bilmagan holda 2-amino-1,3,4-oksadiazol sintez qilgan. U keyingi ishlarida Papov bilan davom ettirib, ushbu birikma tuzilishini gidroksitriazol tuzilishidek deb taklif etishgan. Girard, Boygolt va Papovning "gidroksitriazol" reaksiyasini ishqoriy muhitda olib borib, u sintez qilingan moddani 5-almashingan-3-gidroksi-1,2,4-triazol deb aniqlagan. Shu bilan birga u Boygolt reaksiyasida triazol hosilasi hosil bo'lganligini va ularning tautomerlanish reaksiyalariga o'xshashligini takidlagan. Va nihoyat, 1929 yilda Stolle va Ferenbax 2-amino-1,3,4-oksadiazol to'g'risida ma'lumot berishgan, bunda ular 5-almashingan oksadiazollar xaqida ham ma'lumot bergan. Shu bilan birga, 2-amino-1,3,4-oksadiazolning 5-almashingan holatdagi hosilalarining 1-atsiltiosemikarbazidlarning sikllanishi nitijasida olinishi keyinchalik Xoggort tomonidan bayon etilgan [13, 14, 25].

Simmetrik va nosimmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi

Simmetrik 2,5-diaril-1,3,4-oksadiazollar [26, 27] adabiyotdagi usullarda 2-sxema bo'yicha olinadi.
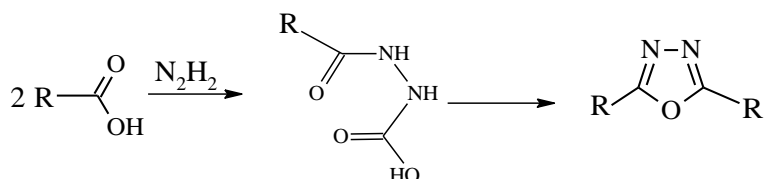
2-Sxema. 2,5-Diaril-1,3,4-oksadiazollarning olinishi. Bu yerda R=aril.

[28] Mualliflar tomonidan dibenzilgidrazinning 250-300°C da siklodegidrogenlanishi natijasida 2,5-difenil-1,3,4-oksadiazol olingan (3-sxema).
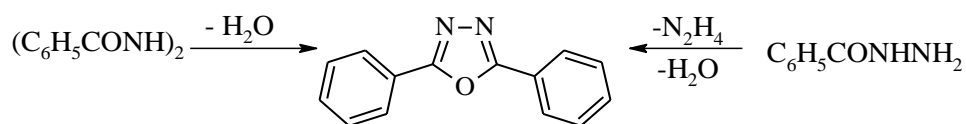
3-Sxema. 2,5-Difenil-1,3,4-oksadiazolning olinishi

1,3,4-Oksadiazol halqasining hosil bo'lishida quyidagi: xlorsulfon kislotasi, oltingugurt xloridi, fosfor pentaoksidi, n-toluolsulfokislota, uning kislota xloridi, tionilxlorid, fosfor oksixloridi, rux xloridi, kislota angidridlari, fosfor pentaxloridi, sulfat kislota kabi gigroskopik vositalar yordam bergan [29-32].
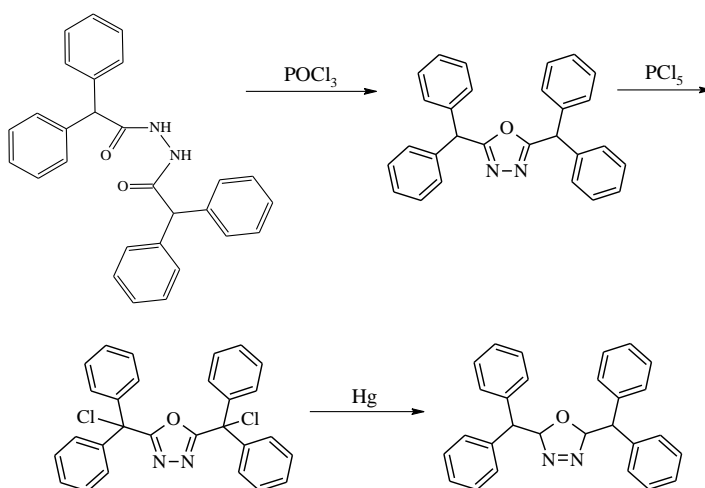
4-Sxema. 2,5-Dibenzgidril-1,3,4-oksadiazol, uning hosilalari olinishi

2,5-Dibenzgidril-1,3,4-oksadiazol va uning hosilalari [16] adabiyotdagi 4-sxema bo'yicha olinadi.

2,5-Diaril-1,3,4-oksadiazol hosilalarini [33] adabiyotdagi metodika bo'yicha, 5-sxemaga muvofiq ham sintez qilish reaksiya unumining yuqoriligi bilan muhim hisoblanadi.
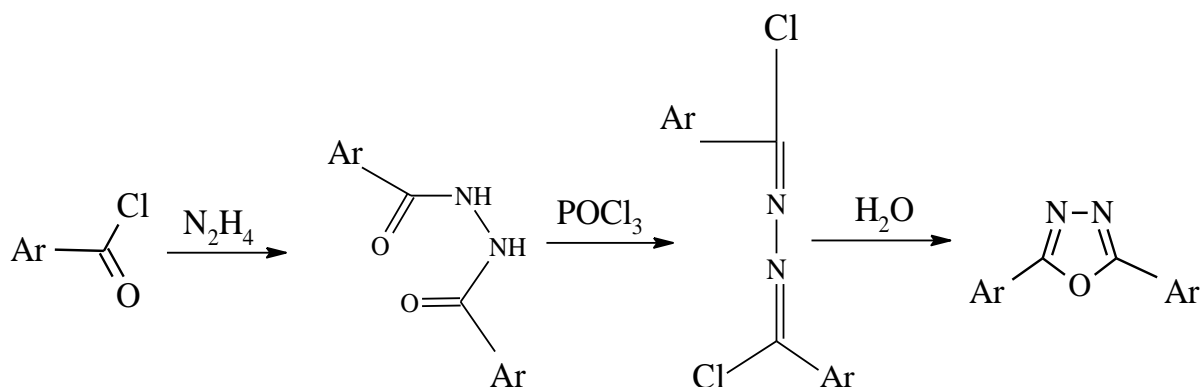
5-Sxema. 2,5-Diaril-1,3,4-oksadiazollarning olinishi

Simmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi [10, 34] mualliflar tomonidan keng o'rganilgan bo'lib, bunda tegishli diarilgidrazinlarning 180-350°C da to'g'ridan-to'g'ri qizdirish yoki ularga fosfor angidrid, tionilxlorid yoki oksalat kislota xloridi ta'siri ostida olingan. Oksadiazol halqasi gidrazidning xlorlovchi vositalar bilan kumush nitrat ishtirokidagi reaksiyasi natijasida sikllangan. 2,5-Diaril-1,3,4-oksadiazollar quyidagi reaksiya tenglamaga muvofiq mono- yoki triatsilgidrazinlarni qizdirish orqali hosil bo'lgan (3-reaksiya).
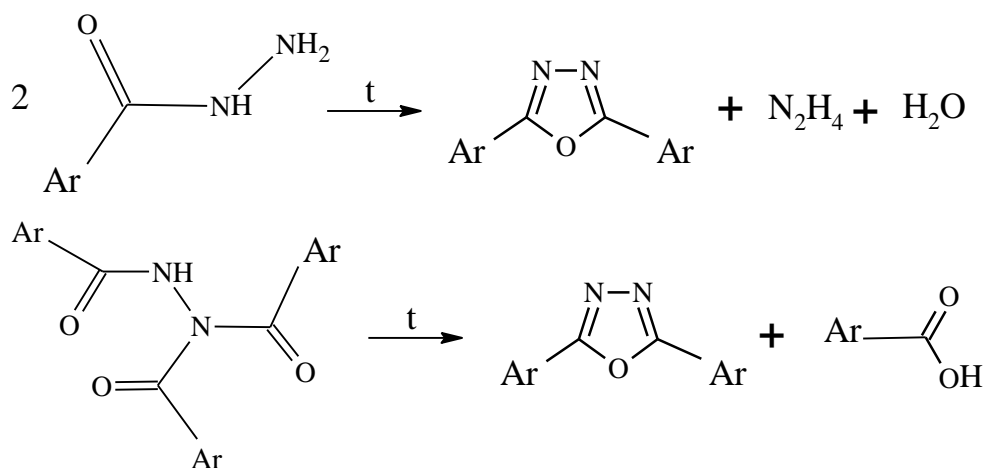
3-Reaksiya. Simmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi

1,2-Diarilgidrazinlarning kumush yoki simob tuzlariga yod ta'sir ettirilganda va diarilgidrazinlarning kumush tuzlari qizdirilganda 2,5-diaril-1,3,4-oksadiazol olingan (6-sxema) [10].
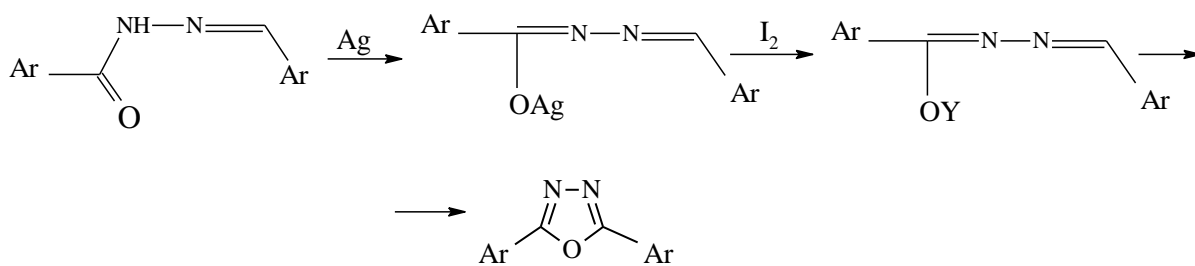
6-Sxema. 2,5-Diaril-1,3,4-oksadiazolni olinishi

Shuningdek, [33] adabiyotda gidrozonlar uglerod tetraxloridida xlorlanganda va ishqoriy muhitda yoki izoamil nitrit bilan kaliy ferrotsianidning suyultirilgan eritmasi bilan qaynatilganda ham 2,5-diaril-1,3,4-oksadiazollar olingan. Gidrazonlarning kumush tuzlariga kislota xlorangidridlarini ta'sir ettirish natijasida oksadiazollarning quyidagi turlari hosil bo'lganligini kurishimiz mumkin.

2,5-Diaril-1,3,4-oksadiazol hosilalari

1,3,4-Oksadiazolning aril hosilalarini olish usullari [33] adabiyotda keltirilgan bo'lib, unda karbon kislota monoatsilgidrazinning 80-160°C da imidoefirgidroxloridlari bilan o'zaro ta'siridan yoki olingan mahsulotni nitrat kislota ishtirokida qayta ishlab 7-sxema bo'yicha olingan.
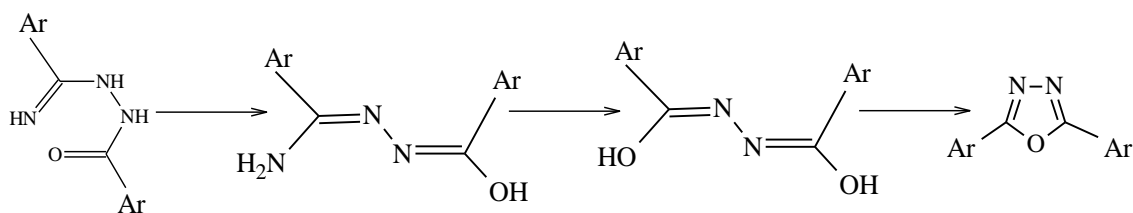
7-Sxema. 1,3,4-Oksadiazolning aril hosilalarini olinishi

[16] Adabiyotda 2,5-diaril-1,3,4-oksadiazollar ham 1,3.4-oksadiazolon-5 hosilalarini 280°C da parchalab olingan (4-reaksiya).
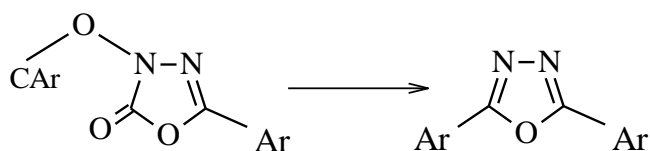
4-Reaksiya. Simmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi

Bunday birikmalarni olish uchun odatda [26] adabiyotdagi keltirilgan sxema qo'llaniladi (8-sxema).
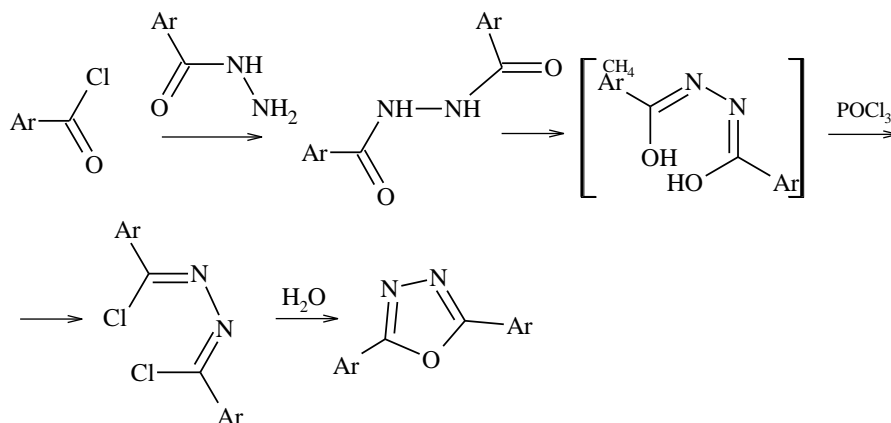
8-Sxema. 2,5-diaril-1,3,4-oksadiazollarning olinishi

8-Sxema yordamida 1,3,4-oksadiazollarning aralash aril hosilalari sintez qilingan, shuningdek, 2,5-difenil-1,3,4-oksadiazolning mono- va bifunksional hosilalarini olish uchun foydalanish mumkinligi o'rganilgan.

Simmetrik 2,5-diaril-1,3,4-oksadiazollar [32, 34] adabiyotda keltirilgan usulda ya'ni, karbon kislotalarni xlorangid-ridlarini 5-almashingan tetrazollar bilan piridin ishtirokida qizdirilganda yuqori unum bilan hosil bo'lgan. Ushbu reaksiyaning sxemasi quyidagicha taklif etilgan (9-sxema).
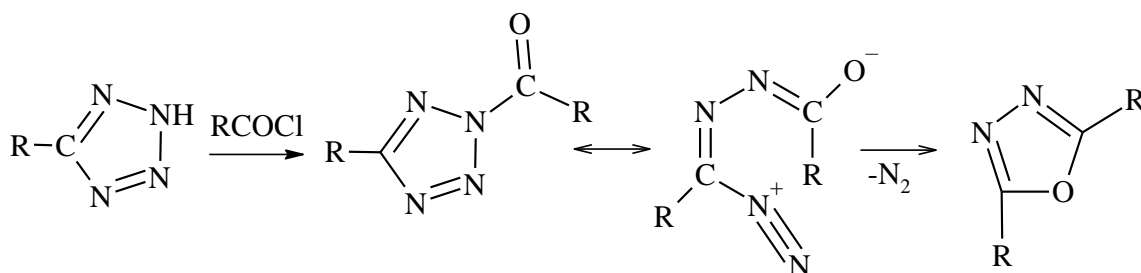
9-Sxema. Simmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi

2,5-Almashingan-1,3,4-oksadiazollarga issiq suv yoki kumush nitrat eritmasi ta'sirida oraliq mahsulot sifatida diatsilgidrazidlar, bis-α-xlorbenzilidengidrazinlar hosil bo'lgan. Shunga o'xshash siklning yopilishi bis-

α-aminobenzilidengidrazinlarga nitrat kislota, kumush nitrat ta'sir ettirilganda simmetrik tuzilishli 2,5-diaril- 1,3,4-oksadiazollarni olish mumkin (5-reaksiya) [35- 37].

$$(n\text{-}BrC_6H_4C(Cl){=}N)_2 \xrightarrow{AgNO_3}$$

PhBr — (oksadiazol halqasi) — PhBr

$$(C_6H_5C(NH_2){=}N)_2 \xrightarrow{HNO_3}$$

H_5C_6 — (oksadiazol halqasi) — C_6H_5

$$C_6H_5C({=}NH)NHNHCOC_6H_5 \xrightarrow{HNO_2}$$

H_5C_6 — (oksadiazol halqasi) — C_6H_5
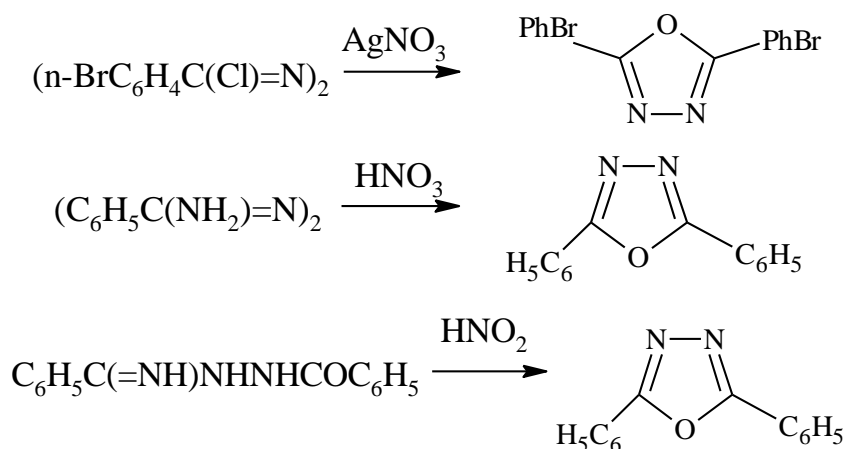
5-Reaksiya. Simmetrik 2,5-diaril-1,3,4-oksadiazollarning olinishi

Kaliy ferritsianid yoki izoamilnitritning ishqoriy eritmalari benzoilgidrazon benzaldegidni 2,5-difenil-1,3,4-oksadiazolga aylantiradi. Ushbu reaksiyada, dastlabki oksidlanish yoki galogenlanish jarayonlari azotga qaraganda uglerod atomida yuqoriroq boradi (6-reaksiya) [37].

$$C_6H_5CH{=}NNHCOC_6H_5 \longrightarrow$$

H_5C_6 — (oksadiazol halqasi) — C_6H_5
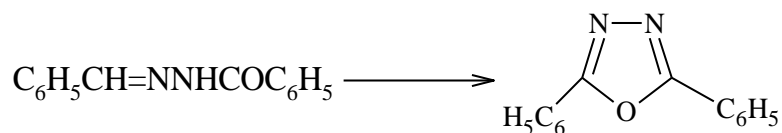
6-Reaksiya. 2,5-Difenil-1,3,4-oksadiazolning olinishi

[37] Adabiyotda benzoilgidrazon benzaldegidning kumushli tuzini atsetil xlorid yoki benzol bilan inert erituvchida qayta ishlash natijasida, quyidagi reaksiya tenglamaga muvofiq 2,5-difenil-4-gidro-3-atsil-1,3,4-oksadiazol hosil bo'ladi (7-reaksiya).

$$Ph\text{-}CN{=}NNHCO\text{-}Ph \xrightarrow{RCOCl}$$

COR — (oksadiazol halqasi) — Ph, Ph
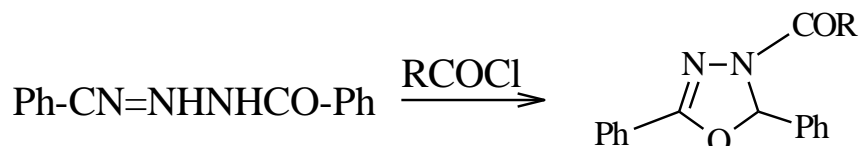
7-Reaksiya. 2,5-Difenil-4-gidro-3-atsil-1,3,4-oksadiazolning olinishi

Yana bir qiziqarli sintez usuli [38, 39] adabiyotda keltirilgan bo'lib, bunda fosfor angidrid, brom, kislorod bilan difenilsirka kislota benzoilgidrazidini qizdirish orqali 5-benzgidril-2-fenil-1,3,4-oksadiazol hosilalarini olinishini ko'rishimiz mumkin (10-sxema).
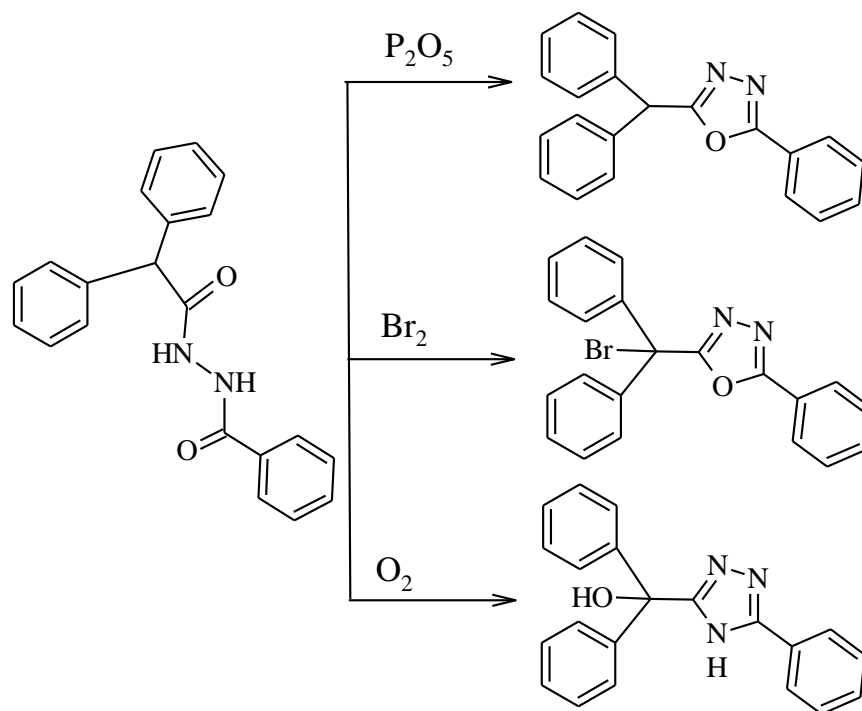
10-Sxema. Oksadiazol hosilalarining olinishi

2-Alkil-5-aril-1,3,4-oksadiazol hosilalarining olinishi

[23, 39-41] Mualliflarning olib borgan tadqiqotlar o'rganilganda, umumiy holatda 2-alkil-5-aril-1,3,4-oksadiazollar quyidagi 11-sxema bo'yicha olingan.
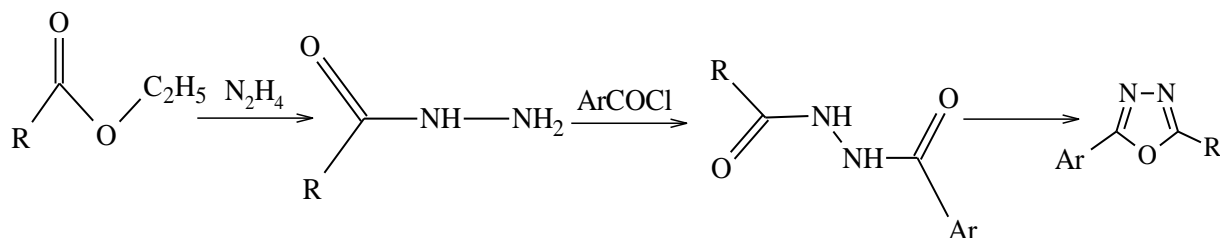
11-Sxema. 2-Alkil-5-aril-1,3,4-oksadiazolning olinishi.

Yuqoridagi 11-sxemadan foydalanish funksional guruhlarning ishlatiladigan reagentlar bilan o'zaro ta'siri natijasida murakkablashishi mumkin. Ushbu hodisani oldini olish uchun [41] mualliflar tomonidan quyidagi sxema ishlab chiqilgan (12-sxema).
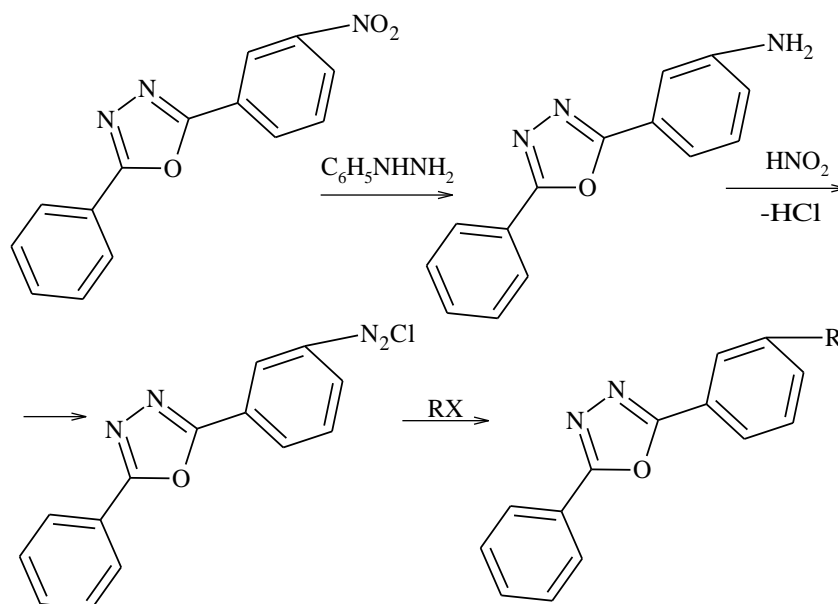
12-Sxema. Oksadiazollarning olinishi

Alifatik gidrazidlarning benzoillanish kinetikasi [42] adabiyotda keltirilgan bo'lib, bunda suyultirilgan eritmalar, xona xaroratida 1,2-diatsilgidrazinning olinishi o'rganilgan. 2-Alkil-5-aril-1,3,4-oksadiazolning hosilalari 2-aril-1,3,4-oksadiazollarning sinteziga o'xshash sharoitlarda gidrazidlarni kislota ortoefirlari bilan reaksiyasi natijasida olingan (13-sxema).
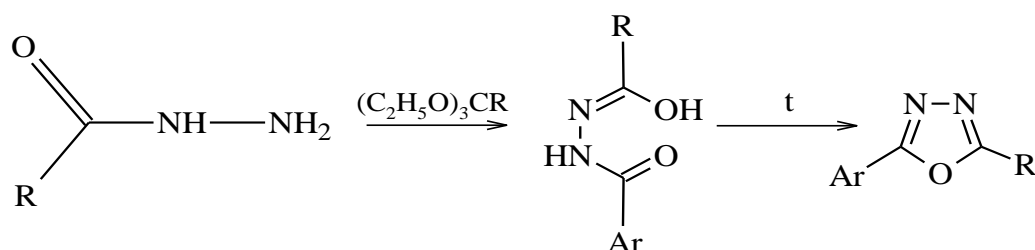
13-Sxema. 2-Alkil-5-aril-1,3,4-oksadiazolning hosilalarining olinishi

2-Alkil-5-aril-1,3,4-oksadiazollarni yuqori ortoefirlardan quyidagi reaksiya tenglamaga muvofiq olish mumkin, bunda ularga tegishli bo'lgan 2-alkil-5-aril-1,3,4-oksadiazollar olinadi (8-reaksiya) [26].

$$C_6H_5CONHNH_2 \quad + \quad RC(OC_2H_5)_3 \quad \longrightarrow \qquad + \quad C_2H_5OH$$

R=H, SN$_3$, S$_2$N$_5$
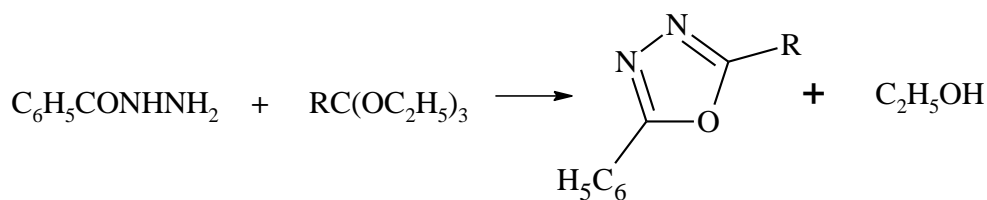
8-Reaksiya. 2-Alkil-5-aril-1,3,4-oksadiazolning olinishi

17

2,5-Almashingan 1,3,4-oksadiazol hosilasining olinishi

2,5-Almashingan 1,3,4-oksadiazol hosilalarini olinish usullarini tahlil qilar ekanmiz, adabiyotlarda 2-amino-1,3,4-oksadiazol hosilalarining olinishi va biologik faolligining yuqoriligi haqida ko'pgina ma'lumotlar keltirilgan.

2-Amino-1,3,4-oksadiazol va uning hosilalari [43, 44] adabiyotdagi quyidagi 14-sxema bo'yicha qo'rg'oshin oksidi yordamida tiosemikarbozidlardan vodorod sulfidni ajratish orqali olingan.
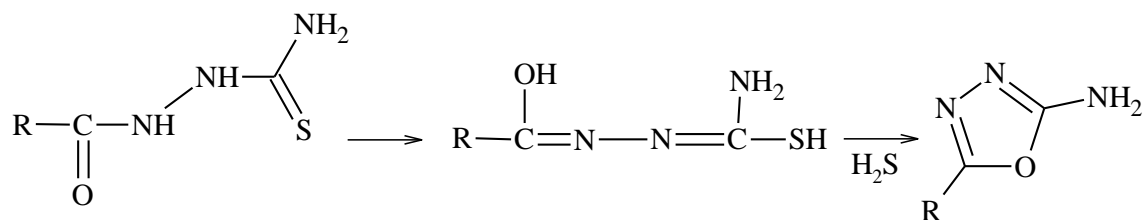
14-Sxema. 2-Amino-1,3,4-oksadiazol hosilalarining olinishi

2-Amino-1,3,4-oksadiazol hosilalarining olinishda sintez tiosemikarbazidning 95% li spirtdagi eritmasi va mo'l miqdordagi qo'rg'oshin oksid ishtirokida uzoq vaqt qizdirish natijasida yuqori unum bilan hosil bo'lishi o'rganilgan [44].

Yuqorida keltirilgan sintez usullaridan tashqari, 2-amino-5-fenil-1,3,4-oksadiazol [44] adabiyotda keltirilgan, quyidagi 15-sxema bo'yicha sintez qilinadi:
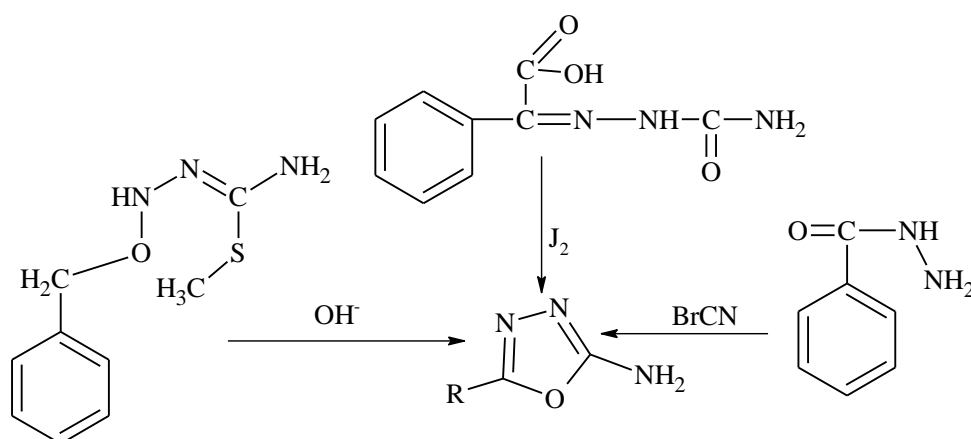
15-Sxema. 2-Amino-5-fenil-1,3,4-oksadiazolning olinishi

Tiosemikarbazid hosilalarini qizdirish yoki gigroskopik moddalar ta'sir ettirib, quyidagi 2,5-almashingan 1,3,4-oksadiazol hosilalari olingan [45]:
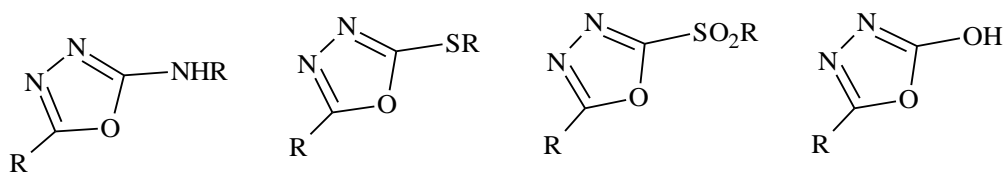
[45] Adabiyotda semikarbazon benzaldegidga 5%li natriy gipobromid eritmasi ta'sir ettirilganda 2-amino-5-fenil-1,3,4-oksadiazol hosil bo'lgan va uning boshqa bir qator hosilalari olingan.

Geterotsiklik kislota gidrazidi va bromsian ishtirokida 2-amino-1,3,4-oksadiazolning geterotsiklik hosilalari sintezi [46] adabiyotda o'rganilgan bo'lib, quyidagi reaksiyaga muvofiq sintez olib borilgan (9-reaksiya):
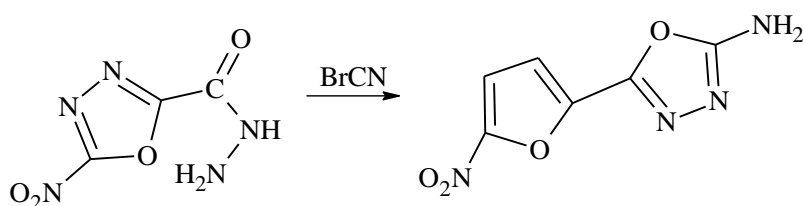
9-Reaksiya. 2-Amino-1,3,4-oksadiazolning geterotsiklik hosilasi sintezi

[46, 47] Ishning mualliflari taklif etgan usul bilan bir qator 1,3,4-oksadiazol hosilalari sintez qilingan. Ushbu usulda geterotsiklik kislota xlorangidridlarini tiosemikarbozid bilan sikllanishi natijasida tegishli oksadiazol hosil bo'lgan.

Semikarbozonga gipoiodit benzaldegid yoki natriy gipobromitning ta'siri natijasida 2-amino-5-fenil-1,3,4-oksadiazol hosil bo'lgan [43]. Ushbu reaksiyada, dastlabki oksidlanish yoki galogenlanish jarayonlari azotga qaraganda uglerod atomida yuqoriroq boradi (10-reaksiya).
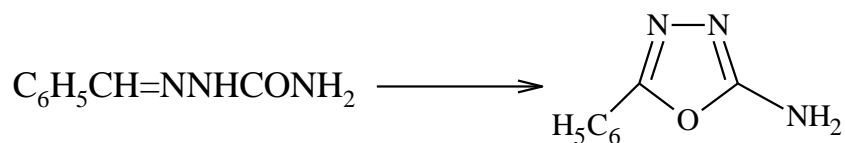
10-Reaksiya. 2-Amino-5-fenil-1,3,4-oksadiazolning olinishi

[43] Mualliflar qo'rg'oshin oksid yoki simob oksidi ishtirokida ba'zi atsiltiosemikarbozidlardan vodorod sulfid ajralib chiqib sikllanishi natijasida 1,3,4-oksadiazollarga aylanishini o'rganishgan. Shunga o'xshash sikllanish jarayoni kaliy ishqori ishtirokida ham kuzatiladi(11-reaksiya).

$$(C_2H_5)_2CHCONHNHCSNH_2 \xrightarrow{Pb_3O_4}$$

$$HCONHNHCSNH_2 \xrightarrow{PbO}$$

$$C_6H_5NHNHCONHNHCSNHC_6H_5 \xrightarrow{KOH\ (20\%)}$$
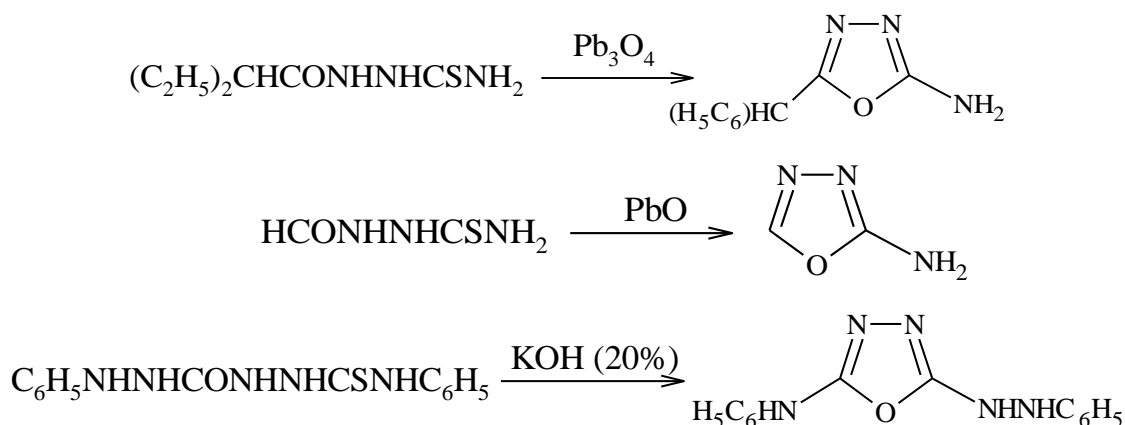
11-Reaksiya. 2,5-Almashingan 1,3,4-oksadiazol hosilalarining olinishi

1-Benzoiltiomochevinaning S-metilhosilasi piroliz paytida metilmerkaptanni yo'qotadi va 2-amino-5-fenil-1,3,4-oksadiazolga aylanadi. Ushbu jarayon yuqori unum bilan boradi (12-reaksiya) [10].

$$C_6H_5CONHNHC(NH)SHCH_3 \xrightarrow{CH_3SH}$$
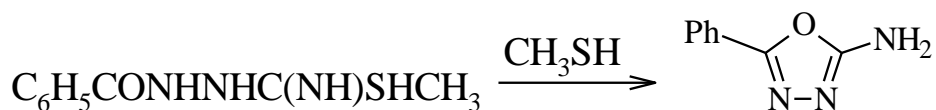
12-Reaksiya. 2-amino-5-fenil-1,3,4-oksadiazolning olinishi

2-Amino-1,3,4-oksadiazollar erituvchi tabiatiga qarab ikki tautomer shaklda reaksiyaga kirishishi mumkin [48]. A tuzilishning oksadiazollari ma'lum benziliden va ftalil hosilalarini tayyorlash bilan aniqlangan.

A   B
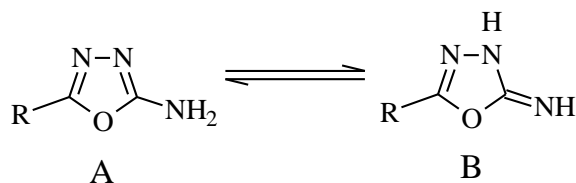
[49] Ishda mualliflar tomonidan 2-amino-1,3,4-oksadiazollarning termik xossalari o'rganilgan, ularning aksariyati kuchsiz qizdirish natijasida eriydi.

Yuqorida keltirilgan usullardan tashqari [50-61] adabiyotlardagi mualliflar tomonidan 2-amino-5-o'rin almashingan-1,3,4-oksadiazollarning olinishi umumiy holatda 16-sxemada keltirilgan. Bunda umumiy holatda 2-amino-5-o'rin almashingan-1,3,4-oksadiazollarni olishda dastlab yarimkarbozid/tiosemikarbozid va tegishli aldegidlarning kondensatsiyasi amalga oshiriladi, so'ngra S-O/C-S bog'ining I_2 ta'sirida oksidlash orqali sintez qilib olinadi.
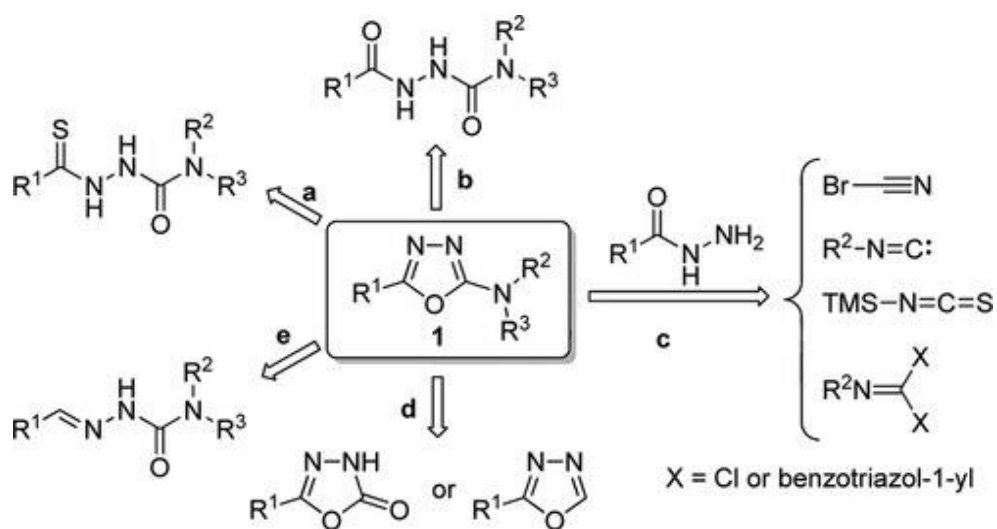
16-Sxema. 2-Amino-5-o'rin almashingan-1,3,4-oksadiazollarning olinishi.

1,3,4-Oksadiazollarning fizik-kimyoviy xossalari

1,3,4-Oksadiazol – suyuqlik, 150° C ga yaqin haroratda qaynaydi. 2,5-Almashingan-1,3,4-oksadiazol hosilalari – rangsiz moddalar. 2,5-Almashingan-1,3,4-oksadiazol nosimmetrik aromatik molekula, uning rezonans energiyasi 167,2 Kj/mol. Uning tarkibidagi bog'lar infraqizil spektroskopiya usulida o'rganilganda C=N bog'ining 1640-1650 sm^{-1} va C-O bog'ining 1020 sm^{-1} da yutilish chiziqlarini aniqlash mumkin. YaMR ma'lumotlariga ko'ra, kimyoviy ekvivalent protonlar $CDCl_3$ da, 8,73 ppm sohada o'zgarish beradi. 1,3,4-Oksadiazollarning eruvchanligi o'rganilganda, turli xil oksadiazol hosilalarining suvda eruvchanligi bir xil emasligi va ularning erish qobilyati o'rinbosarlar tabiatiga bog'liq. Masalan, 2,5-dimetil-1,3,4-oksadiazol har qanday nisbatda suv bilan aralashadi, 2,5-difenil-1,3,4-oksadiazolning suvdagi eruvchanligi atigi 0,03% ni tashkil etadi [62, 63].

1,3,4-Oksadiazolning asosiy fizik ko'rsatkichlari quyidagi 1-jadvalda keltirilgan.

1-Jadval

1,3,4-Oksadiazolning asosiy fizik ko'rsatkichlari

Xossa	Ko'rsatkichi
Molekulyar massa	70.051 g/mol
Molekulyar formula	$C_2H_2N_2O$

21

Zichligi	1.2 g/sm^3
Suyuqlanish harorati	-4.26 °C
Qaynash harorati	150 °C
25 °C bug' bosimi	5.0 mm s.u.
Hosil bo'lish entalpiyasi	31.1 kj/mol
Nur sindirish ko'rsatkichi	1.416

1,3,4-Oksadiazolning nosimmetrik hosilalari ko'p hollarda simmetrik hosilalariga qaraganda past haroratda qaynaydi va suyuqlanadi [64].

1,3,4-Oksadiazolning ba'zi hosilalarning lyuminessiya xossasi [65] mualliflar tomonidan o'rganilgan bo'lib, bunda kuchli elektronoakseptor guruh saqlamagan ba'zi 1,3,4-oksadiazol 2,5-hosilalari kristall holatida, qutbsiz yoki kam qutbli erituvchilarda va polistirolda lyuminessiyalanishi keltirilgan.

1,3,4-Oksadiazol hosilalarining biologik xossalari

Ma'lum bo'lgan birikmalar orasida 1,3,4-oksadiazollar biologik faolligi yuqoriligi bilan katta qiziqish uyg'otgan [7]. 1,3,4-Oksadiazollarning biologik faolligining turlicha bo'lishi ular tarkibidagi radikallarning o'zgartirilishi natijasida sodir bo'ladi.
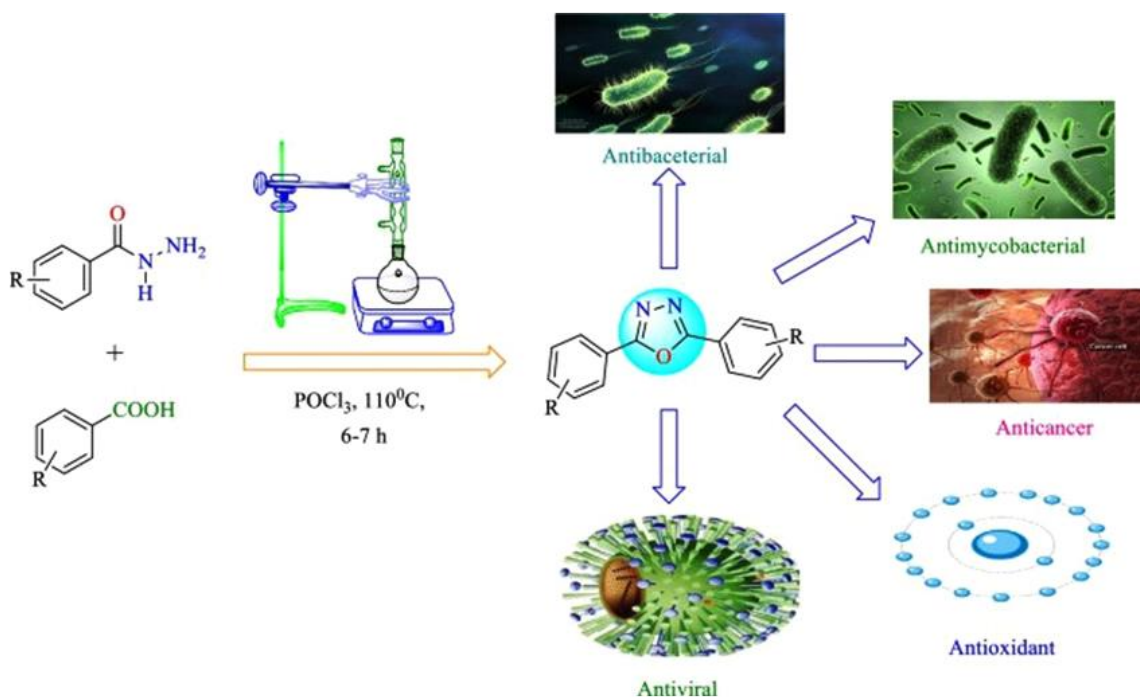
[66-76] Adabiyotlardagi mualliflar tomonidan oksadiazollar penitsillin guruhining vakillari sifatida logorifmik o'sish bosqichida bo'lgan mikroorganizmlarga bakteritsid ta'sir ko'rsatishi o'rganilgan. Bu ularning bakterial xujayra, xujayra devori tarkibiy qismlarining biosintezini ingibirlash qobilyatiga bog'liq bo'lib, ularning boshqarilishida ma'lum bir ferment transpeptidaza ishtirok etganligi, penitsillinlar fermentining peptid substratiga strukturaviy o'xshashligi tufayli antibiotik u bilan transpeptidazaning faol markazi bilan kurashishi o'rganilgan. Antibiotik molekulasini fermentning faol markazi bilan o'zaro ta'siri qaytmas reaksiya hisoblanadi. Azollarning bakterial xujayraga ta'siri xujayra devori tarkibiy qismlarining sinteziga bevosita ta'sir ko'rsatishi bilan bog'liq. 1,3,4-Oksadiazollarning boshqa hosilalari dori-darmonlarni tayyorlashda qo'llanilgan. Sulfoxloridlarning 1,3,4-oksadiazolning aminohosilasi bilan ta'sirlashib sulfamidli preparat sintez qilingan, u esa dori moddalarini olish uchun ishlatiladi (13-reaksiya):
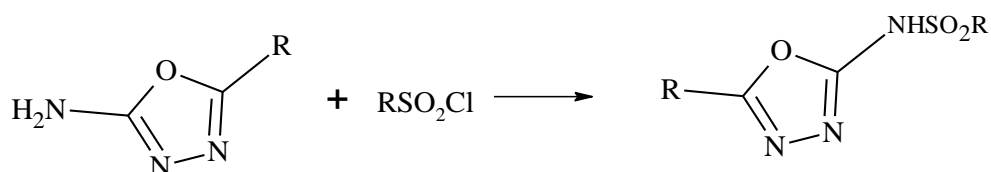
13-Reaksiya. 1,3,4-Oksadiazolning aminohosilasi sulfamidli preparat sintezi

Tibbiyot kimyosida oksadiazol hosilalarini o'z ichiga olgan molekulalar katta ahamiyatga ega. Quyida 1,3,4-oksadiazol hosilalarining biologik ta'siri, o'inbosarning o'zgarishiga qarab turlicha bo'lganligi uchun alohida ko'rib chiqamiz:

Tutqanoqqa qarshi faollik- 2-o'rin almashingan-5-(2-benziltiofenil)-1,3,4-oksadiazollar quyidagi hosilalari sintez qilingan va tutqanoqqa qarshi qarshi vosita sifatida qo'llanilgan. 1,3,4-oksadiazol halqasi va ftor o'rnini bosuvchi benzoilning para- holatiga aminoguruh kiritish orqali tutqanoqqa qarshi faolligini oshganligini ko'rish mumkin [77, 78].
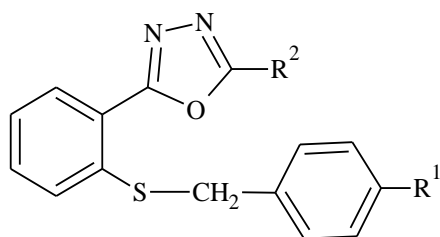
2-o'rin almashingan-5-(2 benziltiofenil)-1,3,4-oksadiazol hosila-lari R_1=H, F, Cl; R_2=NH$_2$, SH, SMe

Ataluren va zibotentan birikmalari mos ravishda pufak fibrozini va prostata saratonini davolash uchun klinik tadqiqotlarning so'nggi bosqichlari o'rganilmoqda [5, 7, 79, 80]. Shunisi etiborga loyiqki, raltegravir aralashmasi OITS infeksiyasini davolash uchun sotuvga chiqarilgan [81].

Fenitoin va tiosemikarbazid, 1,3,4-oksadiazol, 1,3,4-tiadiazol yoki 1,2,4-triazol o'rtasidagi gibridlar sintez qilindi va tutqanoqqa karshi faolligi sinovdan o'tkazildi. Dastlabki tutqanoqqa qarshi faollik standart sichqonlarda elektroshok (MES) va teri osti pentilenetetrazol (scPTZ) skrining yordamida amalga oshirildi, rotorodli sinov yordamida neytrototsiklik aniqlandi. Bular orasida 3-[(5-Sulfanil-1,3,4-oksadiazol-2-il)metil]-5,5-difenilimid-azolidin-2,4-dion birikma 100mg/kg dozada scPTZ testida eng yuqori ximoya (80%) ko'rsatgan [82].
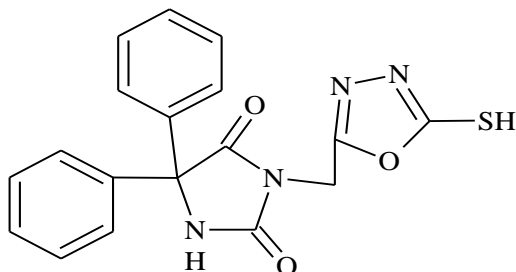
3 - [(5-Sulfanil-1,3,4-oksadiazol-2-il) metil] -5,5-difenilimid-azolidin-2,4-dion

[83-86] Adabiyotlarda yangi 1,3,4-oksadiazol ftalamid hosilalari (1-{5-[(1,3-diokso-1,3-digidro-2N-izoindol-2-il)amino]-1,3,4-oksadiazol-2-il}-3-(4-metoksifen-il)tio-mochevina) hamda 2- (xlorfenil) amino-5- (4-piridil) -1,3,4-oksadiazollar MES tekshiruvida faol va fenitoinga qaraganda kamroq neyrotoksikligi aniqlangan va shu sababli eng istiqbolli antikonvulsantga aylangan.
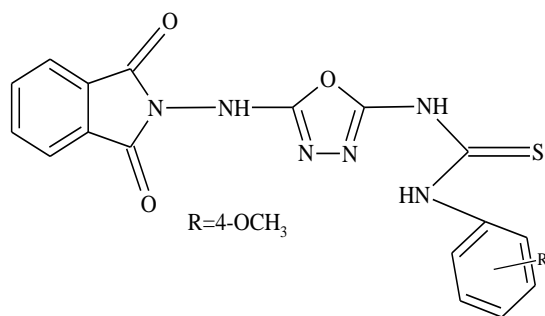
1-{5-[(1,3-diokso-1,3-digidro-2N-izoindol-2-il) amino]-1,3,4-oksadiazol-2-il}-3-(4-metoksifen-il) tiomochevina
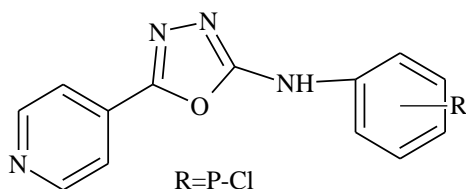
2- (xlorfenil) amino-5- (4-piridil) -1,3,4-oksadiazol

[6, 18, 87-90] Adabiyotlarda yangi sintez qilingan 1,3,4-oksadiazol hosilalarida mikroblarga qarshi faollik ega bo'lgan: 5-(1-/2-naftiloksimetil)-1,3,4-oksadiazol-2(3N)-tion, 2-amino-5-(1-/2-naftiloksimetil)-1,3,4-oksadiazol, 5-(naftiloksimetilning 1-/2-hosilalari) -1,3,4-oksadiazol 2(3H)-1- va/yoki 2-naftollar sintez qilingan. S.stafilokokk , E.koli , R.tayoqchalari , S.Albicans va S.parapsilozlarga qarshi faollikni (konsetratsiya 64–256 mkg/ml) namoyon qiladi.
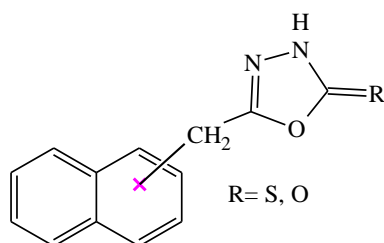
5-(1-/2-naftiloksimetil)- 1,3,4-oksadiazol hosilalari

[81, 91, 92] Adabiyotlarda yangi sintez qilingan birikmalar OITS ga qarshi faollik namoyon qilgan, CEM-SS hujayralari yoki yangi odamning periferik qon mononuklyar hujayralari yordamida OITS mikrotitrator tahlilidan foydalangan holda teskari transkriptaza ingibitori sifatida baholangan. Oksadiazol hosilalari orasida birikma eng yuqori OITS faollikni ko'rsatgan va IC_{50} qiymati 1,44 mkm ga teng.
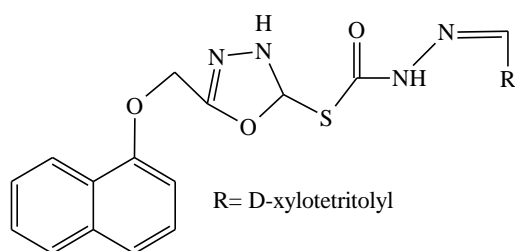
1,3,4-oksadiazolning gidrazid va imidrazon hosilalari

R= D-xylotetritolyl

1,3,4-Oksadiazolning 2-(5-(trifluorometil) piridiloksimetil)-5-aril hosilalari insektitsid faolligikni namoyon qilgan va sintez usuli ishlab chiqilgan va sintez qilingan. Barcha oksadiazollar ko'proq insektitsid faollikka ega, ayniqsa benzol halqasida ftor bo'lganda, muhim insektitsid faollikni namoyon etadi [93; 63-66 b]
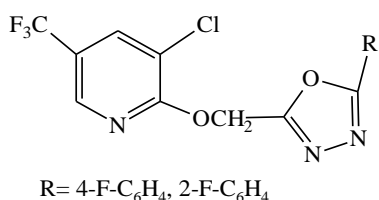
2-(5-(triftormetil) piridiloksilmetil)-5-aril-1,3,4-oksadiazol hosilalari

R= 4-F-C$_6$H$_4$, 2-F-C$_6$H$_4$

[94] Adabiyot mualliflari 2-[3-(4-bromfenil)propan-3-on]-5-(o'rinalmashinganfenil)-1,3,4-oksadiazol hosilalarini 3-(4-brombenzoil)propion kislotlardan sintez qilib olingan, ushbu sintez metodikalarni ishlab chiqishdan asosiy maqsadi nojo'ya ta'sirlarsiz, yallig'lanishga qarshi va og'riq qoldiruvchi faollikka ega ekan bo'lgan dori vositalarini olish bo'lgan va ushbu maqsadga erishilgan. Quyidagi sintez qilingan birikmada yuqori yallig'lanishga qarshi faollik aniqlangan.
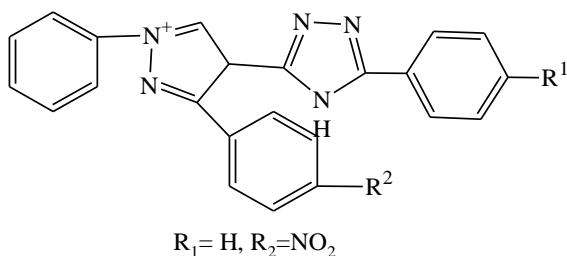
R$_1$= H, R$_2$=NO$_2$

R= C$_6$H$_5$, 2-Cl-C$_6$H$_4$

2-fenil-5- (1,3-difenil-1N-pirazol-4-il) -1,3,4-oksadiazol
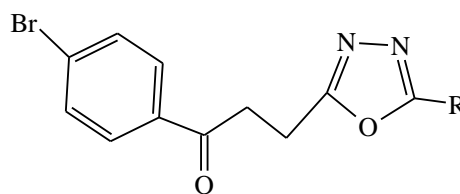
Fenil almashingan 1,3,4-oksadiazollar

[95] Adabiyot o'rganilganda 5- (6-metil-2-almashingan 4-pirimidiniloksimetil)-2,3-digidro-1,3,4-oksadiazol-2-tionlar va ularning 3-morfolinometil hosilalari sintezi va tabiiy sharoitda ularning yallig'lanishga qarshi faollik natijalari tavsiflangan. Sinab ko'rilgan birikmalarning aksariyati yallig'lanishga qarshi ta'sir ko'rsatdi, ularning faolligi va ularning bazilari atsetilsalitsil kislotasiga qaraganda ancha faolligi xulosa qilingan.
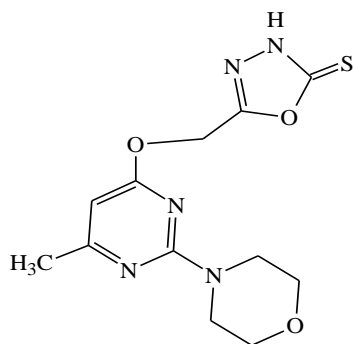
5- (6-metil-2-almashingan-4-pirimidiniloksimetil) -2,3-digidro-1,3,4oksadiazol-2-tionlar

1,3,4-Oksadiazol hosilalarining yuqorida keltirilgan biologik ta'sirlaridan tashqari u yurak-qon tomir kasalliklarida xam qo'llaniladi.

Yurak-qon tomir faoliyatini yaxshilaydigan, imidazol o'rnini bosadigan bir qator yangi oksadiazol hosilalari sintez qilingan va ularning faolligi gepotenziv va o'tkir toksikligi uchun in vivo sinovidan o'tkazilgan. Sinovdan o'tkazilgan birikmalardan imidazol o'rnini bosadigan bir qator yangi oksadiazol hosilalaridan quyida keltirilgan birikma, kolloidinning etalon preparatiga qaraganda eng yuqori faollikni namoyon etgan [96, 97].

Imidazol o'rnini bosadigan bir qator yangi oksadiazol hosilalari

R_1=p-N(CH$_3$)$_2$,
R_2=3(OCH$_3$), 4(OH)-C$_6$H$_3$
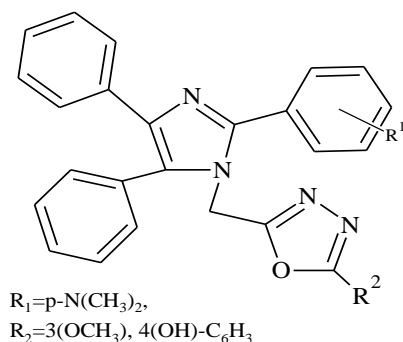
Ko'pgina adabiyotlar o'rganilganda bir qancha 1,3,4-oksadiazol hosilalari tuburkulezga qarshi faollikka ega ekanligi aniqlandi.

[98, 99] Adabiyotda 3-[5-piridin-5-il]-1,3,4-oksadiazol-2-il]-piridin qatori hosilalarining deyarli barchasi tuberkulezga qarshi faollikni namoyon qilgan, (a)-R= -C_5H_4N va (b)- R= -$NH_2C_6H_4$ birikmalari boshqa birikmalarga qaraganda yuqori faollikka egaligi xulosa qilingan.

R=C_5H_4N(a),   -$NH_2C_6H_4$(b)3-[5-piridin-5-il]-1,3,4-oksadiazol-2-il]-piridin
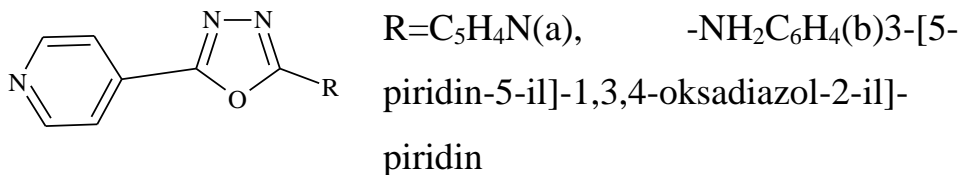
[100] Mualliflar tomonidan sintez qiligan 2-(4-nitropirrol-2-il)-5-aril-1,3,4-oksadiazol hosilalari orasida birikma yuqori tuberkulezga qarshi (0,46 mkg / ml) faollikni namoyon etgan u standart izoniazid (0,40 mkg / ml) dan yuqori ko'rsatkichni namoyon etgan.

R=aryl/heteroaryl

2-(4-nitropirrol-2-il)-5-aril-1,3,4-oksadiazol hosilalari
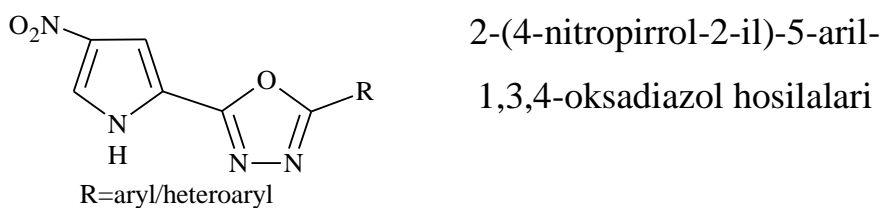
5-Aril-2-tio-1,3,4-oksadiazol hosilalari antimikrobakterial faollik va tuberkulez H37Rv mikrobakteriyasiga qarshi faolligi o'rganilgan. Sintez qilingan 30-37 chi birikmalar yuqori faollikni namoyon qilishi, 12,5 mkg/ml da 90% gacha ingibirlik qilishi aniqlangan [101].

5-aril-2-tio-1,3,4-oksadiazol hosilalari
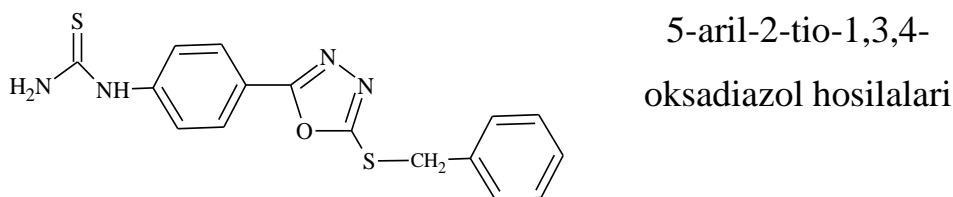
[102- 104] Adabiyotlar tahlili olib borilganda ko'pgina sintez qilingan birikmalarning farmokologik ta'siri molekulyar doking usuli bilan o'rganilganligiga guvohi bo'ldik. Molekulyar doking uchun tanlab olingan ligandning inson organizmida optimal konformatsiyasi tanlab olinadi, bu holat organizmdagi ayrim jarayonlarni sinab ko'rish orqali baholanadi va qaysi

jarayonda bog'lanishning erkin energiyasi minimal qiymatga ega bo'lsa optimal konformatsion holatga erishilgan deb baholanadi. 1,3,4-oksadiazol hosilalarining saratonga qarshi va yallig'lanish qarshi faolliklari dastlab ushbu in vivo usulda baholanib, so'ngra in vitro usulida sichqonlarga ta'sir mexanizmlari o'rganilib dori vositasi sifatida qo'llanilib kelinmoqda.
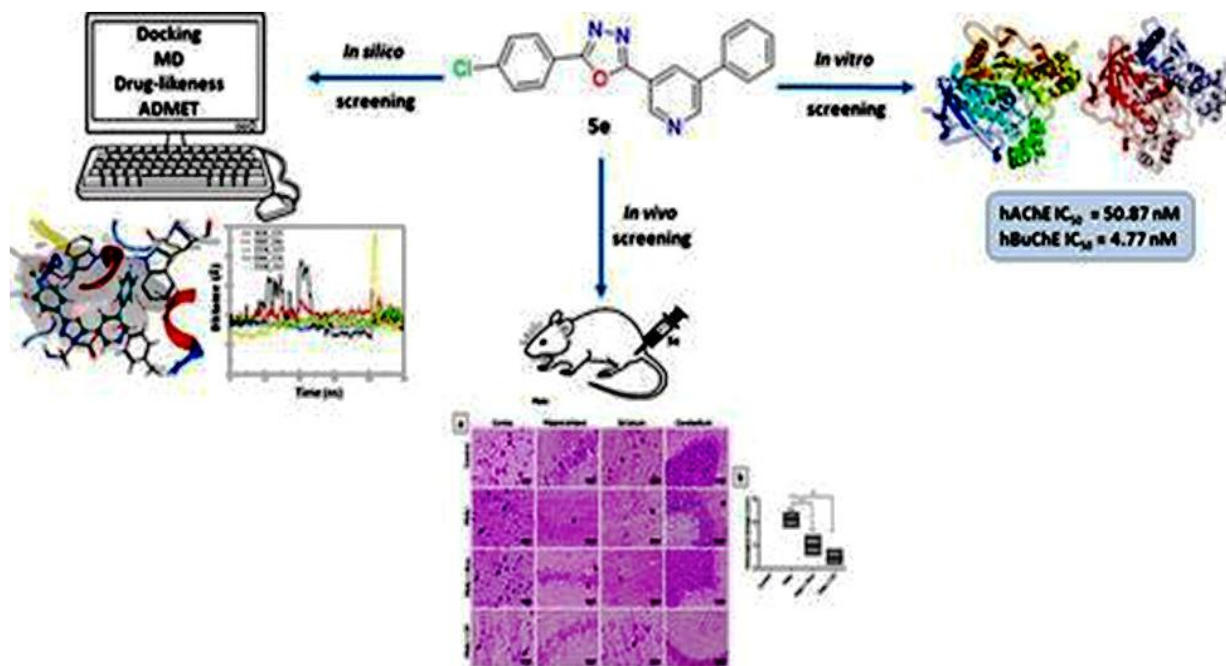
1.2-§. Oksadiazollarning kompleks birikmalari

Miao Du guruhi azolari 2000-yillarning boshlarida koordinatsion polimerlarning sintezi va tavsifiga asoslangan muvafaqqiyatli tadqiqot ishlarini yaratgan, [105- 112] ushbu ishlarda asosiy qurilish bloklari sifatida piridil almashingan 1,3,4-oksadiazollar ishlatilgan. Du va uning hamkasblarining g'oyasi 1,3,4-oksadiazolli ligandlarni turli xil metallar bilan koordinatsiyalanishi, yangi materiallarga bo'lgan qiziqishning ortishi bilan ko'p qirrali koordinatsion birikmalari olingan. Birinchi kompleks birikma Cu^{2+} va 2,5 bis(4-piridil)-1,3,4-oksadiazol (La) yordamida sintezi ishlab chiqilgan bo'lib, markaziy oksadiazol halqasi va ikkita 4-piridinlardagi azot atomlari orasida 137°C burchakka ega ekanligi o'rganilgan. Bunda ikkita birikma olingan, reaksiya ligandning metanol/suvli eritmasi va Cu^{2+} ning perxloratli yoki atsetatli eritmasi 2:1 mol

nisbatda aralashtirib $\{[Cu(La)_2(H_2O)_2](ClO_4)(OH)(H_2O)_{2,5}\}_n$ va $[Cu(La)_2(OAc)_2(H_2O)](H_2O)_2(CH_3\,OH)$ mos ravishda olingan. Xuddi shu reaksiya perxlorat tuzining o'rniga Cu^{2+} atsetat yordamida amalga oshirilganda koordinatsion polimerlarni olishmagan, ammo kutilmagan mononuklyar kompleks, bu yerda Cu^{2+} markaziy atom ikkita oksadiazol ligandlari bilan koordinatsiyalanadi. Ikkita atsetat anioni va bitta suv molekulasi apikal holatda koordinatsiyalangan.

$\{[Cu(La)_2(H_2O)_2](ClO_4)(OH)(H_2O)_{2,5}\}_n$ $[Cu(La)_2(OAc)_2(H_2O)](H_2O)_2(CH_3OH)$
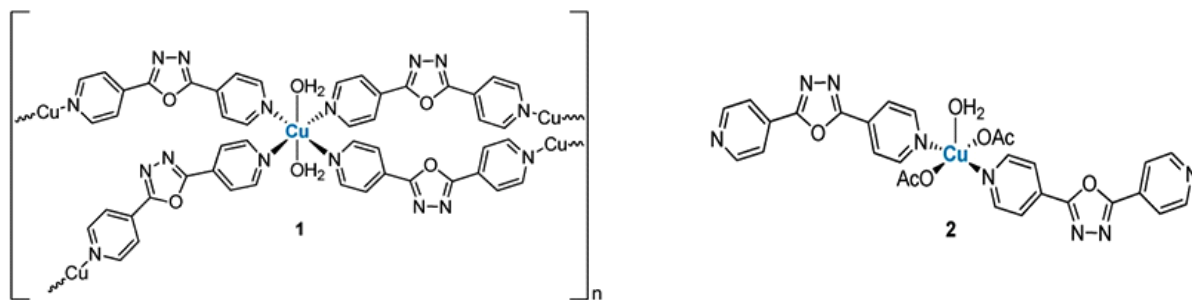
      $\{[Cu(La)_2(H_2O)_2](ClO_4)(OH)(H_2O)_{2,5}\}_n$ muhim ahamiyatga ega ekanligini hisobga olgan holda, Miao Du ushbu kompleks birikmaga anion almashinuvi reaksiyalari yordamida boshqa Cu^{2+} komplekslarini sintez qilgan. NaN_3 va Na_2SO_4 ning suvli eritmasiga $\{[Cu(La)_2(H_2O)_2](ClO_4)(OH)(H_2O)_{2,5}\}_n$ qo'shilgandan so'ng ikkita yangi $\{[CuLa_2\ (N_3)_2](H_2O)1,5\}_n$ va $\{[CuLa_2(H_2O))(SO_4)](H_2O)_2\}_n$ birikma olindi. Ikki yangi birikmaning kristall tuzilishida anion qatlamlari bilan bog'langan chiziqli cheksiz $[-CuL_2-]_n$ zanjirlar mavjudligi aniqlangan [107].

    $\{[CuLa(N_3)_2](H_2O)1,5\}_n$ $\{[CuLa(H_2O))\ (SO_4)]\ (H_2O)_2\}_n$
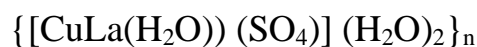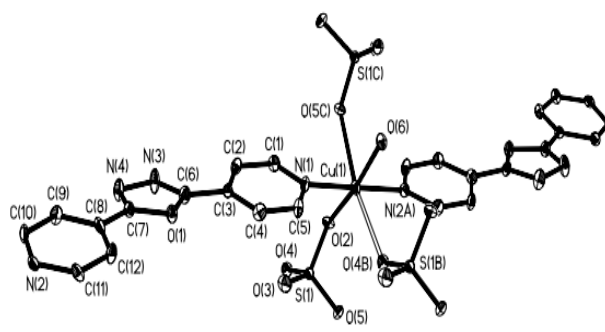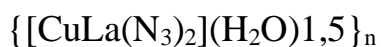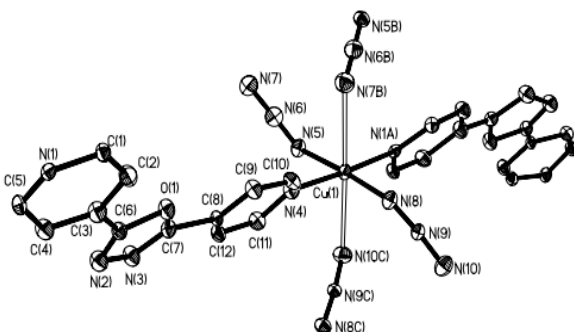
Keyingi ishlarda ham ayni ligand bilan Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+} va Zn^{2+} lar ishtirokida kompleks birikmalar sintez qilingan.
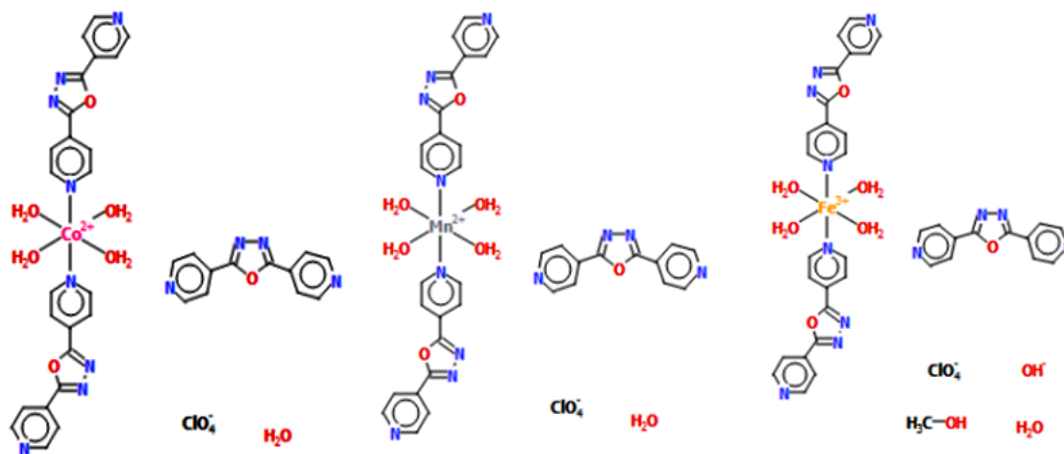
$[CoLa_2(H_2O)_4]$ $\qquad$ $[MnLa_2(H_2O)_4]$ $\qquad$ $[FeLa_2(H_2O)_4]$

Du va uning hamkasblari bundan tashqari boshqa oksadiazol hosilasi asosida sintez olib borgan, yani 2,5 bis(3-piridil)-1,3,4-oksadiazol (Lb) ishtirokida Cu^{2+} ning $[Cu_2(Lb)_2(H_2O)_6](ClO_4)_4$, $[CuLb(NO_3)_2]_2(CH_3CN)_2$, $[Cu_2(Lb)_2(H_2O)_6(SO_4)_2]_n$ komplekslari sintez qilingan, bunda erituvchi (CH_3CN-H_2O) va metall/ligand (1:1) nisbatda turli xil anionlar (ClO_4^-, NO_3^- va SO_4^{2-}) ishtirokida olib borilgan [106]. Bunda uch xil yangi kompleks birikma: $[Cu_2(Lb)_2(H_2O)_6](ClO_4)_4$, $[CuLb(NO_3)_2]_2(CH_3CN)_2$ va $[Cu_2(Lb)_2(H_2O)_6(SO_4)_2]_n$ sintez qilingan.
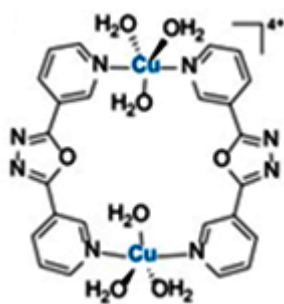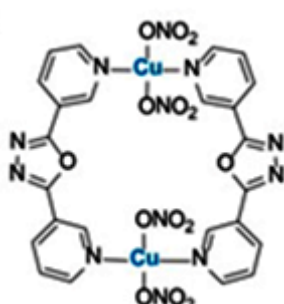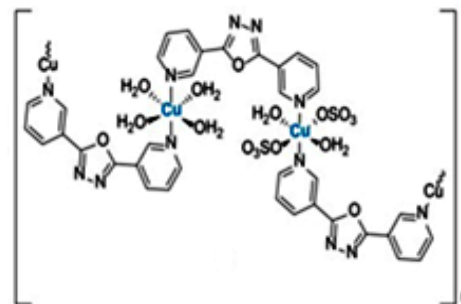
$[Cu_2(Lb)_2(H_2O)_6](ClO_4)_4$ $[CuLb(NO_3)_2]_2(CH_3CN)_2$ $[Cu_2(Lb)_2(H_2O)_6(SO_4)_2]_n$
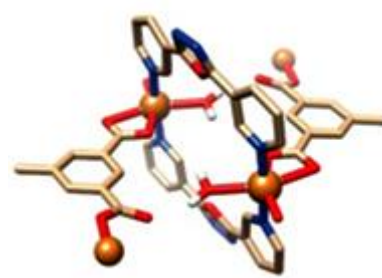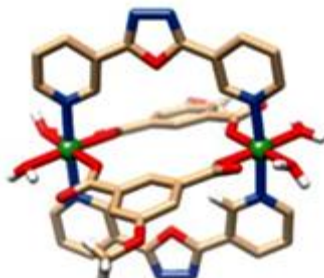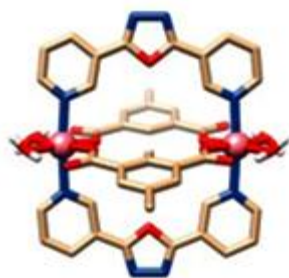
Co^{2+}, Ni^{2+} va Cu^{2+} ning 2,5 bis(3-piridil)-1,3,4-oksadiazol (Lb) ishtirokida olingan kompleksining tuzilishi.

2005 Yilda Du va boshqalar Ag(I)(X=BF$_4^-$, AsF$_6^-$, CF$_3$SO$_3^-$ va SbF$_6^-$) tuzlarining boshqa oksadiazolli ligand, 2,5 bis (pirazin) -1,3,4 -oksadiazol (Lc) bilan reaksiyasi o'rganilgan. Ushbu oksadiazol hosilasining La va Lb ga qaraganda donor markazlari ko'pligi turli xil metallokomplekslar olishga imkon yaratishi sababli tanlab olingan [108]. CHCl$_3$/OH(CH$_2$)$_2$OH/CH$_3$OH muhitida olingan kompleks birimalari umumiy holatda {{Ag(Lc)]-X·erituvchi}$_n$ ko'rinishga ega bo'lgan to'rtta polimer kompleks birikma olingan. {{Ag(Lc)]-X·erituvchi}$_n$ kompleks birimada har bir kumush atomi ikkita ligand bilan (sisoid II konfiguratsiyasida) pirazin azot atomi va oksadiazol azot atomi va ikkita boshqa ligandlardan yana ikkita pirazindagi azot atomlari bilan koordinatsiyalanishi bilan hosil bo'ladi. Shu bilan birga, xar bir oksadiazol ligand to'rtta kumush atomlari bilan koordinatsiyalanib, psevdotetraedrik tugunlarni hosil qilgan[108].
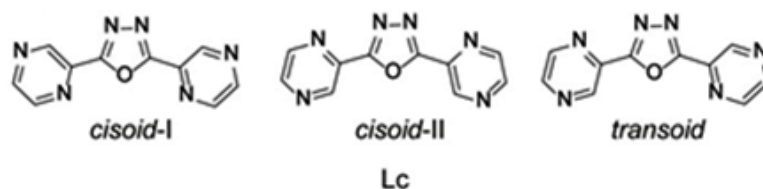
2,5 bis (pirazin) -1,3,4-oksadiazol (Lc) ligand ctrukturasi.
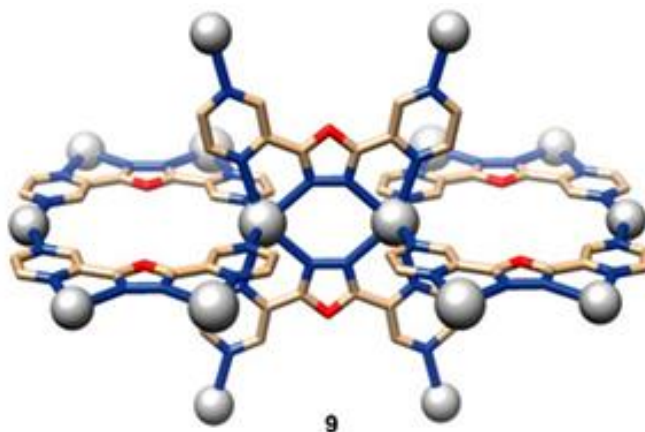
Ag(I) bilan 2,5 bis (pirazin) -1,3,4-oksadiazolning polimer kompleks birikmasi

Bir yil o'tgach, Du va uning hamkasblari tiotsianat ishtirokida Lc ligandi va Cd(II) yoki Co(II) perxlorat tuzlari yordamida yangi sintezni amalga oshirdilar[109].

CH$_3$CN/H$_2$O da teskari sovutgich ulangan holatda 30 daqiqa davomida stixiometrik nisbatda 1:1:3 nisbatda (metall: ligand: SCN) aralashtirib

qizdirilganda ikki xil kompleks birikma olingan: $[Cd (Lc)_2(SCN)_2]_n$ va uch o'lchovli vodorod bog'lanish mavjud bo'lgan $[Co(Lc)_2(SCN)_2(H_2O)_2](CH_3CN)_2(H_2O)_2$ kompleks birimalari xosil bo'lgan. $[Cd (Lc)_2(SCN)_2]_n$ kompleks birikma rentgenstruktur tahlil usuli yordamida o'rganilganda, bu yerda Cd^{2+} bilan Lc bilan hosil qilgan kompleks birikmasi oktoedrik shaklda, ushbu ligand sizoid-I ning shakllanishida monodentat ligand sifatida koordinatsiyalangan (kumush ionlari holatida bo'lganidan farq qilgan). Bundan farqli o'laroq, $[Co(Lc)_2(SCN)_2(H_2O)_2](CH_3CN)_2(H_2O)_2$ kompleksning rentgenstruktur tahlil natijalari shuni ko'rsatdiki, markaziy Co^{2+} atomi ikkita Lc ligandlari bilan monodentant holatda, ikkita azot atomlari SCN va ikkita suv H_2O molekulalari bilan koordinatsiyalangan [109].

$[Cd (Lc)_2(SCN)_2]_n$ $\qquad\qquad$ $[Co(Lc)_2(SCN)_2(H_2O)_2](CH_3CN)_2(H_2O)_2$
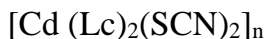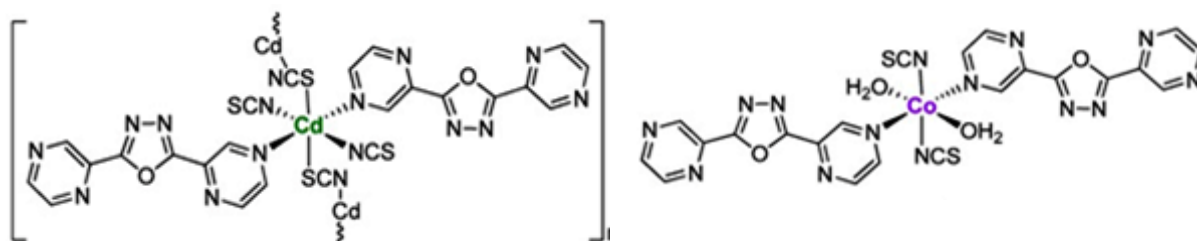
Rakka va leyshmaniyaga qarshi vosita sifatida (5-(4-ftorfenil)-1,3,4-oksadiazol-2-tion va (5-(4-nitrofenil)-1,3,4-oksadiazol-2-tiolato)trifenilfosfinning Au^+ bilan kompleks birikmalari sintez qilingan [108].

Fazoviy guruh: P 1(2),
Yacheyka parametralari:
$a=7,8973$ (2) Å
$b=11,0693$ (3) Å
$c=20,5122$ (5) Å,
$\alpha=96,043$ (2)
$\beta=100,128$ (2)
$\gamma=94,847$ (2)
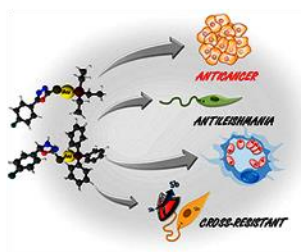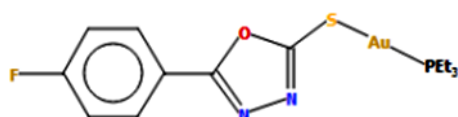
(5-(4-ftorfenil)-1,3,4-oksadiazol-2-tiolato)-(trietilfosfin)-oltin(I)

Fazoviy guruh: P 2_1/ n (14),
Yacheyka parametrlari:
$a=13,2854(2)$Å

b=18,1873(3)Å

c=20,5524 (4) Å,

α=90

β=103,197 (2)

γ=90
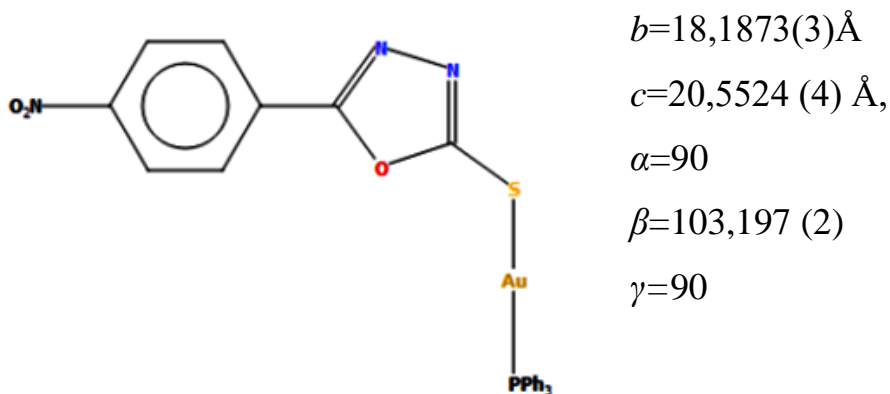
(5-(4-nitrofenil)-1,3,4-oksadiazol-2-tiolato)trifenilfosfin-oltin(I)

2010 va 2011 yillar orasida Terenzi va boshqalar Ni^{2+}, Cu^{2+} va Zn^{2+} larning 3,5-bis-(2-piridil)-1,2,4-oksadiazol va 3-(2-piridil)-5-(fenil)-1,2,4-oksadiazollar asosida, $[M(C_{12}H_8N_4O_2)_2(H_2O)_2)]^{2+}(ClO_4)_2$, $[M(C_{13}H_9N_3O)_2(ClO_4)]^{2+}(ClO_4)_2$ (Cu(II), Zn(II), Ni(II) va $[Pt(C_{17}H_{20}N_2O_3)_2Cl_2)]$, $[Pt(C_{14}H_{10}N_2O_2)_2Cl_2)]$ seriyalari sintez qilingan [20, 109-112].

$[M(C_{12}H_8N_4O_2)_2(H_2O)_2)]^{2+}$ $[M(C_{13}H_9N_3O)_2(ClO_4)]^{2+}$ $[Pt(C_{17}H_{20}N_2O_3)_2Cl_2)]$

$[Pt(C_{14}H_{10}N_2O_2)_2Cl_2)]$
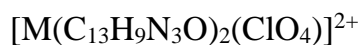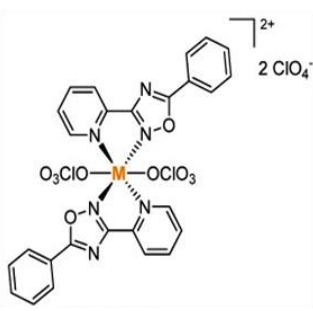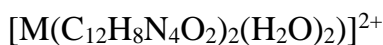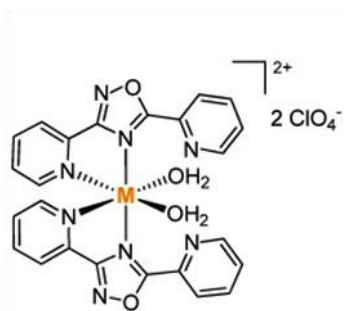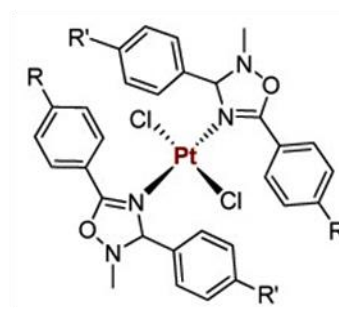
M=Cu(II), Zn(II), Ni(II)   R=OCH$_2$CH$_2$OCH$_3$, (H)

R‛=H (OH⁻)

Mualliflar $[Cu(C_{13}H_9N_3O)_2(ClO_4)]^{2+}(ClO_4)_2$ shish kasalligiga qarshi faollikni namoyon qiluvchi kompleks birikmaga etibor qaratishga qaror qilishgan. Ligand juda faol emas, $[Cu(C_{12}H_8N_4O_2)_2(H_2O)_2)]^{2+}(ClO_4)_2$ kompleks birikmasi har ikkala hujayra hayotiyligini pasaytirgan va 24 soatlik davolanishdan so'ng IC 50 qiymatini tahminan 10 mkM tashkil etgan. Bundan tashqari, [113, 114] adabiyotda hujayra morfologik tahlili va oqim sitometriyasi tahlilida saraton hujayralarining hujayralar siklining G0/G1 bosqichida joylashgan DNK parchalanishi bilan apoptotik o'limi aniqlangan

[109-112] Adabiyotlarda sintez qilingan neytral trans-platina(II) li hosilalari [Pt($C_{17}H_{20}N_2O_3$)$_2$Cl$_2$)] va [Pt($C_{14}H_{10}N_2O_2$)$_2$Cl$_2$)] sisplatinaga chidamli hujayralar modellarida nisbatan faol bo'lgan, tadqiqotchilar fikriga ko'ra geterotsiklik ligandlar sisplatinaga nisbatan qo'shimcha ta'sir o'tkazishga imkon bergan.

[Cu($C_{16}H_{12}N_2O$)($C_6H_{16}N_4$)ClO$_4$]$^{+-}$ [Ru($C_2H_4P_2$(Ph)$_4$)(C_5H_5)($C_8H_3N_2O_6$)]PF$_6$

[Cu($C_{16}H_{12}N_2O$)($C_6H_{16}N_4$)Br]$^+$
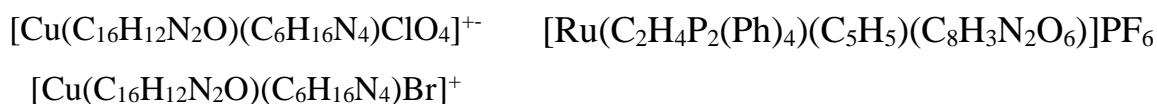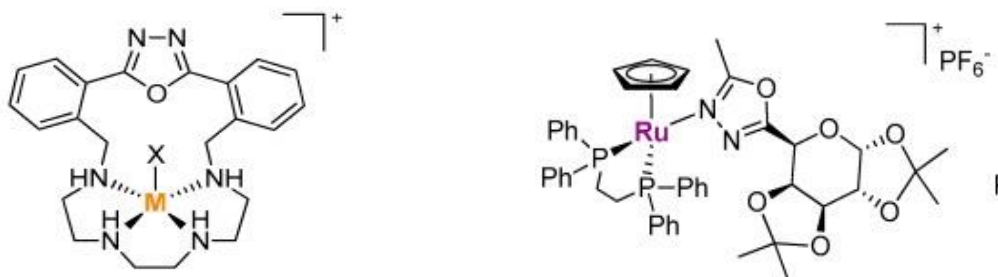
Yaqinda Fernandes guruhi 1,3,4-oksadiazol N-koordinatsion markazlari, mos ravishda [Cu($C_{16}H_{12}N_2O$)($C_6H_{16}N_4$)ClO$_4$]$^{+-}$, [Cu($C_{16}H_{12}N_2O$)($C_6H_{16}N_4$)Br]$^+$ va [Ru($C_2H_4P_2$(Ph)$_4$)(C_5H_5)($C_8H_3N_2O_6$)]PF$_6$ bilan ishlaydigan laktatsiya qilingan galaktozaning fruktoza va uglevodlarning hosilalari ligandlari bilan 5-siklopentadienil, Ru(II) yangi kompleks birikmalarining sintezi va sitotoksilligi haqida ma'lumot berishgan [115].

1.3-§. Metallovanadatlar, olinishi, xossalari

Ushbu ishda biz 1,3,4-oksadiazol hosilalarining vanadatlar ishtirokidagi geterometalli kompleks birikmalarni sintezini amalga oshirishimiz uchun adabiyotlardagi metallovanadatlarning sintezi tahlil qilindi: [116] mualliflar tomonidan 0,25 mmol Cd(Oac)$_2$·2H$_2$O va 0,5 mmol 2,2′ bipiridin va NH$_4$VO$_3$ ishtirokida 1-tetravanadat bis[bis(2,2′ bipiridin)-kadmiy(II)] kompleks birikma sintez qilingan. Sintez qilingan aralash metalli kompleks birikmaning tuzilishi RSA yordamida o'rganilgan.
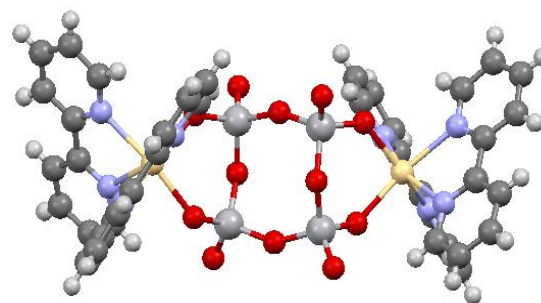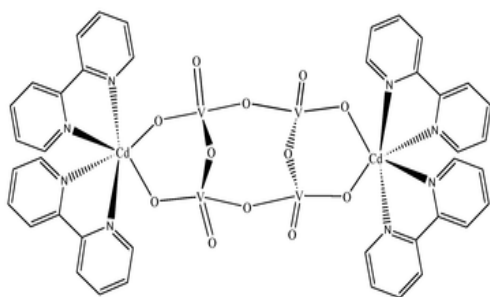
$M_r= 1245.30$; Ortorombik, a= 16.287(7)Å; b= 17.201(9)Å; c= 34.070(16)Å;

V= 9545(8)Å³; Z= 8

Poli[[kobalt(II)-µ-(geksaoksavanadium-*O*:*O'*)]-µ-bipiridin-*N*:*N'*],

$[Cd_2V_4O_{12}(C_{10}H_8N_2)_4]$ tarkibli ikki simmetriya o'qiga ega molekula sintez qilingan. $\{V_4O_{12}\}$ halqasi ikkita $\{Cd(C_{10}H_8N_2)_2\}$ bo'laklari bilan qo'shni vanadiyli qismning okso- guruhlari orqali bog'langan. $C_{10}H_8N_2$ ligandlari ishtirokida π-π o'zaro ta'siri tufayli molekula a va b tekisligiga parallel qatlamlar hosil qilib yig'iladi.

Gidrotermal usulda $[CoV_2O_6(C_{10}H_8N_2)]$ kompleksi olingan va element tahlil, IQ spektroskopiya RSA fizik-kimyoviy tadqiqot usullarida o'rganilgan. Struktura 4,4'-bipiridin ligandlari orqali uch o'lchamli tarmoqlangan $[Co_2V_4O_{12}]$ bimetallik oksidli qatlamidan tuzilgan [117].
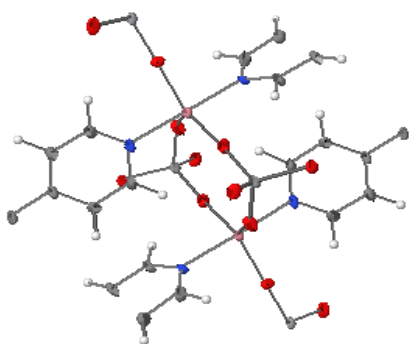
Fazoviy guruh: P1,

Yacheyka parametrlari:

a= 8.1634(9)Å;

b= 8.5720(10)Å;

c= 10.1710(10)Å;

α = 87.079(5);

β = 75.833(4);

γ = 75.233(6);

V= 667.2(2)Å³;   Z= 2

Gidrotermal usulda [118, 119] adabiyotda poli[[[diakva(µ-4,4' bipiridil) - dinikel(II)] bis(µ-4,4' bipiridil)-di-µ-geksaoksodivanadat(2-)] 2.5-gidrat], $[Ni_2-(V_2O_6)_2(C_{10}H_8N_2)_3(H_2O)_2]\cdot2.5H_2O$, sintez qilingan hamda element, IQ- va RS tahlil usullari yordamida o'rganilgan.
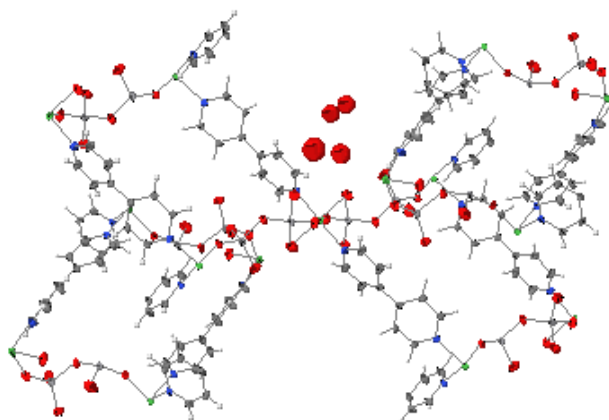
Fazoviy guruh: C2/c,

Yacheyka parametrlari:

a=30.3799(9)Å

b=11.2402(3)Å

c=11.5366(3)Å

β=105.9610(10)

V=3787.6(2)Å³

Z= 4

Struktura [V_2O_6], [Ni (4,4'-bipy)$_4O_2$] va [Ni(H$_2$O)$_2$(4,4'-bipy)$_2O_2$] va kristalizatsion suvdan tashkil topgan. Ni atomi va bitta bipiridil gruppasi simmetriya markazida joylashgan. [Ni(H$_2$O)$_2$(4,4'-bipy)$_2O_2$] kompleks birikma quyi kategoriyali triklin singoniyali, iikilamchi simmetriya o'qiga kompleks birikma hosil qilgan.

Kobalt atsetat, V_2O_5 va 2,5-bis(4-piridil)-1,3,4-tiadiazollarning gidrotermal usulda sintezi olib borilganda, [Co(V_2O_6)(C$_{12}$H$_8$N$_4$S)(H$_2$O)$_3$] -katen-poli[[bis[triakva[2,5 bis(4-piridil)-1,3,4-tiadiazol]kobalt(II)]]-14-tetravanadat] tarkibli kompleks birikmasi, Co^{3+} oksidlanish darajasiga ega bo'lgan buzilgan oktaedrik polimer tuzilishga ega bo'lgan, geterometalli kompleks sintez qilingan [120]. Ushbu kompleks birikmada koordinatsiya piridin halqasidagi azot atomi orqali, tetravanadat qism esa ikkitadan kislorod atomlari orqali borgan.
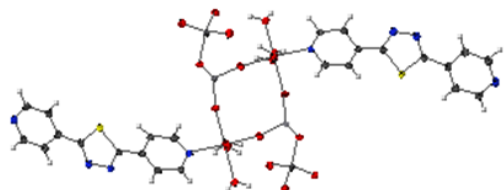
Katen-poli[[bis[triakva[2,5 bis (4-piridil)-1,3,4-tiadiazol] ko-balt(II)]]-14-tetravanadat] kompleks birikmasi

[121] mualliflar tomonidan metavanadat, temir(II) tuzlari va azotdonor saqlagan xelatlanuvchi ligandning gidrotermal sintezi amalga oshirilganda (96) [Fe(C$_{10}$H$_8$N$_2$)$_3$]$_2$[V$_4$O$_{12}$]·10H$_2$O tarkibli, simmetriya markazida bitta [V$_4$O$_{12}$] siklik vanadat mavjud bo'lgan, ikkita disktret oktaedr [Fe(C$_{10}$H$_8$N$_2$)$_3$]$^{2+}$ lari orqali qurshalgan 10H$_2$O solvat molekula bilan qurshalgan murakkab tuzilishli kompleks birikma. Anion va koordinatsion kation qismlari ketma-ketlikda

joylashib alohida qatlamlar hosil qiladi. Anion qatlamida suv molekulalari solvatlangan holatda bo'ladi va anion qism bilan vodorod bog'lanish orqali bog'langan.

$[Fe(C_{10}H_8N_2)_3]_2[V_4O_{12}]\cdot 10H_2O$
kompleks birikmasi
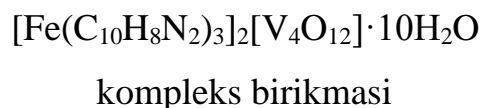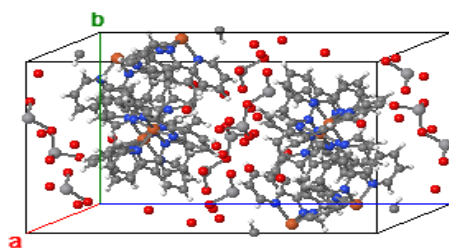
O'rganib chiqilgan adabiyotlar tahlili shuni ko'rsatdiki, 1,3,4-oksadiazol hosilalari asosidagi geterometalli kompleks birikmalar haqida adabiyotlarda xech qanday ma'lumotlar mavjud emas, gomometalli kompleks birikmalari esa kam o'rganilgan, ularning spektral xossalari, tarkibi, komplekslarning amaliyotdagi xossalari va ularning barqarorligi haqidagi yetarli holda o'rganilmagan.

Ushbu tadqiqot ishini amalga oshirishda biz inson organizmi uchun muhim ahamiyatga ega bo'lgan mikrobiogen elementlarni tanlab oldik. Ulardan vanadiy inson organizmida energiya ishlab chiqarishda, uglevodlar va yog'larning metabolizmida, xolesterin ishlab chiqarishni kamaytirishda, ateroskleroz va yurak-qon tomir kasalliklarini davolashda, asab tizimini normal ishlashida, hujayralar bo'linishini boshqarishda va saraton, qandli diabetga qarshi vosita sifatida ishlatishda muhim ahamiyatga ega. Kobalt esa tirik organizmlardagi turli oqsil moddalari, aminokislotalar, platsenta va boshqalar bilan bog'langan bo'ladi hamda nixoyatda katta ahamiyatga ega bo'lgan vitamin B_{12} (kofaktor) tarkibiga kiradi. Kobalt qon hosil bo'lishida ishtirok etadi. U temir ionlarining yangi hosil bo'layotgan qizil qon tanachalardagi gemoglobin tarkibiga kirishini jadallashtiradi. Shu sababli kamqonlik kasalliklarida temirli moddalar bilan birgalikda Cu^{2+} va Co^{2+} tuzlarini qo'llash yaxshi natijalar beradi. Nikel arginaza fermetini faollashtiradi va oksidlanish jarayoniga ta'sir ko'rsatadi. Rux (zink) – barcha fermentlar tarkibiga kiruvchi yagona metall bo'lib, uning o'rnini boshqa metall bosa olmaydi. Rux ko'plab modda almashinuvi jarayonlarida ishtirok etib, tanadagi barcha hujayralarning normal ishlashini ta'minlaydi. Rux insulin gormoni tarkibiga

kirib, uning gipoglikemik ta'sirini oshiradi. Qand kasalligida siydik orqali organizmdan chiqib ketadigan rux miqdori normadagidan 3-4 barobar ortiq bo'ladi. Bu biogen elementning ahamiyatli xususiyatlaridan yana biri uning organizmning immunitetni oshirishda ishtirok etishidir. Mis esa qon hosil bo'lish jarayonida ishtirok etadigan elementdir. U eritrotsitlar tarkibiga kirib, ularning yetilishiga va gemoglobin sinteziga ijobiy ta'sir ko'rsatadi. Bunda mis ta'sirida temirning almashinish jarayonlarining faollashuvi kuzatiladi. Mis organizmdagi karbon suv almashinuviga ta'sir etadi.

I bob bo'yicha xulosalar

Adabiyotlar tahlili shuni ko'rsatadiki, Yaponiya, Avstriya, Turkiya hamda Chexiyaning nufuzli universitetlarida oksadiazol hosilalari sintezi va ularning xossalarini o'rganish ustida ko'plab ilmiy ishlar olib borilmoqda. Oksadiazol hosilalarining saraton, yallig'lanish, infeksiya, diabet, pufak fibrozi, tutqanoqqa qarshi, tuburkulezga qarshi biologik foalligi yuqoriligi sababli oxirgi vaqtda ushbu birikmalarga qiziqish ortmoqda. Nashr etilgan ishlarda ligand tarkibidagi radikallarning turlichaligi va qo'shimcha ligandlar tanlashda aniq birlik bo'lmaganligi sababli, metall va ligand tabiatiga qarab komplekslarning tuzilishi va xossalarini, kompleks hosil qilish xarakterini kuzatish qiyin. Oksadiazol hosilalarining tuzilishi va xossalari batafsil darajada o'rganilgan va ularning yuqori amaliy ahamiyati hisobga olingan bo'lsada, 1,3,4-oksadiazol hosilalari koordinatsion kimyo nuqtai nazaridan yetarlicha o'rganilmagan.

Xozirgi kunga qadar oksadiazol hosilalarining gomometalli kompleks birikmalari tadqiq etilgan, lekin adabiyotlarda Co(II), Ni(II), Cu(II), Zn larning V(V) bilan geterometalli kompleks birikmalari haqida ma'lumotlar yo'q. Geterometalli kompleks birikmalarni sintez qilishda vanadiy metalli katta qiziqish uyg'otadi. Vanadiy inson organizmida energiya ishlab chiqarishda, uglevodlar va yog'larning metabolizmida, ateroskleroz va yurak-qon tomir kasalliklarini davolashda, xolesterin ishlab chiqarishni kamaytiradi, asab tizimini normal ishlashi uchun zarur mikroelement hisoblanadi. Shu munosabat bilan 1,3,4-oksadiazol hosilalari asosidagi gomo- va geterometalli kompleks birikmalarni sintez qilish va ularning fizik-kimyoviy va biologik xossalarini aniqlash muhim ilmiy ahamiyatga ega.

II BOB. 1,3,4-OKSADIAZOL HOSILALARING Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} va VO_2^+ BILAN GOMO- VA GETEROMETALLI KOMPLEKS BIRIKMALARI SINTEZI

2.1-§. Reaktivlar, tadqiqotning metodlari va tahlillari

Kompleks birikmalar sintez qilish uchun metallarning kristalizatsion holatdagi tuzlaridan: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} xlorid, atsetat, nitratlari hamda NH_4VO_3 tuzining «a.u.t.» markasidan foydalanildi. Foydalanilgan organik erituvchilar ma'lum metodika [122] bo'yicha tozalandi va quritildi.

Sintez qilingan birikmalarning elementlar tahlili va mikrostrukturasi Oxford Instruments (Buyuk Britaniya) tizimli mikro analizatorlari yordamida JSM-7001 firma JEOL skanerlovchi-elektron mikroskopida (Yaponiya) tadqiqotlar o'tkazildi. 30 kV kuchlanish bilan 1,2 nm gacha bo'lgan mikroskopning o'lchamlari (ikkilamchi elektronlarda izolyasiya), 0,5dan 30 kV gacha tezlashtirish, ×10 dan ×1000 000 gacha kattalashtirish, 20 nA gacha nur oqimida, B dan U gacha element tahlili olib borildi. O'rganilgan namunalar Jeol (Yaponiya) va Gatan (AQSh) uskunalari majmuasida amalga oshirildi. Natijalar maxsus dasturlar yordamida olingan: elementlarni sifat va miqdoriy tahlil qilish uchun – INCA Point & ID, xaritalash - Mapping va QuantMap, bosqichlarni miqdoriy taqsimlash va kiritish – Feature dasturlarida amalga oshirildi. Element tahlil natijalari Ilg'or texnologiyalar markazi laboratoriyasida olindi.

Birikmalarning yutilish infraqilizil spektrlari 400-4000 sm^{-1} soha oralig'ida Avatar System 360 FT- IR va Rrotege 460 Magna-IR technology firma Nicolet Instrument Corporation (AQSh) spektrofotometrda KBr tabletka ko'rinishidagi diametri 7 mm bo'lgan namunasidan va 4 sm^{-1} aniqlikda foydalanib o'rganildi. IQ-spektr natijalari O'zR FA O.S.Sodiqov nomidagi Bioorganik kimyo instituti "Kompleks birikmalar kimyosi" laboratoriyasida olindi.

Sintez qilingan kompleks birikmalar DQES tahlili UV-2400 (Shimdazu, Yaponiya) spektrofotometrida olindi. Kukun shaklidagi namunalar optik uzunligi 2 mm bo'lgan kvars kyuvetaga joylashtirildi va qaytarilish namunalarining DQES spektrlari 200-880 nm to'lqin uzunligida qayd etildi. DQES spektrlari TKTI Noorganik moddalar kimyoviy texnologiyasi fakulteti "Fizik-kimyoviy tahlillar" laboratoriyasida olindi.

Birikmalar strukturasini aniqlash Malvern Panalytical Empyrean kukunli difraktometri yordamida amalga oshirildi. XRD ma'lumotlar CuK_α radiatsiya bilan (λ=1.54Å) yordamida qayd qilindi. Bu tajribada nurlanish generatorining tezlanuvchan kuchlanishi 45 kV, tok emissiyasi esa 40mA qilib belgilandi. Rentgen difraksion rentgenogrammalari $2\Theta = 20°\text{-}120°$ da Breggo – Brentano nur geometriyasida doimiy ravishda 0,33 daraja / min skanerlash tezligi bilan qayd etildi. Olingan natijalar tahlili VESTA dasturi orqali amalga oshirildi. Rentgenogrammalar O'zRFA Yadro fizikasi instituti "Qattiq jismlar fizikasi" laboratoriyasida olindi.

Termik tahlil termodinamik asbob – Netzsch Simultaneous Analyzer STA 409 PG (Germaniya), K-tipidagi (Low RG Silver) termobug' va alyuminiyli tigelda olib borilgan. Hamma o'lchashlar inert azot atmosferasida azotning oqim tezligi 50ml/min.da olib borilgan. Tahlilning harorat oralig'i 20-400˚C, qizdirish 5K/min tezlikda olib borilgan. Bir o'lchashda namuna miqdori 6-10 mg. O'lchovchi sistema standart moddalar to'plami KNO_3, In, Bi, Sn, Zn, CsCl yordamida tebrandi. Bir vaqtning o'zida namunaning massasi, komplekslarning parchalanish massasi va termik barqarorligi temperatura ortib borishi bilan o'zgarishi aniqlandi.

RSA tahlil Rigaku oxford diffraction XtaLAB Synergy gibrid pikselli massiv detektorli, tezkor kappa goniometri bilan muhrlangan naychadagi bir yoki ikkita mikrofokusli rentgen nurli difraktometrida amalga oshirildi. Tezkor kappa goniometri skanerlash tezligi ma'lumotlarni sekundiga 10° ga olishga qodir. RSA tahlil natijalari O'zR FA O.S.Sodiqov nomidagi Bioorganik kimyo instituti "Kompleks birikmalar kimyosi" laboratoriyasida "Rigaku oxford diffraction XtaLAB Synergy" rentgen nurli difraktometrda olindi.

Rentgenofluoressent o'lchashlar energodispersion rentgenofluoressent analizator NEX CG Applied Rigaku Technologies spektrometri yordamida amalga oshirildi. Ushbu spektrometr qotishma, kukun hamda suyuq holatdagi namunalarni ham tekshirib sifat va miqdor natijalarini beradi. Rentgenofluoressent tahlil TKTI Noorganik moddalar kimyoviy texnologiyasi fakulteti "Fizik-kimyoviy tahlillar" laboratoriyasida olib borildi.
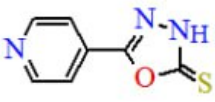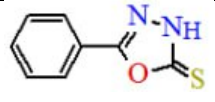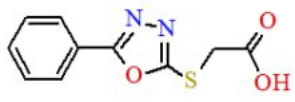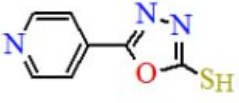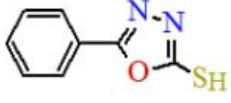
ESI-mass-spektrometriya natijalari O'zR FA Geologiya institutida ESI-mass-spektrometriya (elektrosprey) metodida, "6420 Triple Quad LC/MS (Agilent Technologies, USA)" mass-spektrometida olindi. Namunalarning mass-spektrlari musbat ionlanish usuli bilan ro'yxatga olindi. Fragmentor kuchlanishi 5.0 V, qurutuvchining gaz sarfi 12l/min, gaz temperaturasi 300 ^{0}C, purkagich ninasidagi gaz bosimi 20 psi, bug'latuvchidagi temperatura 300 ^{0}C, kapillyardagi kuchlanish 4000 V da mass-spektr tahlil natijalari olindi.

Metall ionlari bilan ligandlarning koordinatsiyalanish jarayonlarini o'rganish bo'yicha tajriba natijalarini yanada mukammalroq izohlash uchun elektron strukturalarini hisoblash amalga oshirildi. Molekulaning kvant-kimyoviy hisoblashlari Gaussian09 programmasining B3LYP nazariyasi doirasidagi LanL2DZ bazisida to'liq geometrik parametrlarni optimatsiya qilish orqali o'rganildi.

Komplekslarning antioksidantlik faolligi Agilent Technologies Cary 60 UV-Vis spektrofotometrda aniqlandi. Moddalarning antioksidantlik faolligi *in vitro* usulida aniqlanadi. Anitioksidantlik hususiyatlarini tadqiq qilish uchun 2ml 0,2 M li Na$_2$CO$_3$ va NaHCO$_3$ larning pH=10,65 bo'lgan bufer tayyorlanadi, unga 56mkl 0,1%li adrenalingidroxlorid (epenifrin), 30 mkl antioksidant (preparat) solinadi va aralashtirilib spektrofotometr Cary 60 UV-Vis Agilent Technologies da o'rganildi. Antioksidantlik faolligi O'zR FA O.S.Sodiqov nomidagi Bioorganik kimyo institutida o'rganildi, olingan komplekslarda korroziyaga karshi ingibitorlik xossasi mavjudligi aniqlandi.

2.2-§. Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ionlarning 1,3,4-oksadiazol hosilalari asosidagi kompleks birikmalari sintezi

Ushbu tadqiqot ishini amalga oshirishda quyidagi ligandlardan foydalanildi:

L^1-5-(4-piridil)-1,3,4-oksadiazol-2(3H)-tion/tiol	L^2-5-fenil-1,3,4-oksadiazol-2(3H)-tion/tiol	L^3-2-karboksimetiltio-5-fenil-1,3,4-oksadiazol

L^{1,2} ligandlarda tautomeriya xodisasining mavjudligi, turli erituvchilarda eruvchanligi va erituvchi tabiatiga qarab tion yoki tiol holatda reaksiyaga kirishish ehtimolligi borligi sabab turli sintez usullari qoʻllanildi.

2.2.1. Co^{2+}, Ni^{2+}, Cu^{2+} va Zn^{2+} larning L^1 asosidagi kompleks birikmalari sintezi

L^1 asosida gomometalli kompleks birikmalarning sintezi:

1-Usul. Co^{2+} xlorid kristallogidratning 5 ml 0,2 M li etanoldagi eritmasi ustiga 5 ml 0,4 M L^1 etanoldagi eritmasi tomichilatib qoʻshildi. Eritma teskari sovutgich ulangan holatda 1,5 soat davomida magnitli aralashtirgichda aralashtirilib, T=70ºC da qaynatildi. Hosil boʻlgan qizgʻish-qoʻngʻir choʻkma filtrlab ajratib olindi, etanolda bir necha marta yuvildi va ochiq havoda quritildi. T$_s$=240°C. Unum 69%.
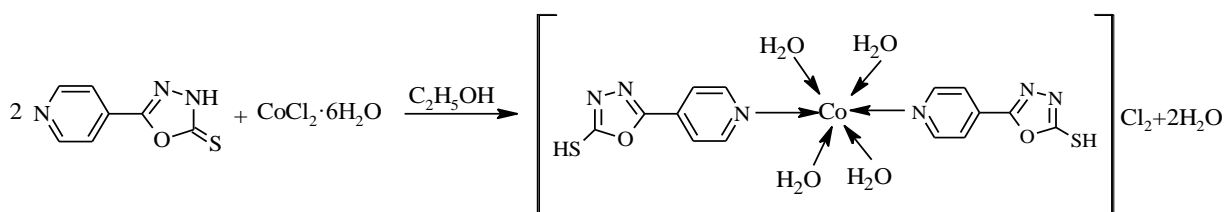
2.1-Sxema. L^1 ning CoCl$_2$·6H$_2$O bilan kompleks birikmasi sintezi

Zn^{2+}, Ni^{2+} va Cu^{2+} xlorid tuzlari ishtirokidagi sintez ham ushbu metodika boʻyicha quyidagi reaksiyaga muvofiq olib borildi (2.1-sxema).

2-Usul. 5 ml 0,4 M li L^1 ning etanoldagi eritmasiga KOH (0,01 M, 1 ml) suvli eritmasi qoʻshildi. CoCl$_2$·6H$_2$O ning 5 ml 0,2 M li etanoldagi eritmasi ustiga eritmasiga ligandning spirtli eritmasi tomchilatib qoʻshildi va teskari sovutgich ulangan holatda T=70ºC da 40 min magnitli aralashtirgichda aralashtirilib qaynatildi. Hosil boʻlgan toʻq qizil rangdagi choʻkma filtrlab ajratib olindi, etanolda bir necha marta yuvildi va ochiq havoda quritildi. T$_s$=251°C. Unum 76%.
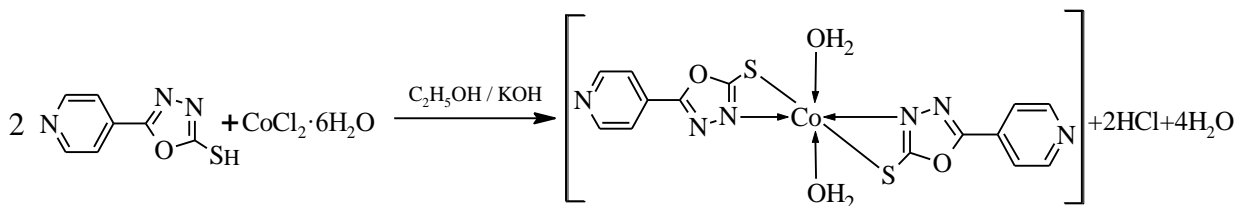
2.2-Sxema. L^1 ning CoCl$_2$·6H$_2$O bilan kompleks birikmasi sintezi

Zn^{2+}, Ni^{2+} va Cu^{2+} xlorid tuzlari ishtirokidagi sintez ham quyidagi reaksiyaga muvofiq olib borildi (2.2-sxema).

3-Usul. 5 ml 0,4 M li L^1 ning DMFA dagi eritmasiga Co(NO$_3$)$_2$·6H$_2$O ning 0,2 M li spirtli eritmasidan 5 ml tomchilatib qo‘shildi va teskari sovutgich ulangan holatda T=70°C da, 30 min davomida magnitli aralashtirgichda aralashtirilib qaynatildi. Hosil bo‘lgan to‘q qizil rangdagi mayda cho‘kma filtrlab olindi, bir necha marta etanolda yuvildi va ochiq havoda quritildi. T$_s$=220°C. Unum 75%.
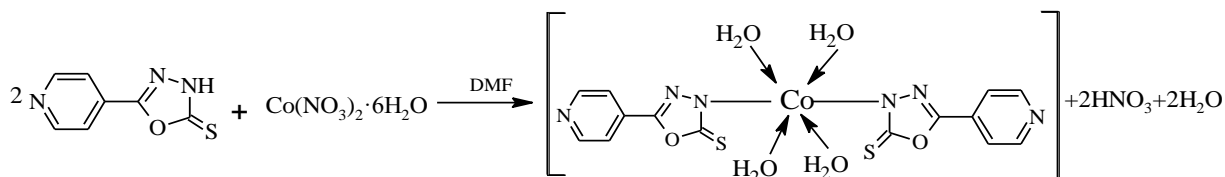
2.3-Sxema. L^1 ning Co(NO$_3$)$_2$·6H$_2$O bilan kompleks birikmasi sintezi

Zn^{2+}, Ni^{2+} va Cu^{2+} nitrat tuzlari ishtirokidagi sintez ham quyidagi reaksiyaga muvofiq olib borildi (2.3-sxema).

4-Usul. Co(OAc)$_2$·2H$_2$O ning 5 ml 0,2 M li spirtli eritmasiga 5 ml 0,4 M li L^1 ning etil spirtdagi eritmasi bir necha tomchi MEA tomichilatib qo‘shilgan eritmasi qo‘shildi. Eritma teskari sovutgich ulangan holatda 1soat davomida magnitli aralashtirgichda aralashtirilib qaynatildi. Hosil bo‘lgan oq-sarg‘ish cho‘kma filtrlab olindi, bir necha marta etanolda yuvildi va ochiq havoda quritildi. T$_s$=215°C. Unum 52%.
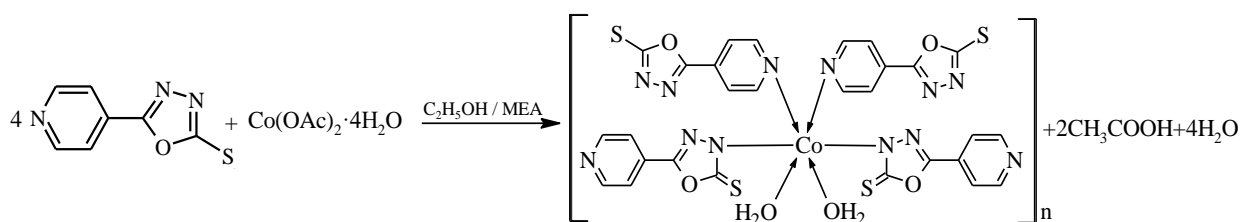
2.4-Sxema. L^1 ning Co(OAc)$_2$·4H$_2$O bilan kompleks birikmasi sintezi

Zn^{2+}, Ni^{2+} va Cu^{2+} atsetat tuzlari ishtirokidagi sintez ham quyidagi reaksiyaga muvofiq olib borildi (2.4-sxema).

Kompleks birikmalarni sintez qilishning 4 ta usuli batafsil tahlil qilinganda, ligandning tautomer shakliga erituvchilarning ta’sir qilishi o‘rganildi. Bunda L^{1,2} proton erituvchilarda tiol S-H holatda, aproton erituvchilarda esa tion C=S holatda bo‘lishi aniqlandi.

45

Proton erituvchilar:	Aproton erituvchilar:
$H_2O, CH_3OH, C_2H_5OH, HF, HCOOH$	$DMFA, DMSO, O(CH_2CH_2)_2O$

Etil spirti boshqa erituvchilarga nisbatan uchuvchanligining yaxshiligi va kristallanish uchun kamroq vaqt talab etilishini inobatga olgan holda, keyingi sintezlar (2.2-sxema) asosida olib borildi.

NH_4VO_3 ning L^1 bilan hosil qilgan kompleks birikmasi sintezi:

Vanadiyli $[V_4O_{12}](L^1+H)_4$ tarkibli kompleks birikmaning sintezi suvli spirtli muhitda olib borilib, V:L 1:1 molyar nisbatda 5 ml 0,2 M li NH_4VO_3 ning suvli eritmasiga 5ml 0,2 M li L^1 ligandning spirtli eritmasi qo'shildi (pH=6-8).

Reaksiya T=70ºC da 20 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan och yashil rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida quritildi. Mahsulot unumi 64%. $T_s = 184-185^OC$ (2.5-sxema).
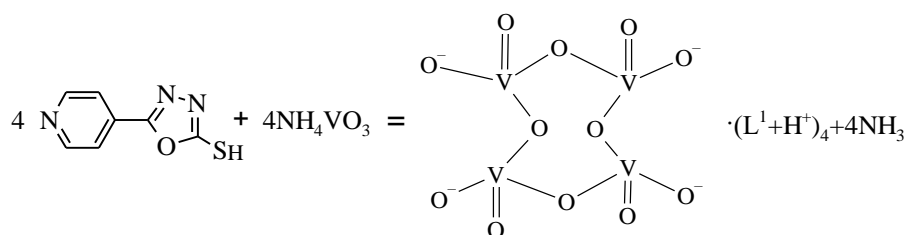
2.5-Sxema. NH_4VO_3 ning L^1 bilan kompleks birikmasi sintezi

L^1 asosida geterometalli kompleks birikmalarning sintezi:

$[Co_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ tarkibli geterometalli kompleks birikmaning sintezi uchun 5ml 0,4M li ammoniy vanadatning suvli eritmasiga 5ml 0,4M li L^1 ligandning spirtli eritmasi qo'shildi va uning ustiga 5ml 0,2 M li Co^{2+} xloridning spirtli eritmasi ($M:VO_2^+:L^1$=1:2:2 mol nisbatda) qo'shildi, pH=6-8. Reaksiya T=70ºC da 40 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan to'q yashil rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida ochiq havoda quritildi. Mahsulot unumi 71%, T_{suyuq}=196-197°C ni tashkil qildi (2.6-sxema).
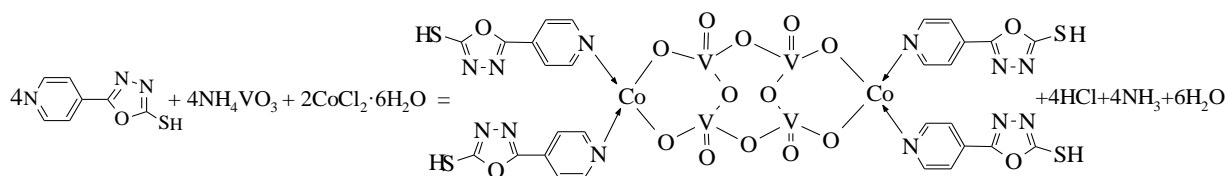
2.6-Sxema. L^1 ning CoCl$_2$·6H$_2$O bilan geterometalli kompleks birikmasi sintezi

L^1 ning boshqa Zn^{2+}, Ni^{2+} va Cu^{2+} metall xloridlari bilan yuqoridagi 2.6-sxemadagi reaksiya tenglamasiga muvofiq geterometalli kompleks birikmalarining sintezi amalga oshirildi.

2.2.2. Co^{2+}, Ni^{2+}, Cu^{2+} va Zn^{2+} larning L^2 asosidagi kompleks birikmalar sintezi

L^2 asosida gomometalli kompleks birikmalarning sintezi:

5 ml 0,4 M li L^1 ning etanoldagi eritmasiga KOH (0,01 M, 1 ml) suvli eritmasi qo'shildi. CoCl$_2$·6H$_2$O ning 5 ml 0,2 M li etanoldagi eritmasi ustiga eritmasiga ligandning spirtli eritmasi tomchilatib qo'shildi va teskari sovutgich ulangan holatda T=70ºC da 40 min magnitli aralashtirgichda aralashtirilib qaynatildi. Hosil bo'lgan oq rangdagi cho'kma filtrlab ajratib olindi, etanolda bir necha marta yuvildi va ochiq havoda quritildi. Qurigan cho'kma DMFA:atseton (1:1) erituvchilarida qayta kristallandi, 7 kundan so'ng oq sarg'ish mayda kristallar ajratib olindi. T_s=343-344°C. Unum 49%.
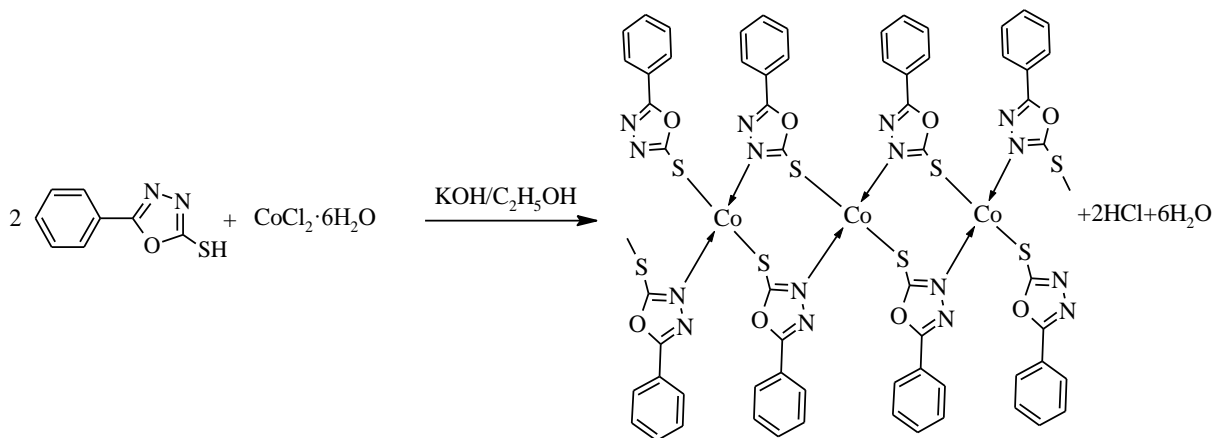
2.7-Sxema. L^2 ning CoCl$_2$·6H$_2$O bilan kompleks birikmasi sintezi

L^2 ning boshqa Zn^{2+}, Ni^{2+} va Cu^{2+} metall xloridlari bilan yuqoridagi 2.7-sxema reaksiya tenglamasiga muvofiq amalga oshirildi.

NH$_4$VO$_3$ ning L^2 bilan hosil qilgan kompleks birikmasi sintezi:

Vanadiyli $[V_4O_{12}](L^2+H)_4$ tarkibli kompleks birikmaning sintezi suvli spirtli muhitda olib borilib, VO_2^+:L=1:1 molyar nisbatda 5 ml 0,2 M li NH_4VO_3 ning suvli eritmasiga 5ml 0,2 M li L^2 ligandning spirtli eritmasi qo'shildi (pH=6-8).

Reaksiya T=70°C da 20 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan och yashil rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida quritildi. Mahsulot unumi 80%. T_s = 149-150°C (2.8-sxema).
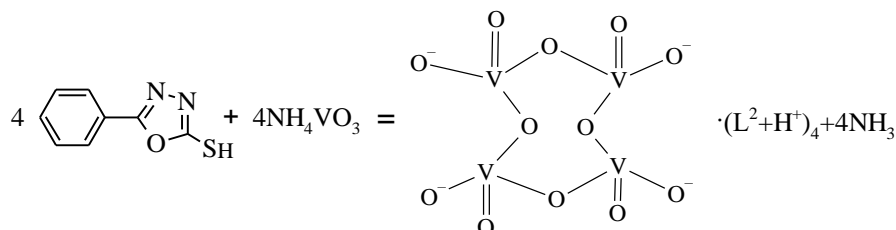
2.8-Sxema. NH_4VO_3 ning L^2 bilan kompleks birikmasi sintezi.

L^2 asosida geterometalli kompleks birikmalarning sintezi:

$[Co_2V_4O_{12}(L^2)_4]\cdot 2H_2O$ tarkibli geterometalli kompleks birikmaning sintezi uchun 5ml 0,4M li ammoniy vanadatning suvli eritmasiga 5ml 0,4M li L^2 ligandning spirtli eritmasi qo'shildi va uning ustiga 5ml 0,2 M li Co^{2+} xloridning spirtli eritmasi (M:VO_2^+:L^2=1:2:2 mol nisbatda) qo'shildi, pH=6-8. Reaksiya T=70°C da 40 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan to'q ko'k rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida ochiq havoda quritildi. Mahsulot unumi 67%, T_{suyuq}=188-189°C ni tashkil qildi (2.9-sxema).
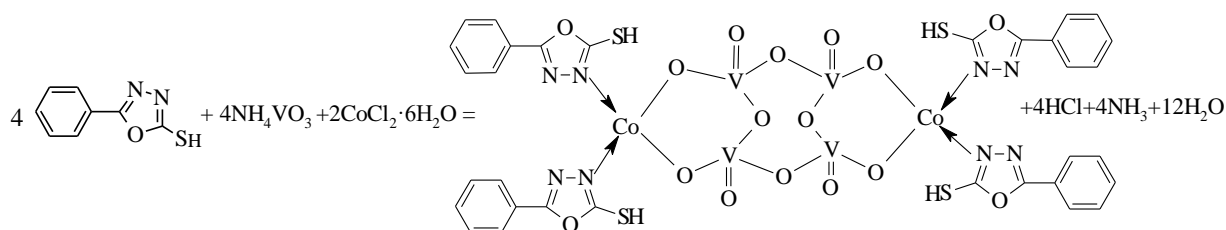
2.9-Sxema. L^2 ning $CoCl_2\cdot 6H_2O$ bilan geterometalli kompleks birikmasi sintezi

L^2 ning boshqa Zn^{2+}, Ni^{2+} va Cu^{2+} metall xloridlari bilan yuqoridagi 2.9-sxemadagi reaksiya tenglamasiga muvofiq geterometalli kompleks birikmalarining sintezi amalga oshirildi.

2.2.3. Co^{2+}, Ni^{2+}, Cu^{2+} va Zn^{2+} larning L^3 asosidagi kompleks birikmalar sintezi

L^3 asosida olib borilgan gomometalli kompleks birikmalarning sintezi:

5 ml 0,4 M li L^1 ning etanoldagi eritmasiga KOH (0,01 M, 1 ml) suvli eritmasi qo'shildi. CoCl$_2$·6H$_2$O ning 5 ml 0,2 M li etanoldagi eritmasi ustiga eritmasiga ligandning spirtli eritmasi tomchilatib qo'shildi va teskari sovutgich ulangan holatda T=70ºC da 40 min magnitli aralashtirgichda aralashtirilib qaynatildi. Hosil bo'lgan to'q jigarrang rangdagi cho'kma filtrlab ajratib olindi, etanolda bir necha marta yuvildi va ochiq havoda quritildi. T$_s$=178-179°C. Unum 49%.
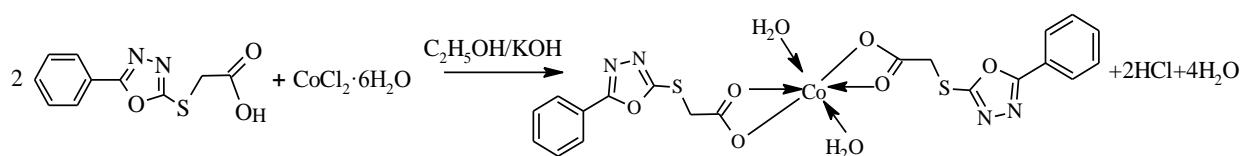
2.10-Sxema. L^3 ning CoCl$_2$·6H$_2$O bilan kompleks birikmasi sintezi

L^3 ning boshqa Zn^{2+}, Co^{2+} va Cu^{2+} metall xloridlari bilan yuqoridagi 2.10-sxemadagi reaksiya tenglamasiga muvofiq amalga oshirildi.

NH$_4$VO$_3$ ning L^3 bilan hosil qilgan kompleks birikmasi sintezi:

Vanadiyli [V$_4$O$_{12}$](L^3+H)$_4$ tarkibli kompleks birikmaning sintezi suvli spirtli muhitda olib borilib, V:L 1:1 molyar nisbatda 5 ml 0,2 M li NH$_4$VO$_3$ ning suvli eritmasiga 5ml 0,2 M li L^3 ligandning spirtli eritmasi qo'shildi (pH=6-8).

Reaksiya T=70ºC da 20 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan to'q sariq rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida quritildi. Mahsulot unumi 65%. T$_s$ = 149-150°C (2.11-sxema).
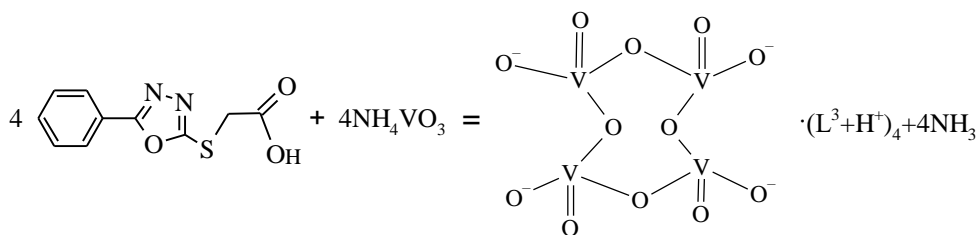
2.11-Sxema. NH_4VO_3 ning L^3 bilan kompleks birikmasi sintezi

L^3 asosida geterometalli kompleks birikmalarning sintezi:

$[Co_2V_4O_{12}(L^3)_4]\cdot 2H_2O$ tarkibli geterometalli kompleks birikmaning sintezi uchun 5ml 0,4M li ammoniy vanadatning suvli eritmasiga 5ml 0,4M li L^2 ligandning spirtli eritmasi qo'shildi va uning ustiga 5ml 0,2 M li Co^{2+} xloridning spirtli eritmasi ($M:VO_2^+:L^3=1:2:2$ mol nisbatda) qo'shildi, pH=6-8. Reaksiya $T=70^oC$ da 40 minut davomida suv hammomida magnitli aralashtirgichda aralashtirilib qaynatish bilan olib borildi. Hosil bo'lgan to'q ko'k rangdagi cho'kma issiq holatda filtrlab olindi va bir necha bor etanolda yuvildi va xona haroratida ochiq havoda quritildi. Mahsulot unumi 61%, $T_{suyuq}=174-175°C$ ni tashkil qildi (2.12-sxema).
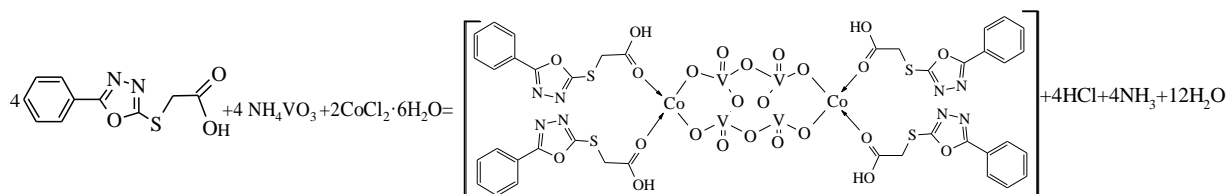
2.12-Sxema. L^3 ning $CoCl_2\cdot 6H_2O$ bilan geterometalli kompleks birikmasi sintezi

L^3 ning boshqa Zn^{2+}, Ni^{2+} va Cu^{2+} metall xloridlari bilan yuqoridagi 2.12-sxemadagi reaksiya tenglamasiga muvofiq geterometalli kompleks birikmalarining sintezi amalga oshirildi.

Sintez qilingan koordinatsion birikmalarning hosil bo'lish unumi, suyuqlanish xarorati, Brutto formulasi hamda turli erituvchilardagi eruvchanligi 2.2-2.9 jadvallarda keltirilgan.

2.3-§. Kompleks birikmalar tarkibidagi elementlar miqdorini SEM – EDT va rentgenofluoressent tahlil usullari bilan aniqlash

Moddalar tarkibidagi elementlar miqdorini energiya dispersion tahlil (EDT) skanerlovchi elektron mikroskop (SEM) yordamida aniqlash materiallarni tahlil

qilish uchun yuqori axborot mazmuni va olingan tadqiqot natijalarining ishonchliligi tufayli aniq ilmiy texnologik muammolarni hal qilishda keng qo'llaniladi [123].

Hosil bo'lgan kompleks birikmalardagi azot, kislorod va metallarning miqdorlarini SEM-EDT usulida aniqlandi (2.2-2.3-jadvallar). SEM-EDT natijasida olingan ma'lumotlar asosida shunday xulosaga kelish mumkinki, ligandlar bilan metall ionlarining koordinatsiyalanishi ligandlar mikrostrukturasining o'zgarishiga olib keladi, xususan, uni ko'plab metall cho'qqilar qayd etildi, bu esa EDT tomonidan tasdiqlandi (2.1-2.5 rasmlar)[124].
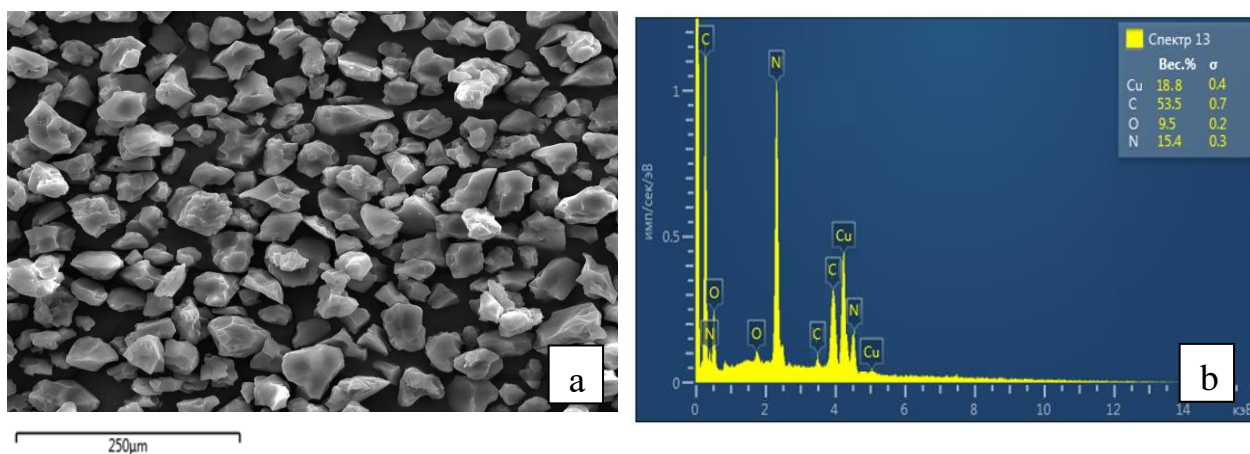
2.1-Rasm. $[Cu(L^1)_2(H_2O)_2]$ mikrostrukturasi (a) va EDT natijasi (b)
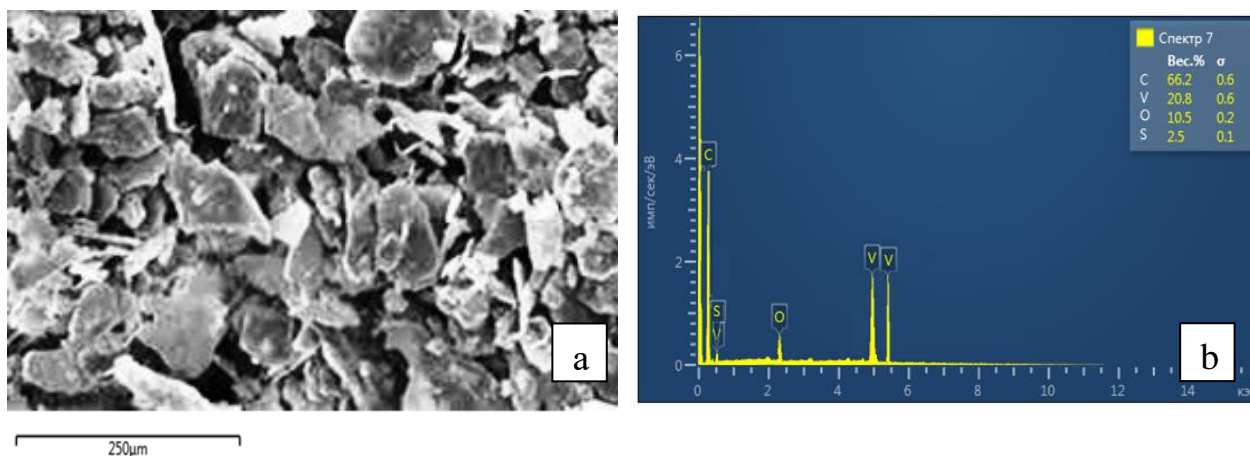
2.2-Rasm. $[V_4O_{12}](L^1+H)^+_4$ mikrostrukturasi (a) va EDT natijasi (b)
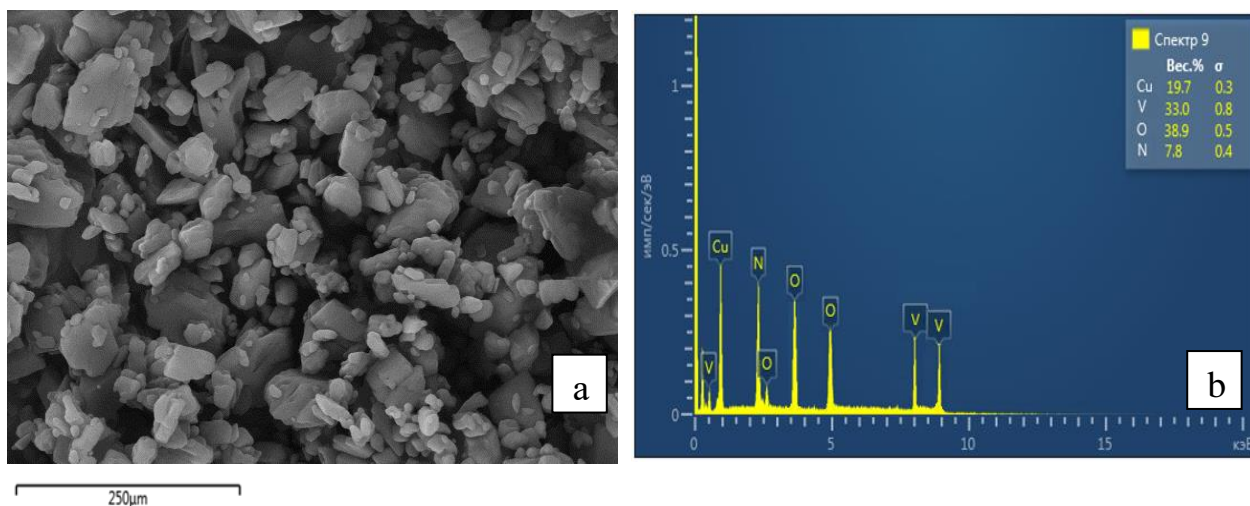
2.3-Rasm. $[Cu_2V_4O_{12}(L^1)_4]·2H_2O$ mikrostrukturasi (a) va EDT natijasi (b)
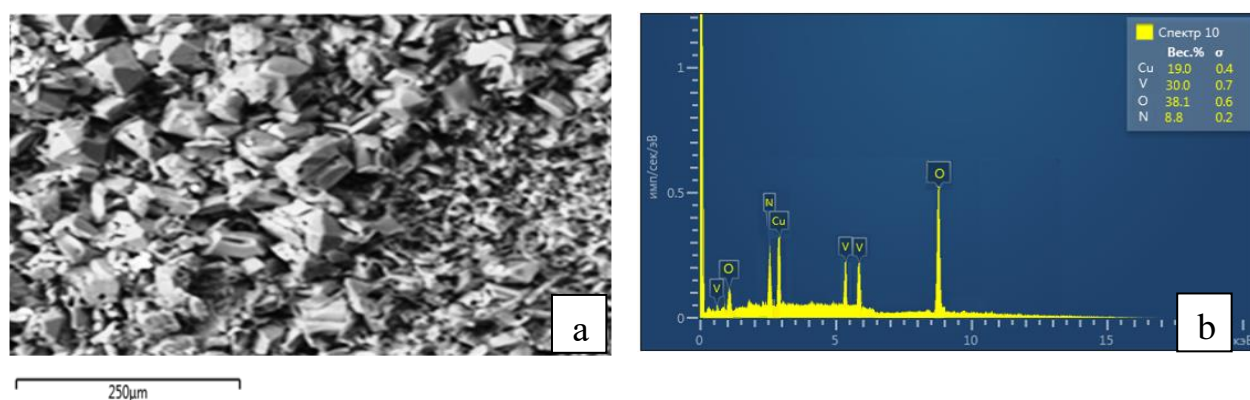
2.4-Rasm. $[Cu_2V_4O_{12}(L^2)_4]·2H_2O$ mikrostrukturasi (a) va EDT natijasi (b)
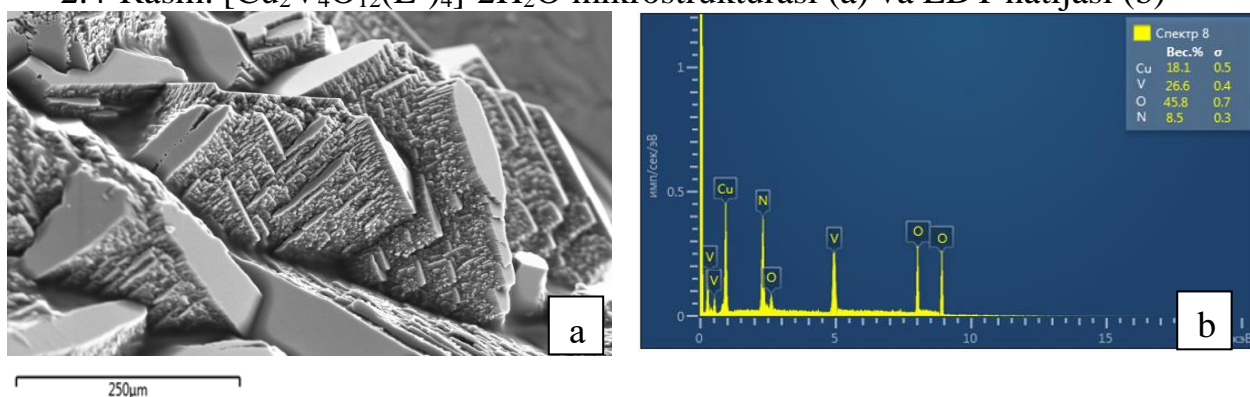
2.5-Rasm. $[Cu_2V_4O_{12}(L^3)_4]·2H_2O$ mikrostrukturasi (a) va EDT natijasi (b)

Rentgenofluoressent tahlil moddaning elementar tarkibi, ya'ni element analiz tahlilini olish uchun qo'llaniladigan zamonaviy spektroskopik usullardan biri [125, 126].

Sintez qilingan koordinatsion birikmalar tarkibidagi metallarning mol nisbatlarini aniqlash maqsadida rentgenofluoressent tahlil amalga oshirildi (2.6-rasm; 2.1-jadval).

$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$, $[Cu_2V_4O_{12}(L^2)_4]\cdot 2H_2O$ va $[Cu_2V_4O_{12}(L^3)_4]\cdot 2H_2O$ kompleks

birikmalarining rentgenofluoressent tahlil usuli bo'yicha olingan natijalar

№	Birikmalar	Cu (%)	V (%)	S (%)	Mol nisbat
1	$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	4,3	8,36	5,5	1:2:2
2	$[Cu_2V_4O_{12}(L^2)_4]\cdot 2H_2O$	4,6	8,2	3,5	1:2:2
3	$[Cu_2V_4O_{12}(L^3)_4]\cdot 2H_2O$	8,6	10,8	6,8	1:2:1
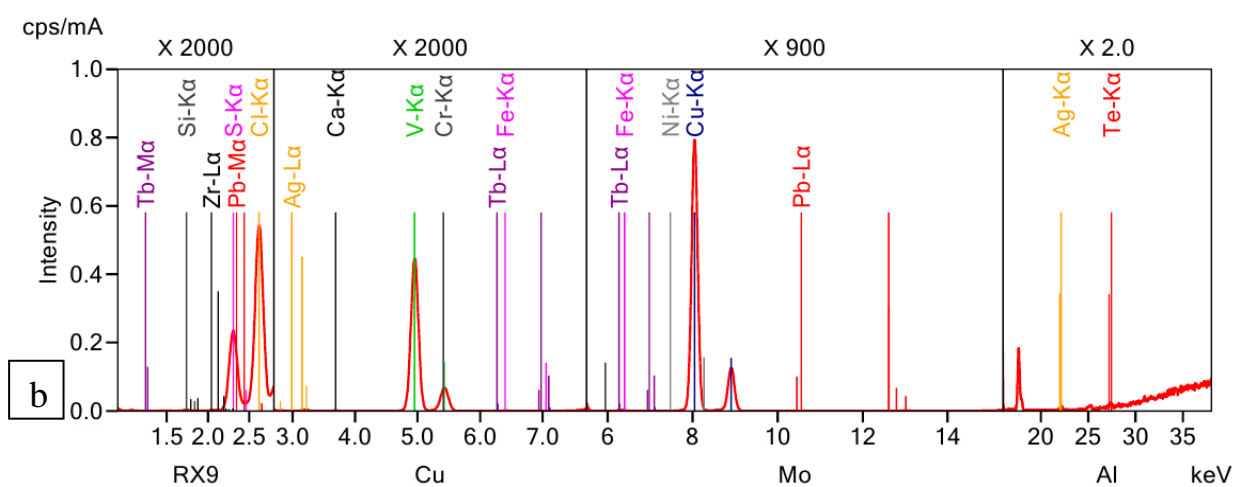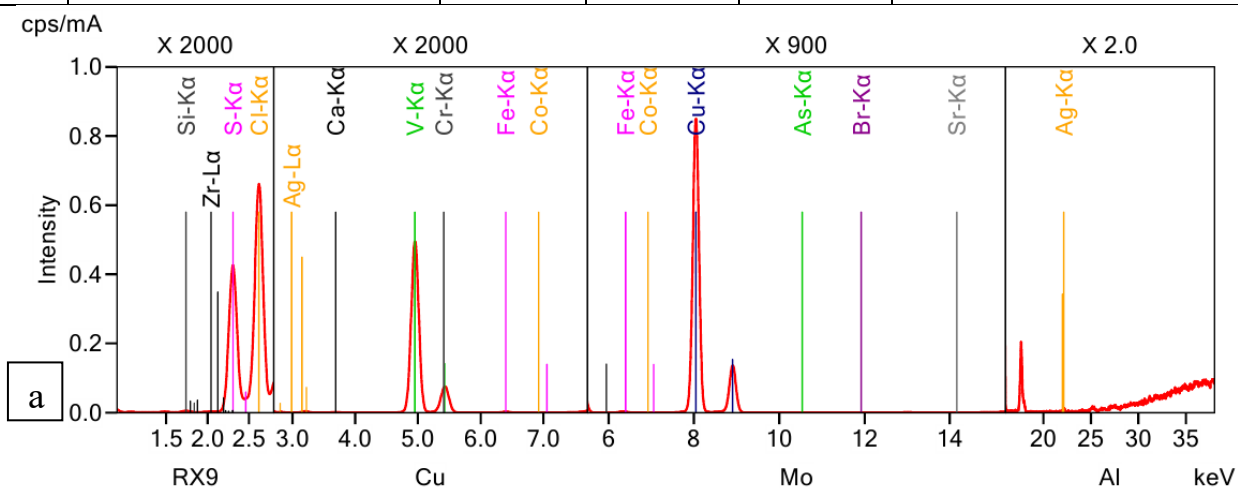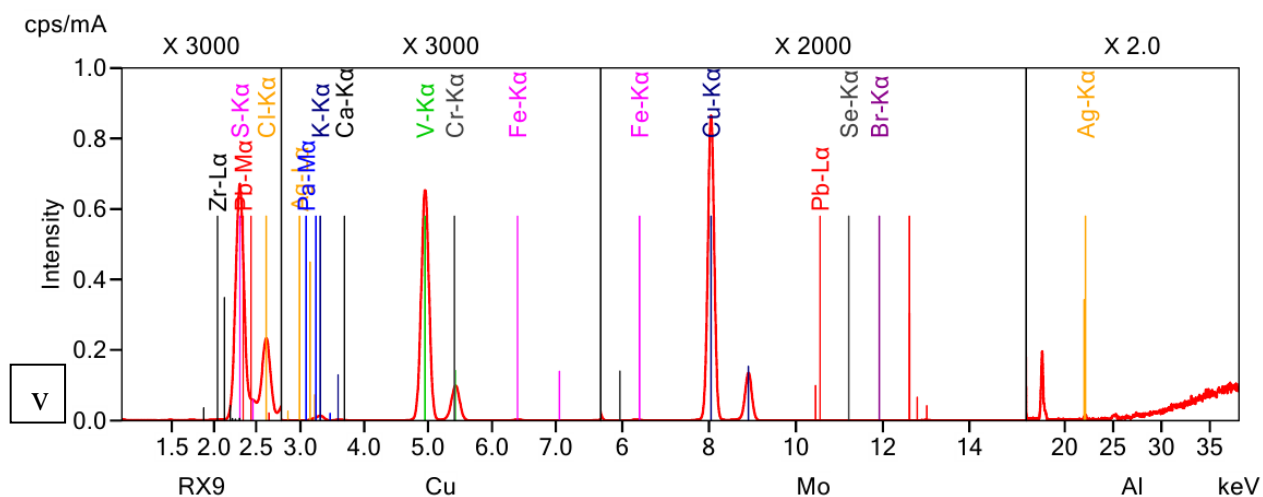
2.6-Rasm. $[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ (a), $[Cu_2V_4O_{12}(L^2)_4]\cdot 2H_2O$ (b) va $[Cu_2V_4O_{12}(L^3)_4]\cdot 2H_2O$ (v) kompleks birikmalarining rentgenofluoressent tahlil usuli bo'yicha olingan spektrlar

Ushbu 2.6-rasm va 2.1-jadvalda rentgenofluoressent tahlil natijalari keltirilgan bo'lib, koordinatsion birikmalar tarkibidagi M:V:S larning foizlari taqqoslanib, 1:2:2 nisbatda birikkanligi aniqlandi.

L^1 ligand asosida sintez qilingan gomometalli kompleks birikmalarning xarakteristikasi

Erituvchi	Birikma	Rangi	Unum %	Topildi, %				Hisoblandi, %				
				C	H	N	M	Brutto formula	C	H	N	M
	L^1	Sariq	-	46,92	2,81	23,45		C$_7$H$_5$N$_3$OS	47,16	2,93	23,76	
C$_2$H$_5$OH (Cl$^-$)	[Ni(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	To'q yashil	80	31,89	4,15	15,97	11,14	NiC$_{14}$H$_{22}$N$_6$O$_8$S$_2$	32,0	4,19	16,0	11,23
	[Co(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	Qizil qo'ng'i	69	31,75	4,17	15,64	11,20	CoC$_{14}$H$_{22}$N$_6$O$_8$S$_2$	32,0	4,19	16,0	11,23
	[Zn(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	Och sariq	74	31,60	4,11	15,73	12,19	ZnC$_{14}$H$_{22}$N$_6$O$_8$S$_2$	31,63	4,14	15,82	12,24
	[Cu(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	Jigarrang	80	31,65	4,11	15,79	12,03	CuC$_{14}$H$_{22}$N$_6$O$_8$S$_2$	31,69	4,15	15,85	12,07
C$_2$H$_5$OH /KOH(Cl$^-$)	[Ni(L^1)$_2$(H$_2$O)$_2$]	To'q yashil	71	37,0	1,73	18,0	13,1	NiC$_{14}$H$_8$N$_6$O$_4$S$_2$	37,1	1,76	18,5	13,0
	[Co(L^1)$_2$(H$_2$O)$_2$]	To'q qizil	76	37,1	1,75	18,6	12,9	CoC$_{14}$H$_8$N$_6$O$_4$S$_2$	37,1	1,76	18,5	13,1
	[Zn(L^1)$_2$(H$_2$O)$_2$]	Novotrang	83	36,4	1,71	18,12	14,0	ZnC$_{14}$H$_8$N$_6$O$_4$S$_2$	36,6	1,74	18,3	14,2
	[Cu(L^1)$_2$(H$_2$O)$_2$]	Qo'ng'ir	88	36,2	1,79	18,33	14,5	CuC$_{14}$H$_8$N$_6$O$_4$S$_2$	36,7	1,78	18,4	14,4
DMF (NO$_3^-$)	[Ni(L^1)$_2$(H$_2$O)$_4$]	Och yashil	73	34,43	3,21	17,12	12,07	NiC$_{14}$H$_{16}$N$_6$O$_6$S$_2$	34,49	3,29	17,25	12,11
	[Co(L^1)$_2$(H$_2$O)$_4$]	Pushti	75	34,39	3,23	17,18	12,03	CoC$_{14}$H$_{16}$N$_6$O$_6$S$_2$	34,49	3,29	17,25	12,11
	[Zn(L^1)$_2$(H$_2$O)$_4$]	Sariq	73	39,97	3,20	17,01	13,11	ZnC$_{14}$H$_{16}$N$_6$O$_6$S$_2$	34,07	3,24	17,04	13,18
	[Cu(L^1)$_2$(H$_2$O)$_4$]	To'q qizil	79	34,08	3,21	17,03	12,97	CuC$_{14}$H$_{16}$N$_6$O$_6$S$_2$	34,14	3,25	17,07	13,01
C$_2$H$_5$OH / MEA (CH$_3$COO$^-$)	{[Ni(L^1)$_4$(H$_2$O)$_2$]}$_n$	Och yashil	60	41,49	2,69	20,78	7,23	NiC$_{28}$H$_{22}$N$_{12}$O$_6$S$_4$	41,54	2,74	20,76	7,25
	{[Co(L^1)$_4$(H$_2$O)$_2$]}$_n$	To'q sariq	52	41,52	2,71	20,72	7,18	CoC$_{28}$H$_{22}$N$_{12}$O$_6$S$_4$	41,54	2,74	20,76	7,25
	{[Zn(L^1)$_4$ (H$_2$O)$_2$]}$_n$	Sariq	51	41,18	2,63	20,50	8,00	ZnC$_{28}$H$_{22}$N$_{12}$O$_6$S$_4$	41,20	2,72	20,59	8,01
	{[Cu(L^1)$_4$ (H$_2$O)$_2$]}$_n$	To'q sariq	62	41,27	2,68	20,59	7,74	CuC$_{28}$H$_{22}$N$_{12}$O$_6$S$_4$	41,30	2,72	20,64	7,8

Ligandlar (L^1, L^2, L^3) va sintez qilingan gomometalli kompleks birikmalarning xarakteristikasi

Birikma	Unum %	Rangi	Suyuq. har. ^{0}C	Brutto formula	Topilgan / hisoblangan, %			
					C	O	N	M
L^1-$C_7H_5N_3OS$	-	Och sariq	268-270	$C_7H_5N_3OS$	47,1/46,9	17,4/ 17,87	23,22/23,46	-
$[Ni(L^2)_2(H_2O)_2]$	71	To'q yashil	242	$C_{14}H_8N_6O_4S_2Ni$	37,0/37,1	1,73/1,76	18,0/18,5	13,0/13,0
$[Co(L^1)_2(H_2O)_2]$	76	To'q qizil	221	$C_{14}H_8N_6O_4S_2Co$	37,1/37,1	1,75/1,76	18,6/18,5	12,9/13,1
$[Zn(L^1)_2(H_2O)_2]$	83	Novotrang	239	$C_{14}H_8N_6O_4S_2Zn$	36,4/6,6	1,71/1,74	18,12/18,3	14,0/14,2
$[Cu(L^1)_2(H_2O)_2]$	88	Qo'ng'ir	268	$C_{14}H_8N_6O_4S_2Cu$	36,236,7	1,791,78	18,33/18,4	14,5/14,4
$[V_4O_{12}](L^1 +H^+)_4$	64	Och yashil	250-251	$C_{28}H_{20}N_{12}O_{16}S_4V_4$	30,20/30,21	11,46/11,51	14,97/15,10	18,30/18,34
L^2- $C_8H_6N_2OS$	-	Oq	223-224	$C_8H_6N_2OS$	40,8/ 40,4	16,4/17,9	15,1/15,7	-
$[Co(L^2)_2]$	73	To'q qizil	225-226	$C_{16}H_{12}N_4O_2S_2Co$	55,0/56,6	8,9/9,4	14,7/16,5	12,8/17,4
$[Cu(L^2)_2]$	69	Qo'ng'ir	280-281	$C_{16}H_{12}N_4O_2S_2Cu$	53,5/55,8	9,5/9,3	15,4/16,27	18,8/18,6
$[Ni(L^2)_2]$	51	To'q yashil	245-246	$C_{16}H_{12}N_4O_2S_2Ni$	29,5/56,6	4,8/9,4	9,8/16,5	16,3/17,4
$[Zn(L^2)_2]$	79	Oq	343-344	$C_{16}H_{12}N_4O_2S_2Zn$	51,2/55,6	8,3/9,27	16,1/16,23	17,9/18,8
$[V_4O_{12}](L^2+H^+)_4$	80	Och yashil	196-197	$C_{32}H_{28}N_8O_{16}S_4V_4$	66,2/64,9	10,5/11,4	2,5/2,8	20,8/20,5
L^3- $C_{10}H_8N_2O_3S$	-	Oq	117-118	$C_{10}H_8N_2O_3S$	50,8/ 50,2	13,6/13,5	11,9/11,7	-
$[Co(L^3)_2(H_2O)_2]$	56	To'q qizil	167-168	$C_{20}H_{14}N_4O_6S_2Cl_2Co$	40,0/38,9	10,7/10,3	9,3/8,9	9,8/9,0
$[Cu(L^3)_2(H_2O)_2]$	62	Qo'ng'ir	190-191	$C_{20}H_{14}N_4O_6S_2Cl_2Cu$	39,6/39,0	10,5/10,3	9,3/9,2	10,6/10,3
$[Ni(L^3)_2(H_2O)_2]$	49	Yashil	178-179	$C_{20}H_{14}N_4O_6S_2Cl_2Ni$	40,0/39,4	10,7/10,5	9,3/8,7	9,8/9,4
$[Zn(L^3)_2(H_2O)_2]$	53	Sariq	204-205	$C_{20}H_{14}N_4O_6S_2Cl_2Zn$	39,5/39,1	10,6/10,5	9,5/9,1	10,5/10,7
$[V_4O_{12}](L^3+H^+)_2$	65	To'q sariq	149-150	$C_{40}H_{36}N_8O_{24}S_4V_4$	35,71/ 35,0	9,52/ 9,50	8,33/ 8,8	15,17/15,04

Sintez qilingan geterometalli kompleks birikmalarning xarakteristikasi

Birikma	Unum %	Rangi	Suyuq. har. ^{0}C	Brutto formula	Topilgan / hisoblangan, %			
					O	N	V	M
L^1-$C_7H_5N_3OS$	-	Och sariq	268-270	$C_7H_5N_3OS$	47,1/46,9	17,4/17,87	23,22/23,46	-
$[Co_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	71	To'q qizil	196-197	$C_{28}H_{16}N_{12}O_{16}S_4V_4Co_2$	34,12/34,31	21,82/22,52	26,48/27,34	15,47/15,81
$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	78	Qo'ng'ir	244-245	$C_{28}H_{16}N_{12}O_{16}S_4V_4Cu_2$	33,27/33,86	20,24/22,22	26,39/26,98	16,27/16,93
$[Ni_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	59	To'q yashil	266-267	$C_{28}H_{16}N_{12}O_{16}S_4V_4Ni_2$	33,92/34,31	22,21/22,52	27,11/27,34	15,13/15,81
$[Zn_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	72	Och yashil	258-259	$C_{28}H_{16}N_{12}O_{16}S_4V_4Zn_2$	10,29/10,30	13,26/13,29	16,40/16,43	10,30/10,32
L^2- $C_8H_6N_2OS$	-	Oq	223-224	$C_8H_6N_2OS$	16,4/17,9	15,1/15,7	-	-
$[Co_2V_4O_{12}(L^2)_4]\cdot 2H_2O$	67	Ko'k	188-189	$C_{32}H_{24}N_8O_{16}S_4V_4Co_2$	36,8/37,1	16,10/16,23	28,40/29,56	16,50/17,1
$[Cu_2V_4O_{12}(L^2)_4]\cdot 2H_2O$	83	To'q yashil	224-226	$C_{32}H_{24}N_8O_{16}S_4V_4Cu_2$	38,9/39,75	7,8/8,69	33,0/31,67	19,70/19,87
$[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O$	74	To'q sariq	174-175	$C_{32}H_{24}N_8O_{16}S_4V_4Ni_2$	35,9/37,04	16,17/16,12	29,33/29,42	16,81/17,0
$[Zn_2V_4O_{12}(L^2)_4]\cdot 2H_2O$	71	Sarg'ish	184-185	$C_{32}H_{24}N_8O_{16}S_4V_4Zn_2$	31,42/36,46	14,83/15,95	21,78/29,05	15,37/18,85
L^3- $C_{10}H_8N_2O_3S$	-	Oq	117 -118	$C_{10}H_8N_2O_3S$	13,6/13,5	11,9/11,7	-	-
$[Co_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	61	Pushti	174-175	$C_{40}H_{36}N_8O_{26}S_4V_4Co_2$	48,57/48,94	12,58/13,17	23,74/24,0	12,90/13,88
$[Cu_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	84	Qo'ng'ir	227-228	$C_{40}H_{36}N_8O_{26}S_4V_4Cu_2$	48,51/48,37	13,0/13,02	23,06/23,27	14,51/14,88
$[Ni_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	68	Och yashil	180-181	$C_{40}H_{36}N_8O_{26}S_4V_4Ni_2$	48,22/48,92	12,66/13,09	23,92/23,98	13,70/13,84
$[Zn_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	59	Sariq	230-231	$C_{40}H_{36}N_8O_{26}S_4V_4Zn_2$	48,19/48,25	12,67/12,99	23,44/23,66	14,99/15,08

L^1 ligand asosida sintez qilingan gomometalli kompleks birikmalarning eruvchanligi

Erituvchi	Birikma	Suv	Metanol	Etanol	Xloroform	DMFA
	L^1	EM	E	E	OE	E
C$_2$H$_5$OH (Cl$^-$)	$[Ni(L^1)_2 (H_2O)_4]*2H_2O$	Э	E	E	OE	E
	$[Co(L^1)_2 (H_2O)_4]*2H_2O$	Э	E	E	OE	E
	$[Zn(L^1)_2 (H_2O)_4]*2H_2O$	Э	E	E	OE	E
	$[Cu(L^1)_2 (H_2O)_4]*2H_2O$	OE	OE	OE	EM	E
C$_2$H$_5$OH /КOH(Cl$^-$)	$[Ni(L^1)_2(H_2O)_2]$	E	E	E	OE	E
	$[Co(L^1)_2(H_2O)_2]$	E	E	E	OE	E
	$[Zn(L^1)_2(H_2O)_2]$	E	E	E	OE	E
	$[Cu(L^1)_2(H_2O)_2]$	OE	OE	OE	EM	E
DMF (NO$_3^-$)	$[Ni(L^1)_2 (H_2O)_4]$	OE	OE	E	OE	E
	$[Co(L^1)_2 (H_2O)_4]$	OE	OE	E	OE	E
	$[Zn(L^1)_2 (H_2O)_4]$	OE	E	E	OE	E
	$[Cu(L^1)_2 (H_2O)_4]$	OE	OE	OE	EM	E
C$_2$H$_5$OH / MEA (CH$_3$COO$^-$)	$\{[Ni(L^1)_4(H_2O)_2]\}_n$	E	E	E	OE	E
	$\{[Co(L^1)_4 (H_2O)_2]\}_n$	E	E	E	OE	E
	$\{[Zn(L^1)_4 (H_2O)_2]\}_n$	OE	E	E	OE	E
	$\{[Cu(L^1)_4 (H_2O)_2]\}_n$	OE	OE	OE	EM	OE

Izoh: E. – Eriydi, OE. –Oz eriydi, EM – Erimaydi

Ligandlar (L^1, L^2, L^3) va sintez qilingan gomometalli kompleks birikmalarning eruvchanligi

Birikmalar (Dipol momenti)	Suv (1,83 D)	Metanol (1,65 D)	Etanol (1,7 D)	Xloroform (1,01 D)	DMFA (3,82 D)
L^{1-} (2,876 D)	EM	E	E	OE	E
$[Ni(L^1)_2(H_2O)_2]$	E	E	E	OE	E
$[Co(L^1)_2(H_2O)_2]$	OE	E	E	OE	E
$[Zn(L^1)_2(H_2O)_2]$	E	E	E	OE	E
$[Cu(L^1)_2(H_2O)_2]$	OE	E	E	EM	E
$[V_4O_{12}](L^1 + H^+)_4$	E	OE	OE	EM	E
L^2 - (2,667 D)	EM	E	E	OE	E
$[Co(L^2)_2]$	E	E	E	EM	E
$[Cu(L^2)_2]$	OE	OE	OE	EM	E
$[Ni(L^2)_2]$	E	E	E	EM	E
$[Zn(L^2)_2]$	E	E	E	EM	E
$[V_4O_{12}](L^2 + H^+)_4$	E	OE	OE	EM	E
L^3 - (3,944 D)	EM	E	E	EM	E
$[Co(L^3)_2(H_2O)_2]$	E	E	E	EM	E
$[Cu(L^3)_2(H_2O)_2]$	OE	OE	OE	EM	E
$[Ni(L^3)_2(H_2O)_2]$	E	E	E	OE	E
$[Zn(L^3)_2(H_2O)_2]$	E	E	E	OE	E
$[V_4O_{12}](L^3 + H^+)_2$	E	OE	OE	EM	E

Izoh: E. – Eriydi, OE. –Oz eriydi, EM – Erimaydi

Sintez qilingan geterometalli kompleks birikmalarning eruvchanligi

Birikmalar (Dipol momenti)	Suv (1,83 D)	Metanol (1,65 D)	Etanol (1,7 D)	Xloroform (1,01 D)	DMFA (3,82 D)
L^{1-} (2,876 Д)	EM	E	E	OE	E
$[Co_2V_4O_{12}(L^1)_4] \cdot 2H_2O$	E	E	E	EM	E
$[Cu_2V_4O_{12}(L^1)_4] \cdot 2H_2O$	OE	E	E	EM	E
$[Ni_2V_4O_{12}(L^1)_4] \cdot 2H_2O$	E	E	E	EM	E
$[Zn_2V_4O_{12}(L^1)_4] \cdot 2H_2O$	E	E	E	EM	E
L^{2-} (2,667 Д)	EM	E	E	OE	E
$[Co_2V_4O_{12}(L^2)_4] \cdot 2H_2O$	OE	E	E	EM	E
$[Cu_2V_4O_{12}(L^2)_4] \cdot 2H_2O$	OE	E	E	EM	E
$[Ni_2V_4O_{12}(L^2)_4] \cdot 2H_2O$	E	E	E	EM	E
$[Zn_2V_4O_{12}(L^2)_4] \cdot 2H_2O$	E	E	E	EM	E
L^{3-} (3,944 Д)	EM	E	E	EM	E
$[Co_2V_4O_{12}(L^3)_2] \cdot 2H_2O$	E	E	E	EM	E
$[Cu_2V_4O_{12}(L^3)_2] \cdot 2H_2O$	OE	E	E	EM	E
$[Ni_2V_4O_{12}(L^3)_2] \cdot 2H_2O$	E	E	E	EM	E
$[Zn_2V_4O_{12}(L^3)_2] \cdot 2H_2O$	E	E	E	EM	E

Izoh: E. – Eriydi, OE. –Oz eriydi, EM – Erimaydi

II – bob bo'yicha xulosalar

Ushbu bobda dissertatsiya tadqiqoti doirasida foydalanilgan asbob-uskunalar va reaktivlarning tavsifi, maqsadli birikmalarni sintez qilish usullarini tanlashga yondashuv, bir va aralash metalli kompleks birikmalarni olish hamda ularning fizik – kimyoviy xossalarini aniqlash usullari keltirilgan. Yangi koordinatsion birikmalar sintez qilishning optimal usullari ishlab chiqildi va Co(II), Ni(II), Cu(II), Zn(II) larning 27 ta gomo- va VO_2^+ bilan 12 ta geterometalli koordinatsion birikmalari sintez qilindi. Komplekslar sintezining optimal sharoitini ishlab chiqish maqsadida dastlab L^1 asosida 4 ta metodika bo'yicha sintez olib borildi. Ushbu 4 xil metodikada o'rganishdan asosiy maqsad ligand tarkibida tion-tiol tautomerlanish xolatining mavjudligidir. Kompleks xosil bo'lish jarayonida atsidoligand tabiatining ta'siri kuzatilmadi, ammo liganddagi o'rinbosar proton erituvchilarda tiol S-H holatda, aproton erituvchilarda esa tion C=S holatda bo'lishini ko'rsatdi. Sintez jarayonida reaksiya muhitiga ko'ra kompleks hosil bo'lishida rangning o'zgarishi kuzatildi, bu ligand va 3d-metall tuzi o'zaro kompleks hosil qilganligini ko'rsatdi. Kompleks birikmalarning tarkibi element va rentgenofluoressent tahlili o'tkazildi, element tahlil natijalari shuni ko'rsatdiki, M:L molyar nisbati reaktivlarning dastlabki nisbatiga mos keladi.

Olingan kompleks birikmalarning rangi, reaksiyaning unumi va suyuqlanish haroratlari aniqlandi. Kompleks birikmalarning suyuqlanish harorati boshlang'ich birikmalar, ya'ni ligand va oraliq metallarning tuzidan farq qilishi aniqlandi. Sintez qilingan kompleks birikmalarning turli erituvchilarda eruvchanligi o'rganildi.

Olingan kompleks birikmalarning element tarkibi SEM-EDT usuli bilan o'rganildi, organik ligandlar bilan metall ionlarining murakkab shakllanishi ularning mikro tuzilishining o'zgarishiga olib keladi degan xulosaga kelish mumkin, xususan, ko'plab metall va oltigugurt, azot, kislorod cho'qqilari qayd etilgan, bu EDT tomonidan tasdiqlangan. Natijalarga ko'ra gomometalli kompleks birikmalarning M:L 1:2 nisbatda, geterometalli kompleks birikmalar esa L^{1-3} M:V:L:1:2:2 mol nisbatda reaksiyaga kirishganligi xulosa qilindi. Ushbu SEM-EDT ma'lumotlari, rentgenofluoressent tahlil natijalari bilan tasdiqlandi.

III BOB. 1,3,4-OKSADIAZOL HOSILALARI ASOSIDAGI GOMO-, GETEROMETALLI KOMPLEKS BIRIKMALARINI FIZIK-KIMYOVIY TADQIQOT USULLARI YORDAMIDA O'RGANISH

3.1-§. Ligandlarning reaksion qobiliyatini yarim emperik kvant-kimyoviy usulda o'rganish

Kompleks hosil bo'lish jarayonini o'rganish uchun ko'p funksional oksadiazol hosilalari, jumladan 2,5-almashingan 1,3,4-oksadiazol (L^1, L^2, L^3) hosilalari ishlatildi. Ligandning tuzilishi kvant-kimyoviy hisoblash, IQ-spektroskopiya, rentgenfazaviy va termik tahlil usullari bilan o'rganilgan.

1,3,4-Oksadiazol va ularning oraliq metallar bilan hosil qilgan kompleks birikmalari biologik faollikka ega bo'lib, hozirda tibbiyotda qo'llanilayotgan ko'plab dorivor moddalarning tarkibiga kiradi. 1,3,4-Oksadiazol hosilalarini mikroelement sifatida qo'llaniladigan metallar bilan koordinatsion birikmalarini sintez qilishda, biofaol ligand va mikroelementlarning koordinatsion birikma holida faolligi o'zgaradi va ta'sir qilish xususiyatlari yaxshilanishi mumkin. Kvant-kimyoviy tahlil polifunksional ligandlarning koordinatsiyaga uchraydigan raqobatdosh donor markazlarni oldindan aytib berish imkonini beradi [127-129].

Ushbu ishda geteroatomli ligand 1,3,4-oksadiazol hosilalaridan: 5-(4-piridin)-1,3,4-oksadiazol-2(3N)-tion (L^1), 5-fenil-1,3,4-oksadiazol-2(3H)-tion (L^2) va 2-karboksimetiltio-5-fenil-1,3,4-oksadiazol (L^3) kvant-kimyoviy hisoblashlar orqali elektron tuzilishi o'rganildi. Kvant-kimyoviy tahlil Gaussian09 dasturiy paketida B3LYP nazariyasi doirasida LanL2DZ bazisida amalga oshirildi. Kvant-kimyoviy tadqiqotlar bir nechta bosqichda: o'rganilayotgan moddalarning nazariy modelini tuzib olish, optimizatsiyalash va fizik-kimyoviy ko'rsatkichlarni hisoblash, olingan natijalarni qayta ishlash va vizualizatsiyalash ketma ketligida olib borildi.

3.1-Jadvalda 1,3,4-oksadiazol hosilalarini optimizatsiyalash bo'yicha kvant-kimyoviy o'rganish natijalari va 3.1-rasmda ligandlarning optimizatsiya qilingan strukturalari keltirilgan.

3.1-Jadval

1,3,4-Oksadiazol hosilalarini optimizatsiyalash natijasida olingan ayrim
fizik-kimyoviy koʻrsatkichlar

Ligand	E_{sis}, Ha	μ, Debay	α, a.u.	E_T, kkal/mol	C_v, kkal/mol-K	S, kkal/mol-K
L^1	-519,2	2,876	115,886	80,003	34,611	96,915
L^2	-445,2	2,667	110,978	89,965	37,662	95,533
L^3	-732,2	3,944	149,016	130,818	54,276	126,410

Kvant-kimyoviy tadqiqotlar davomida 1,3,4-oksadiazol hosilalarining Malliken
zaryadlari taqsimoti oʻrganildi. 3.1-Rasmda keltirilgan ma'lumotlardan koʻrish
mumkinki, barcha hosilalarda konyugirlanish kuzatiladi. Konyugirlanish benzol va
piridin halqalaridagi *p-, p-* elektronlar hamda oksadiazol halqasidagi amin (–NH),
imin (=NH), merkapto (=S) guruhlari elektronodonor atomlar va kislorod atomidagi
(faqat L^3 molekulasida) taqsimlanmagan elektron juftlari (musbat mezomer (+ M)
effekti) hisobiga amalga oshadi. Konyugirlanish oqibatida elektron zichliklarining
qayta taqsimoti kuzatiladi. L^1 va L^2 ligandlarning amin guruhining azot atomi
oksadiazol halqasidagi eng yuqori manfiy zaryadga (L^1=-0.151, L^2=-0.351) ega
boʻlib qoladi (3.2-rasm). Shuningdek, oksadizaol halqasidagi kislorod atomida ham
elektron zichlik ancha yuqori. E'tiborlisi shundaki, L^1 va L^2 ligandlarda
konyugirlanishda S atomi ham ishtirok etadi va bu holatlarda musbat mezomer (+M)
effekt manfiy induktiv (- I) effektni amaliy jihatdan neytrallaydi, oqibatda bu
birikmalardagi S atomida elektron zichligi mos ravishda L^1=– 0,277, L^2= – 0,302,
gacha ortadi. Imin guruhidagi azot atomi (N14) elektron zichligi juda siyrak (L^1=-
0.207, L^2=-0.038,). L^3 ligand molekulasidagi elektron zichligi taqsimotiga karboksil
guruhi sezirlarli darajada ta'sir koʻrsatadi. Karboksil guruhining manfiy induktiv
(- I) effekti natijasida oltingugurt atomida elektron zichligi tanqisligi kuzatiladi
(0.099).
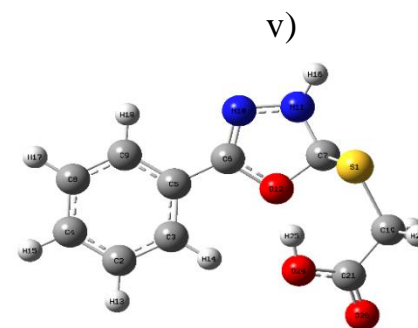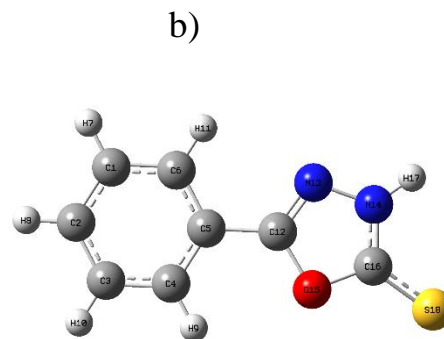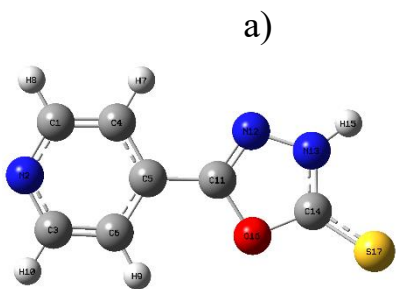
	a)	b)	v)
Optimizatsiya qilingan strukturalar:			
Malliken zaryadlari taqsimoti			
Bog' uzunliklari			
Bog' tartiblari			
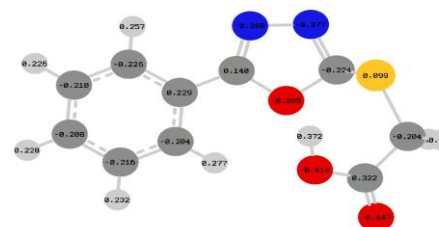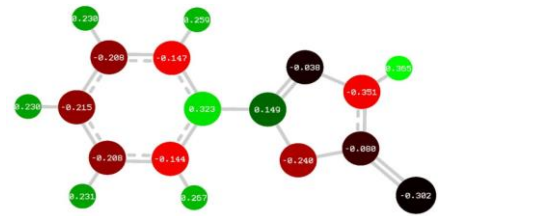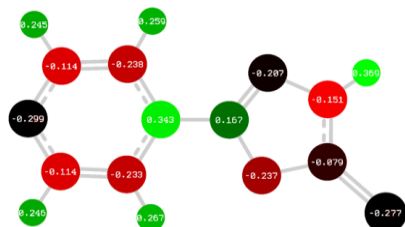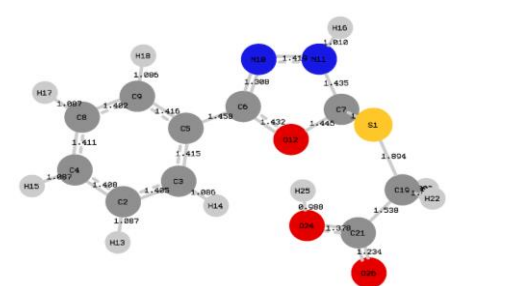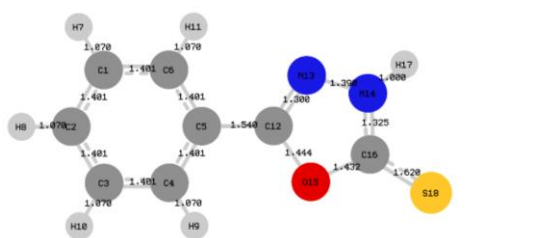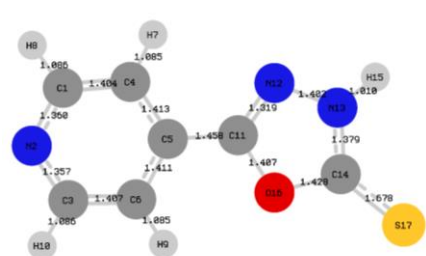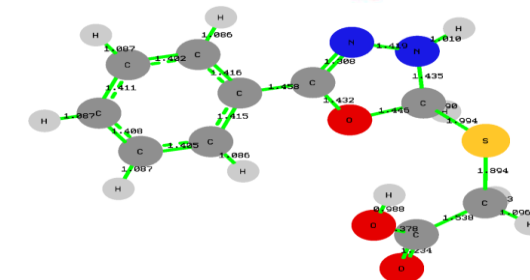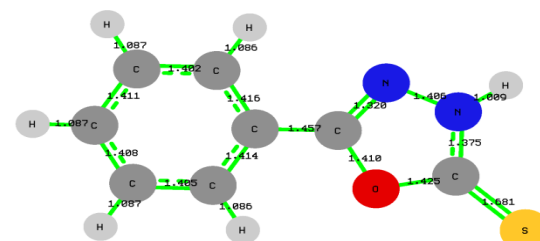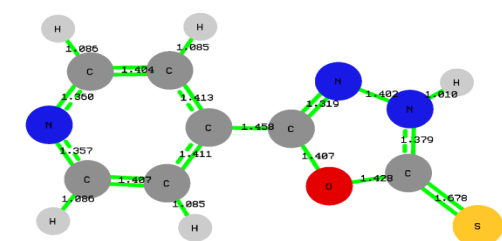
3.1-Rasm. Ligandlarning reaksion qobiliyatini yarim emperik kvant-kimyoviy o'rganish: a – L^1, b – L^2, v – L^3.

1,3,4-Oksadiazol halqasiga birikkan oʻrinbosarlar tabiatining oʻzgarishi ligandlarning qutblanuvchiligiga ham ta'sir etadi. 3.1-Jadvalda keltirilgan ma'lumotlardan koʻrish mumkinki, ligandlarning dipol momenti qiymatlari $L^2 \to L^1 \to L^3$ tartibida oshib boradi.

Yuqorida keltirilgan ma'lumotlarga asoslangan holda L^1 va L^2 ligandlar kislorod atomi va imin guruhi hisobida bidendatlikni, L^3 esa polidentatlikni namoyon qilishi mumkinligini ta'kidlash mumkin. Umumiy koordinatsiyalash qobiliyati ligandlarning $L^2 \to L^1 \to L^3$ qatori koʻrinishida oshib borishi borishi aniqlandi.

Ammo shunga qaramasdan, real sharoitlarda metall kationlari, anionlar va erituvchi molekulalari ta'siri ostida geterohalqalardagi geteroatomlar elektron zichligining qayta taqsimlanishi oqibatida ularning koordanatsion qobiliyati oʻzgarishlarga uchrashishi mumkin. Shu sababli kvant-kimyoviy hisoblashlarni turli d-metall tuzlari hamda erituvchilar ishtirokida amalga oshirish yanada koʻproq ma'lumot olishga imkon yaratadi.

Ligandlardagi konyugirlanish, ya'ni manfiy induktiv (-I) va musbat mezomer (+M) effektlar tufayli ularda ayrim bogʻ uzunliklari va tartiblarida oʻzgarishlar kuzatiladi. Jumladan, C=S bogʻ uzunligi odatdagi 1,55 Å (uglerod disulfidda) dan ancha farq qiladi va mos ravishda 1,628 va 1,678 Å ga teng boʻlib qoladi (3.1-rasm). Ligandlardagi bogʻ tartiblarida ham Malliken zaryadlariga muvofiq keluvchi oʻzgarishlar kuzatiladi. Jumladan, L^1 ligand tarkibidagi N13-C14 va C14-S17 bogʻlari, L^2 ligand tarkibidagi N14-C16 va C12-O15, shuningdek L^3 liganddagi C6-O12 bogʻ uzunliklari 1,5 ga tengdir (3.1-rasm).

Nazariy kvant-kimyoviy tadqiqotlar doirasida barcha ligandlar molekulalarining asosiy va qoʻzgʻalgan holatlaridagi molekulyar orbitallari holati va elektron qoʻzgʻalishlarning energetik koʻrsatkichlari aniqlandi.

Kvant-kimyoviy tadqiqotlar davomida oʻrganilayotgan ligandlarning asosiy va qoʻzgʻalgan holatdagi frontal (chegaraviy) molekulyar orbitallari (MO) tadqiq etildi (3.2-rasm va 3.2-jadval).
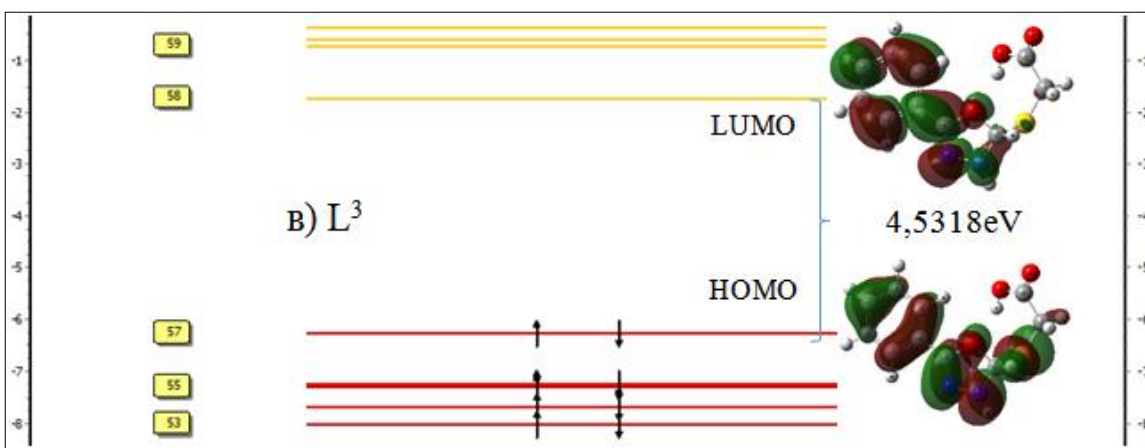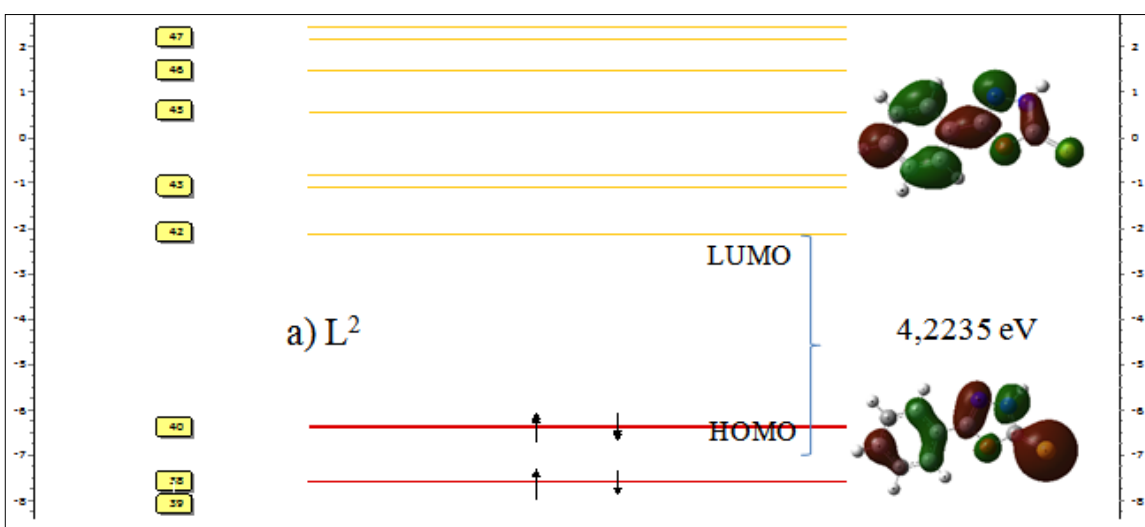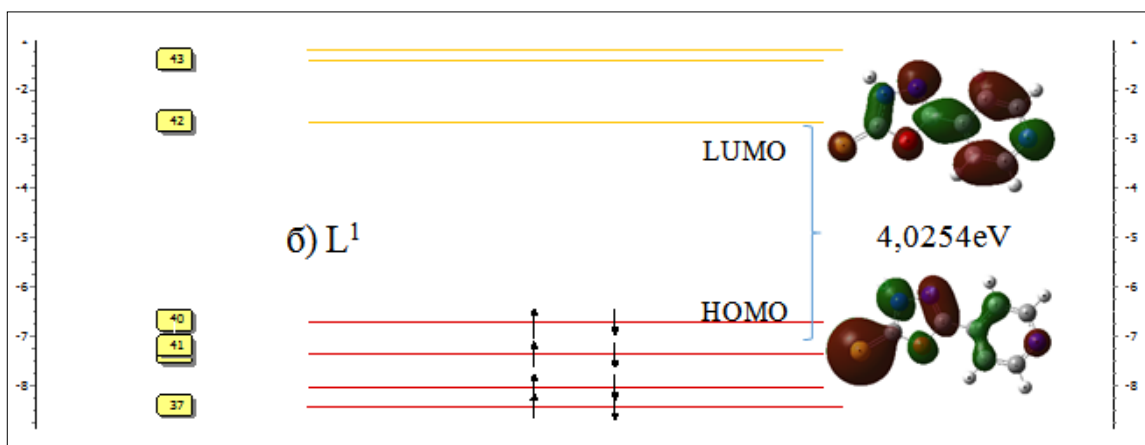
3.2-Rasm. Ligandlar MO energetik qavatlari diagrammasi

3.2-Rasm va 3.2-jadvalda keltirilgan ma'lumotlardan ko‘rinib turibdiki, ta'qiqlangan zona (HOMO – LUMO farqi) ning kengligi bo‘yicha eng yuqori qiymat (4,5318 eV) L^3 ligandda namoyon bo‘ladi, ya'ni bu ligand molekulasi asosiy holatdan (HOMO) qo‘zg‘algan holatga (LUMO) o‘tishi uchun ko‘proq energiya talab etiladi.

Ligandlarda chegaraviy molekulyar orbitallar va ta'qiqlangan zona
energiyalari

Ligand	HOMO, eV	LUMO, eV	E_g, eV
L^1	-6,7044	-2,6790	4,0254
L^2	-6,3430	-2,1195	4,2235
L^3	-6,2744	-1,7426	4,5318

3.2-Rasmdan ko'rish mumkinki, barcha ligandlarda elektron bilan to'lgan eng yuqori MO lar singlet holatga ega, ya'ni qarama-qarshi spinli ikkita elektron bilan to'lgan. Qo'zg'algan holatdagi eng quyi MO lar esa bo'sh turibdi. Shu sababli, barcha ligandlar elektron spinlari bo'yicha simmetrik ko'rinishga, boshqacha qilib aytganda, "yopiq" elektron qobiqlarga ega.

Yuqorida keltirilgan ma'lumotlarga muvofiq ravishda, 3.3-rasmdan ko'rinib turibdiki, umumiy olganda $\sim -6,3 \div -1,7$ eV oraliqda elektron qobiqlari zichligi 0 ga teng, ya'ni yuqorida ta'kidlagandek, elektron mazkur energetik oraliqda mavjud bo'la olmaydi. Ya'ni ligandlar molekulalari molekulyar orbitallari energiya diagrammasi uzluksiz ravishda, balki diskret ravishda o'zgaradi. Boshqacha qilib aytganda, ligandlar molekulyar orbitallari istalgan qiymatlarni emas, balki cheklangan diskret qiymatlarni qabul qiladi. Shu sababli, L^1, L^2 va L^3 ligandlar molekulalari asosiy holatdan qo'zg'algan holatga o'tishi uchun talab etiladigan minimal energiya qiymati mos ravishda: $L^1 = 41$ MO (HOMO) – 42 MO (LUMO) = 4,0254 eV (388,392kJ/mol), $L^2 = 41$ MO (HOMO) – 42 MO (LUMO) = 4,2235 eV (407,5057kJ/mol) va $L^3 = 57$ MO (HOMO) - 58 MO (LUMO)= 4,5318 eV (437,2521 kJ/mol) tashkil etadi.

a) L^1

b) L^2

v) L^3
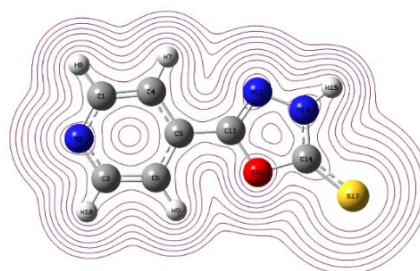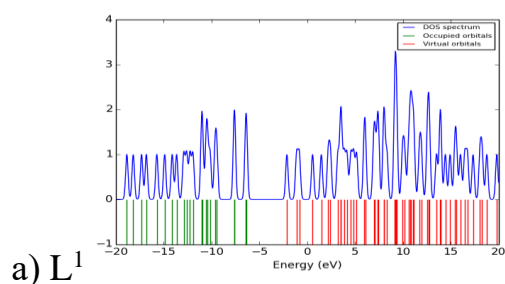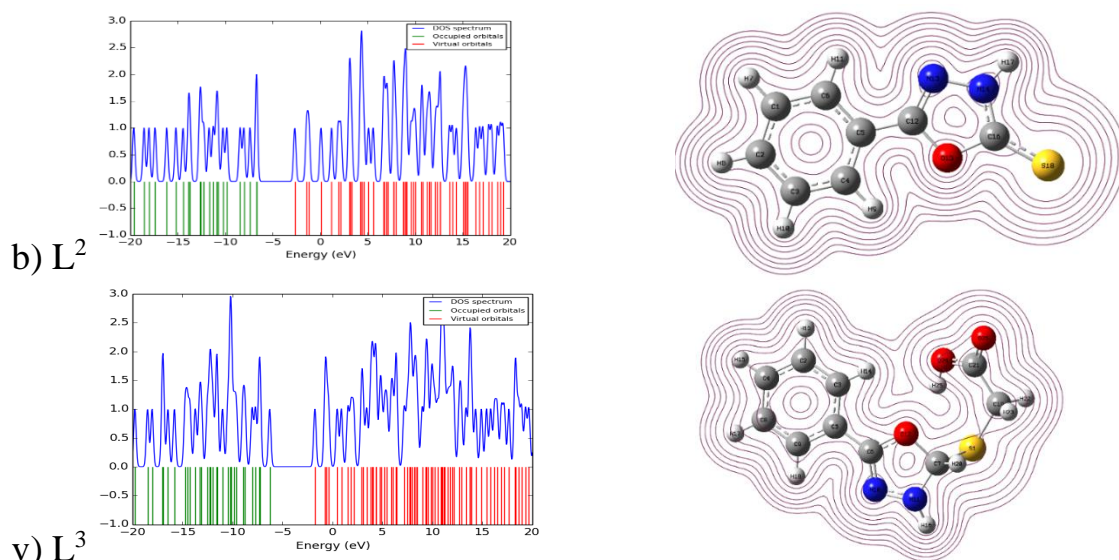
3.3-Rasm. L^1 (a), L^2 (b), L^3 (v) Ligandlarning molekulyar orbital qavatlarining umumiy zichligi va zichlik spektri (DOS – density of orbital state) grafiklari

(koʻk rang – DOS spektri, yashil rang – asosiy holatdagi orbitallar, qizil rang – qoʻzgʻalgan holatdagi orbitallar).

Ligandlar molekulalarining toʻlqin funksiyalarini hisoblash orqali aniqlangan elektrostatik potensial (ESP) konturlari 3.4-rasmda tasvirlangan. ESP elektron zichligi bilan bogʻlangan boʻlib, kimyoviy reaksiyalarda elektrofil va nukleofil hujumlar tabiatini yoki hududini aniqlashga yordam beradi. Tasavvur qilaylik, agarda musbat zaryad molekulaga yaqinlashayotganda u musbat hududlarni chetlab oʻtib, manfiy hududlarni ma'qul koʻradi. Ya'ni, ESP dipol momentga aloqador boʻlib, u molekulaning nisbiy qutblanuvchanligini hamda lokal musbat va lokal manfiy hududlarni vizual koʻrsatib berishga xizmat qiladi. Chunki elektrostatik kuchlar birinchi galda molekulalaro uzoq ta'sirlarga (nokovalent, elektrostatik, Van-der-Vaals bogʻlar) javobgardir.

a)L^1

b)L^2

v)L$_3$

(I)   (II)
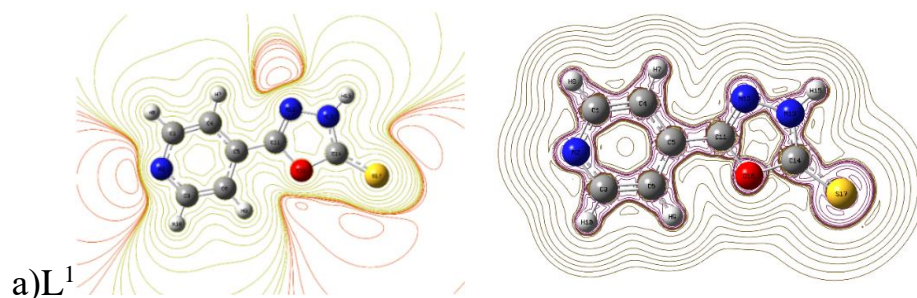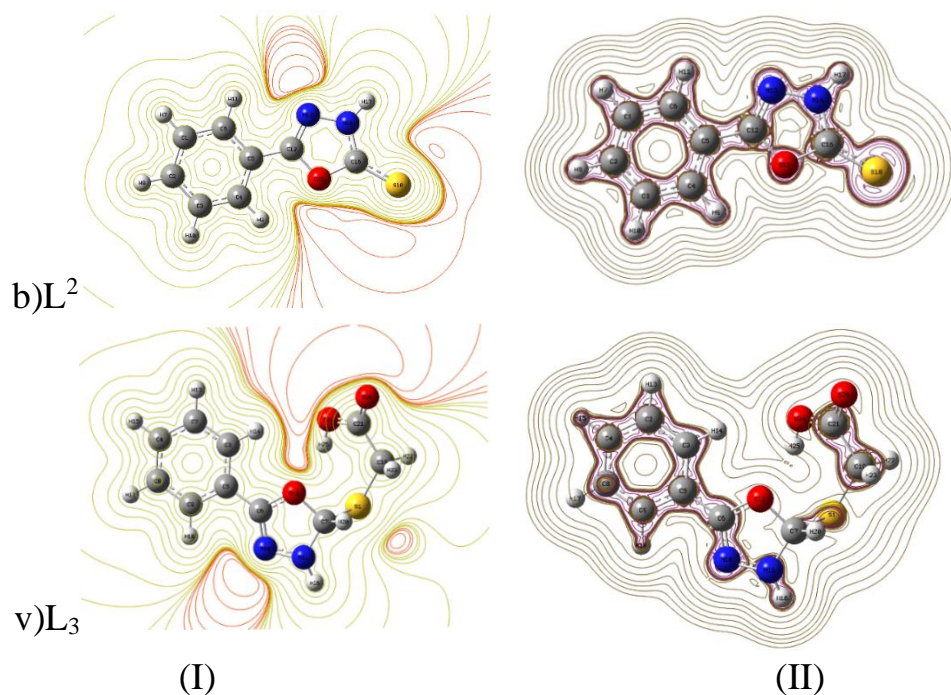
3.4-Rasm. L^1 (a), L^2 (b), L^3 (v) Ligandlar molekulalarining:

I) elektrostatik potensial (ESP) konturlari; II) Laplasian konturlari

ESP konturidagi qizil konturlar elektrostatik potensialning minimal qiymatlariga mos keladi hamda bu hududlar elektrofil hujumga, masalan, anionlar – kislota qoldiqlariga moyil bo'ladi. Yashil rang esa elektrostatik potensialning yuqoriligidan dalolat beradi. Bu hududlar nukleofil hujumga (metall kationlari ta'siriga) moyil bo'ladi. Ushbu xulosalar Malliken zaryadlarining taqsimoti borasidagi natijalarga mos keladi.

Haqiqatdan ham imin-, merkapto- guruhlari hamda oksadiazol halqasidagi kislorod atomi atrofida manfiy zaryad zichligi juda past (qizil konturlar). Shunday holatni L^1 molekulasidagi piridin halqasi azot atomi (N2) hamda L^3 ligand molekulasi karboksil guruhi va oltingugurt atomi (S1) atrofida ham ko'rish mumkin. Bu esa mazkur hududlarda donor-akseptor bog'larning hosil bo'lish ehtimolligining pasayganligidan dalolat beradi.

Shuningdek, kvant-kimyoviy tadqiqotlar davomida elektron zichlikning umumiy taqsimoti kontur chiziqlari hamda Laplasian konturlari aniqlandi (3.4-rasm).

3.4-Rasmdan ko'rinib turibdiki, Laplasian manfiy qiymatlarga ega bo'lgan hududlarda (binafsha rang) manfiy zaryad zichlashgan bo'lib, potensial energiya dominantlik qiladi. Laplasian musbat hududlarda esa kinetik energiya dominantlik qiladi, manfiy zaryad esa siyraklashadi. Bu natijalar yuqorida bayon qilingan xulosalarni tasdiqlaydi.

3.3-Jadval

Ligand o'rinbosarlarini elektrodonor atomlari va oksadiazol halqasining donor atomlarida hisoblangan elektron zichliklari

Ligand	O'rinbosar	Oksadiazol halqasi				Py
		-NH(C)	= O	= S	=N(N)	(C)-N=(C)
B3LYP/ LanL2DZ						
L^1	– Py	-0.151	-0.237	-0.277	-0.207	-0.299
L^2	– Ph	-0.351	-0.240	-0.302	-0.038	-
L^3	– Ph, -(S)-CH$_2$-COOH	-0.377	-0.285 -0.447(C=O) -0.414(C-O)	0.099	-0.306	-

3.3-Jadvaldagi ma'lumotlar asosida, L^{1-3}- lar uchun ularning reaksion qobiliyati va elektron zaryadlarni kamayishiga, oksadiazol halqasidagi o'rinbosarlarning umumiy elektron ta'siriga ko'ra quyidagi qatorda joylashtirilishi: $L^2<L^1<L^3$ (– Ph <– Py <– Ph, -(S)-CH$_2$-COOH) xulosa qilindi.

Bundan tashqari, 5-o'rin almashgan-1,3,4-oksadiazol-2-tion/tiol hosilasi tautomer shakllarini mavjudligini inobatga olib, ushbu ikki holatning reaksion qobiliyatini va barqaror holatini aniqlash maqsadida kvant-kimyoviy hisoblash olib borildi. DFT/B3LYP/6-311+G(d,p) bazisidagi, LanL2DZ metodi bilan 5-o'rin almashgan-1,3,4-oksadiazol-2-tion/tiol hosilasining geometrik tuzilishi MEP va zaryadlarining taqsimlanishi, elektrofil va nukleofil jarayonlarning reaksiya markazlarini aniqlash uchun optimizatsiyalashtirilgan geometriyasi bilan sirt elektrostatik potensiallari hisoblandi. Sirt elektrostatik potensiallaridagi turli hil qiymatlar har xil ranglar bilan ifodalanadi va potensiallar qiymati quyidagi tartibda oshib boradi: qizil <to'q sariq <sariq <yashil <ko'k.

Tiol   Tion

3.5-Rasm. 5-O'rin almashgan-1,3,4-oksadiazol-2-tion/tiol hosilasining DFT /
B3LYP metodi bo'yicha hisoblangandagi geometrik tuzilishi MEP va
zaryadlarining taqsimlanishi

MEP ning manfiy (qizil) sohalari nukleofil reaksion qobiliyati bilan, musbat
sohalari (ko'k) esa elektrofil reaksion qobiliyati bilan bog'liq. L^1–tiol tautomer
holatda nukleofil va elektrofil markazlar mavjud bo'lib, uning reaksion faolligi
yuqori bo'ladi.

3.4-Jadval

5-O'rin almashgan-1,3,4-oksadiazol-2-tion/tiol hosilasi tautomer shakllarini
optimallashtirishning natijalari

Parametrlar	Tiol	Tion
Bazis	6-311+G(d, p)	6-311+G(d, p)
Ichki energiya (E)	68,138 kkal/mol	67,453 kkal/mol
Dipol momenti	3,04 D	2.24 D
Qutblanish qobilyati	113,78	109.48
Entalpiya (H)	68,72 kkal/mol	68,04 kkal/mol
Entropiya (S)	0,106429 kkal/mol *K	0,104163 kkal/mol *K
Issiqlik sig'imi (Cv)	0,040669 kkal/mol *K	0,039845 kkal/mol *K

L^1-tion holatda esa faqatgina oksadiazol halqasidagi azot atomi atrofidagi
vodorod atomida elektrofil markaz mavjud bo'lishi, uni nisbatan barqaror holatda
bo'lishini ifoda etadi va adabiyotdagi ma'lumotlaga ham mos keladi (3.5-rasm,
3.4-jadval).

5-o'rin almashgan-1,3,4-oksadiazol-2-tion/tiol hosilalaridan L^1, L^2 larning -tiol tautomer holatda nukleofil va elektrofil markazlar mavjud bo'lib, uning reaksion faolligi yuqori bo'lishi aniqlandi.

3.2-§. Ba'zi 3d-metallarni NH_4VO_3 bilan oksadiazoltion hosilalari asosida gomo- va geterometalli kompleks birikmalarini IQ-spektroskopiya usulda o'rganish

Ligandlar va sintez qilingan kompleks birikmalarning tuzilishini va individualligini aniqlash maqsadida IQ-spektroskopik tahlil o'tkazildi. 3.5-3.8-jadvallarda va 3.6-3.10-rasmlarda 1,3,4-oksadiazol hosilalari asosida sintez qilingan kompleks birikmalarning IQ-spektroskopiya natijalari keltirilgan.

IQ-spektr natijalari L^{1-3} ligandlar bo'yicha umumiy holatda tahlil qilib chiqilganda, aromatik halqaga tegishli bo'lgan C-H bog'i valent tebranishlari ~2925-3100 sm^{-1} sohada kuzatildi. L^{1-2} da C=N funksional guruhining simmetrik va assimetrik tebranishlarining yutilish chiziqlari o'rtacha 1595 sm^{-1} (ν_{as}C=N), ~1616 sm^{-1} (ν_sC=N) chastotaga ega, L^3 ligandda esa S=N guruhi 1524-1564 sm^{-1} sohada joylashgan bo'lib, L^{1-2} ligandlarga nisbatan yutilish chizig'ining bunday siljishi karboksil guruhining ta'siri bilan izohlanadi. L^2 ligand tarkibida boshqa ligandlar tarkibida mavjud bo'lmagan, koordinatsiyalanish ehtimolligi yuqori bo'lgan piridil halqasidagi ν(C-N=C) bog' yuqori intensivlik bilan 1006 sm^{-1} sohada kuzatildi. L^3 da karboksil guruhiga tegishli assimetrik va simmetrik valent tebranish chiziqlari 1617-1638 sm^{-1} sohada joylashgan bo'lib, bu karboksil guruhi uchun odatda qabul qilingan chastotalardan biroz pastroqdir, bu holatni molekuladagi ichki molekulyar vodorod bog'lanish orqali izohlash mumkin. Ushbu karboksil guruhiga tegishli assimetrik va simmetrik valent tebranish sohalari ayirmasi $\Delta=\nu_{as}$ (COO)-ν_s (COO)=200 va undan yuqori bo'lsa bidentat, 200 dan kam bo'lsa monodentat birikishini ko'rsatadi [130-134].

a)

b)

v)
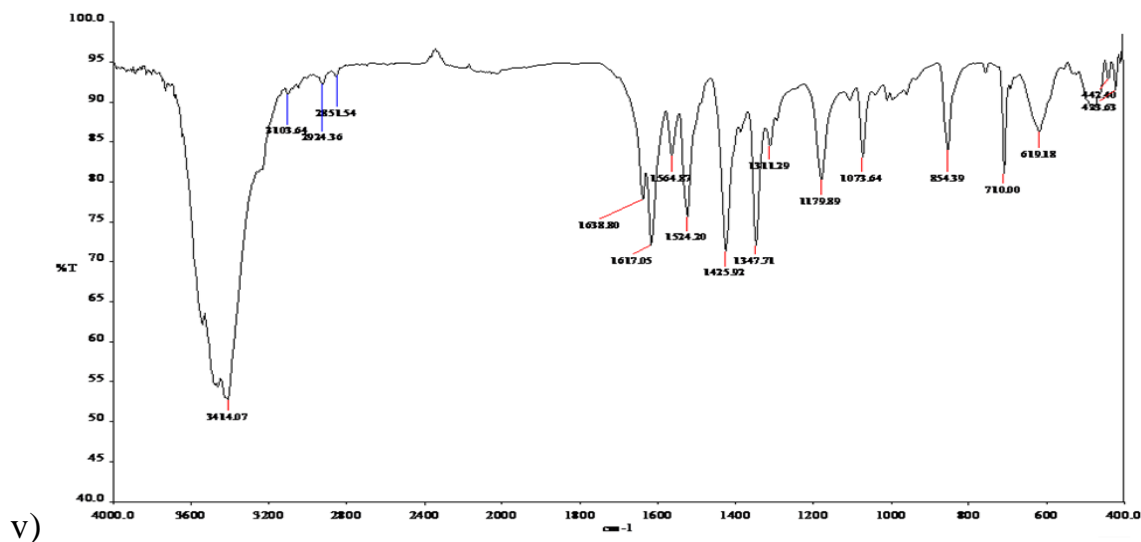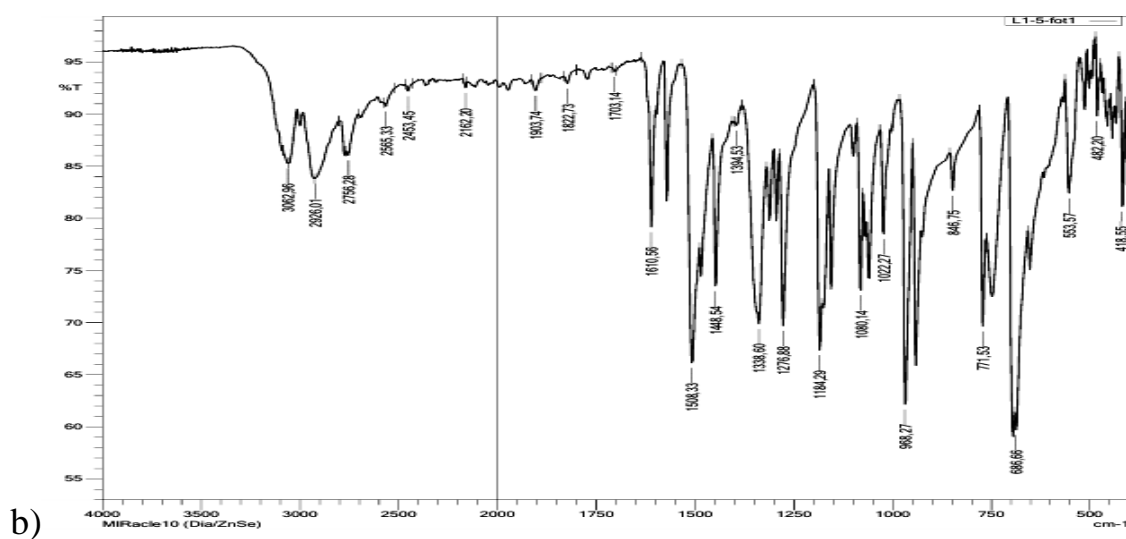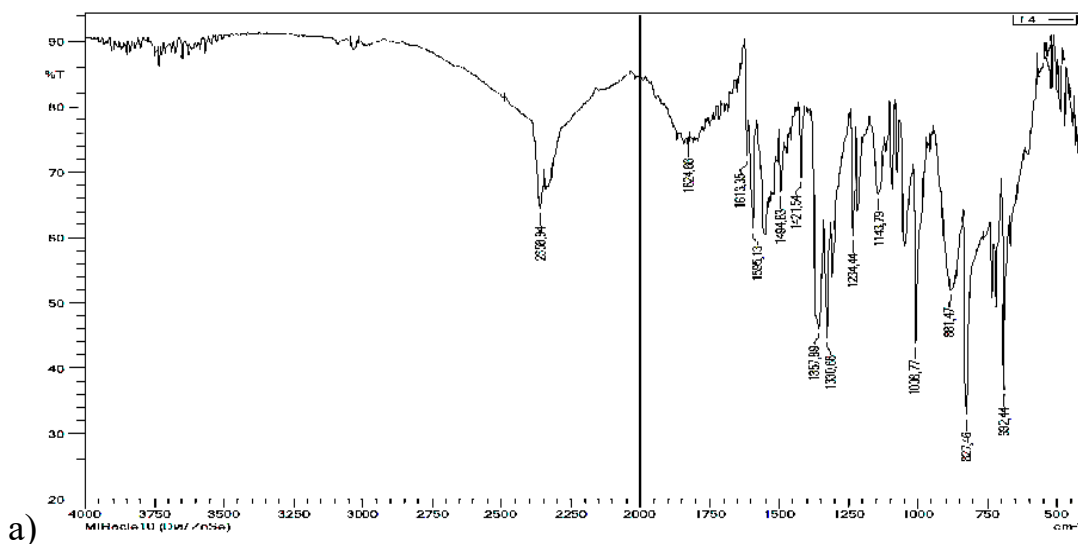
3.6-Rasm. a)L^1; b) L^2; v) L^3 larning IQ spektrlari;

Tion/tiol holatda mavjud bo'lish ehtimolligi bo'lgan L$^{1-2}$ ning IQ-spektrlari

tahlil qilinganda ~1494-1421 sm^{-1} sohada oksadiazol halqasidagi =N-N- bog'iga

tegishli xarakterili chiziqlar aniqlandi. Ushbu L^{1-2} ligandlarda 3100-3200 sm^{-1} sohada iminoguruhga tegishli valent tebranish chastotasiining yo'qligi, L^{1-2} ning quruq holatda tiol holatda bo'lishidan darak beradi. Bu ligandning IQ-spektridagi muhim xarakterli chiziqlardan biri S-H valent tebranishlari bilan tasdiqlanadi, u 2358 sm^{-1} sohada paydo bo'ladi. Ammo shuni takidlash kerakki, L^1 ning turli erituvchilarda erishi natijasida tautomer shaklini o'zgartirishi mumkin. Turli erituvchilarda olib borilgan tadqiqotlar natijasida qaysi tautomer shaklning ustunligi haqida qaror qabul qilish mumkin.

Sintez qilingan kompleks birikmalarning infraqizil spektrlarida ligandlarning funksional guruhlarining xarakterli yutilish sohalarida kompleks hosil bo'lishi tufayli mos siljishlar kuzatildi. Erkin ligandda 1595 sm^{-1} sohada kuzatiladigan vC=N bog'ining valent tebranish chiziqlari, kompleks birikmalarda past chastota tomon siljiydi va 1516-1573 sm^{-1} soha oralig'ida kuzatildi. Bu chiziqlar vC=N bog' intensivligining qisqarishiga to'g'ri keladi. Buni metallning elektron zichligini ligandning π-holati bilan delokallashishi deb izohlash mumkin, bu azotning (C=N) metall atomlari bilan koordinatsiyalanganligini ko'rsatadi. L^{1-2} ligandlar asosida sintez qilingan barcha gomometalli kompleks birikmalarda vS-H ga tegishli xarakterli chiziq yo'qoladi. Bu esa metall kationi va oltingugurt o'rtasida ion bog'lanish hosil bo'ladi degan xulosaga kelishga imkon beradi. Geterometalli kompleks birikmalarda esa vS-H funksional guruhiga mos keladigan yutilish chizig'i saqlanadi. Gomo- va geterometalli kompleks birikmalardagi bog'lanishlarning bunday farqli jihatlarini ushbu birikmalarning sintez usullarini turlichaligi bilan izohlash mumkin. Ligand L^3 tarkibidagi karboksil guruhiga tegishli yutilish chiziqlarining gomo- va geterometalli kompleks birikmalar infraqizil spektrlarida quyi sohaga tomon 10-40 sm^{-1} gacha siljiganligi, ushbu ligand metall atomiga karboksil guruhi orqali koordinatsiyalanganligidan dalolat beradi.

Bundan tashqari ba'zi gomometalli kompleks birikmalarning IQ-spektrlarida 3000 sm^{-1} - 3700 sm^{-1} gacha sohalarga cho'zilgan o'rtacha intinsivlikdagi kengaygan valent chiziqlar kuzatildi. Bu esa -OH guruhiga tegishli

bog'ni, ya'ni 3000 sm^{-1} - 3400 sm^{-1} sohalarda koordinatsiyalangan hamda 3500 sm^{-1} - 3700 sm^{-1} soha oralig'idagi o'rtacha intensivlikdagi valent chiziqlar kristalizatsiyalangan suv molekulasi mavjudligini ko'rsatadi.

[V$_4$O$_{12}$](L+H$^+$)$_4$ tarkibli oniyli kompleks birikmalar tahlil qilinganda, L$^{1-3}$ ligandlarda uchramagan ν(V-O) 650-700 sm^{-1} , ν(V=O) 900-980 sm^{-1} va ν(N-H) 3251-3202 sm^{-1} sohalar o'rtacha intensivlikdagi valent chiziqlar kuzatildi, bu esa ligand molekulasi protonlangan holatda ekanligini va markaziy atom vanadiy siklik vanadil holatidaligidan dalolat beradi. Bunda oniyli kompleksning hosil bo'lishi molekulalararo vodorod bog'lanish hisobiga ekanligi aniqlandi [130; 536 b, 131; 528 b, 132; 305-358 b, 133; 189 b, 134; 234 b].

L$^{1-2}$ ligandlarning IQ-spektridan farqli o'laroq, barcha sintez qilingan gomometalli kompleks birikmalarda 500 sm^{-1} soha atrofida M-N bog'linishiga mos keladigan tebranish chiziqlari mavjud bo'lib, bu chiziqlar oksadiazol halqasining imin guruhi va L^1 ligandining piridil halqasidagi azot atomi metall ioni bilan koordinatsiyalanishda ishtirok etishi mumkin degan xulosani beradi. Ligand L^3 ning gomometalli kompleks birikmalarida (M-O) bog'i karboksil guruhidagi Δ=ν$_{as}$ (COO)-ν$_s$ (COO) farqi 200 sm^{-1} dan yuqoriligi aniqlandi, bu esa karboksil guruhidagi kislorod atomlari orqali bidentat koordinatsiya ketganligidan dalolat beradi. L$^{1-2}$ ligandlar asosidagi gomometalli kompleks birikmalarning IQ-spektrlarida ~450 sm^{-1} chastotada M-S bog'iga mos keladigan yutilish chiziqlari kuzatildi. Oniyli va geterometalli kompleks birikmalarda ~680 sm^{-1} (V-O) va 595 sm^{-1} (M-O) chastotalarda M-O bog'iga mos keladigan yutilish chiziqlari aniqlandi. L^1-L^2-ligandlar geterometalli kompleks markazida joylashgan oksovanadiyli (oniyli) qismga oksadiazol halqasidagi uchinchi azot atomi orqali koordinatsiyalanadi, L^3 esa tarkibidagi karboksil guruhidagi kislorod atomlari orqali oksovanadiyli qism bilan donor-akseptor bog'lanish hosil qilishi aniqlandi (3.11-3.16 rasmlarda kompleks birikmalarning IQ spektrlari keltirilgan).
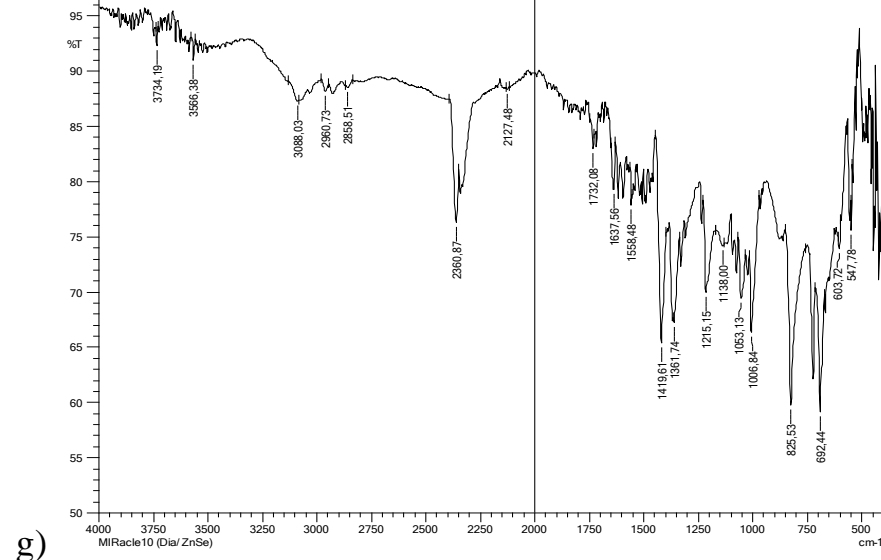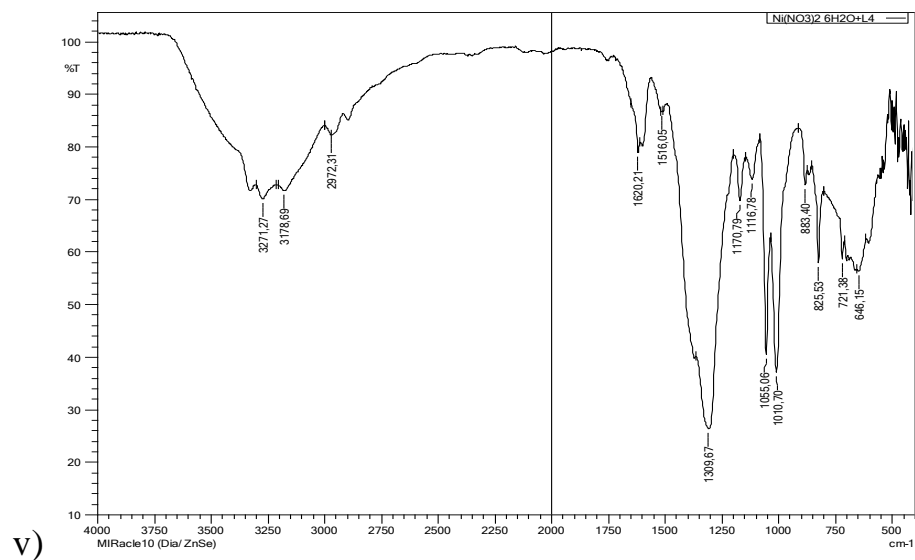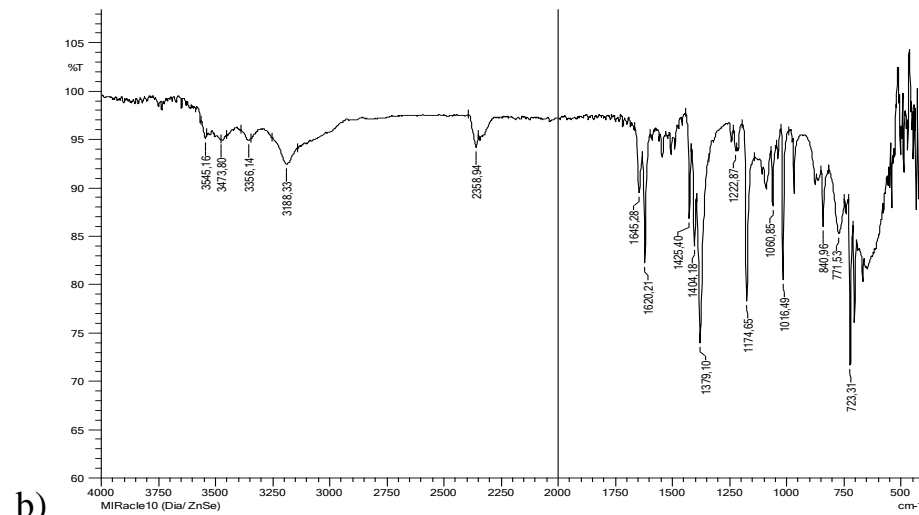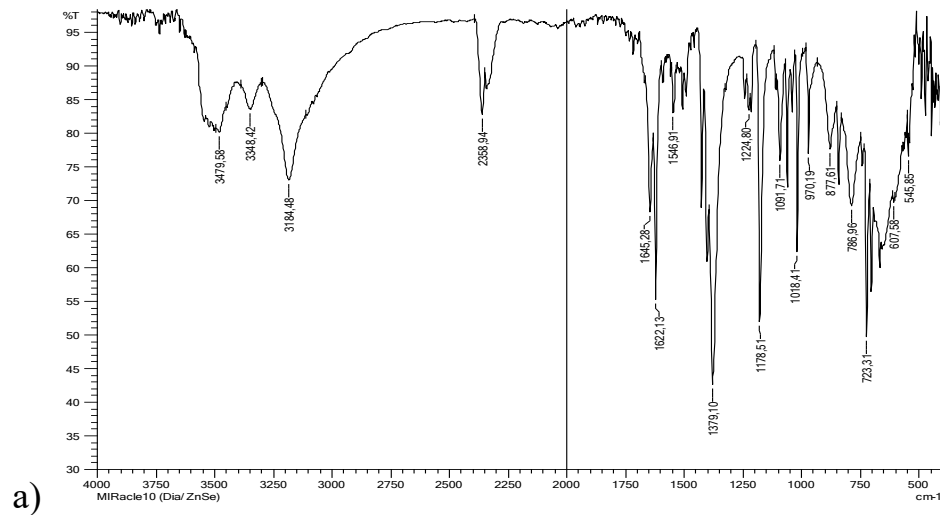
3.7-Rasm. L^1 ning turli erituvchilardagi kompleks birikmalari IQ-spektri

a)[Ni(L^1)$_2$(H$_2$O)$_4$]·2H$_2$O;   b) [Ni(L^1)$_2$(H$_2$O)$_2$];   v) [Ni(L^1)$_2$(H$_2$O)$_4$];   g) {[Ni(L^1)$_4$(H$_2$O)$_2$]}$_n$

L^1 va uning turli erituvchilarda olingan kompleks birikmalarining IQ-spektridagi muhim qiymatlari (sm^{-1})

Birikma	ν_s (C=N)	ν_{as} (C=N)	ν (S=C)	ν (C-O-C)	ν S-H	ν O-H	ν (N-M)
L^1 –	1595	1616	-	1421	2358		-
[Ni(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	1546	1645	-	1379	2358	3479-3348	490
[Co(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	1550	1645	-	1379	2358	3545-3473	493
[Zn(L^1)$_2$(H$_2$O)$_4$]*2H$_2$O	1558	1637	-	1361	2360	3566	507
[Cu(L^1)$_2$ (H$_2$O)$_4$]*2H$_2$O	1550	1635	-	1396	2360	3649	500
[Ni(L^1)$_2$(H$_2$O)$_2$]	1562	1630	-	1384	-	3243	501 462(M-S)
[Co(L^1)$_2$(H$_2$O)$_2$]	1553	1642	-	1392	-	3275	510 458(M-S)
[Zn(L^1)$_2$(H$_2$O)$_2$]	1556	1637	-	1369	-	3266	506 467(M-S)
[Cu(L^1)$_2$(H$_2$O)$_2$]	1555	1621	-	1390	-	3254	511 479(M-S)
[Ni(L^1)$_2$ (H$_2$O)$_4$]	1516	1620	1170	1404	-	3271-3178	487
[Co(L^1)$_2$ (H$_2$O)$_4$]	1573	1633	1170	1396	-	3242	515
[Zn(L^1)$_2$ (H$_2$O)$_4$]	1550	1639	1165	1415	-	3250	511
[Cu(L^1)$_2$ (H$_2$O)$_4$]	1556	1612	1178	1400	-	3367-3161	500
{[Ni(L^1)$_4$(H$_2$O)$_2$]}$_n$	1552	1600	1157	1404	2362	3261-2951	487
{[Co(L^1)$_4$ (H$_2$O)$_2$]}$_n$	1537	1637	1170	1406	2358	3074	486
{[Zn(L^1)$_4$ (H$_2$O)$_2$]}$_n$	1573	1633	1205	1396	2358	3242-2924	495
{[Cu(L^1)$_4$ (H$_2$O)$_2$]}$_n$	1539	1645	1178	1404	2358	3200-3000	490
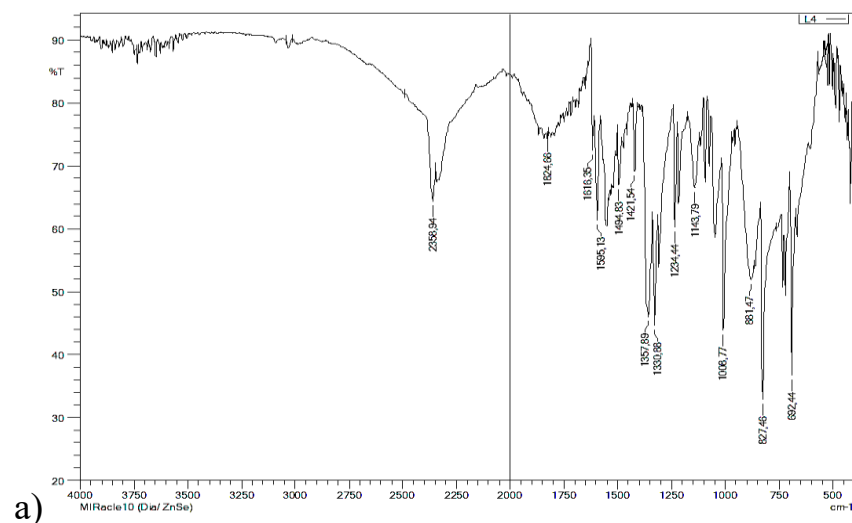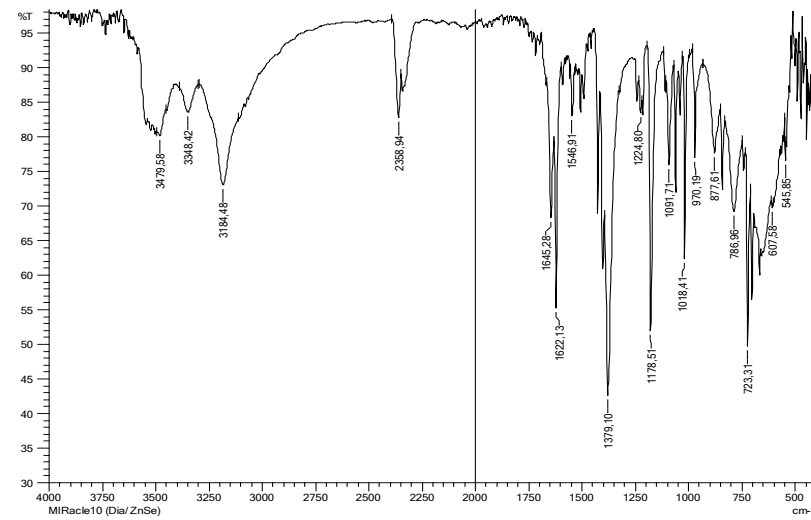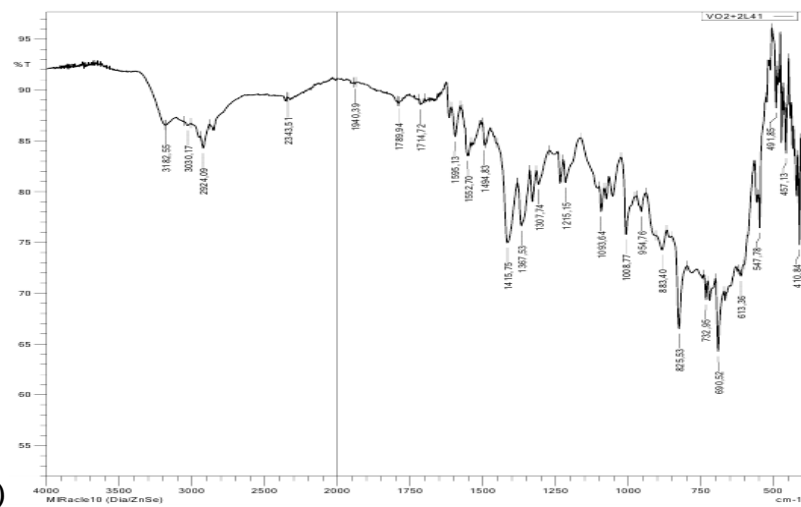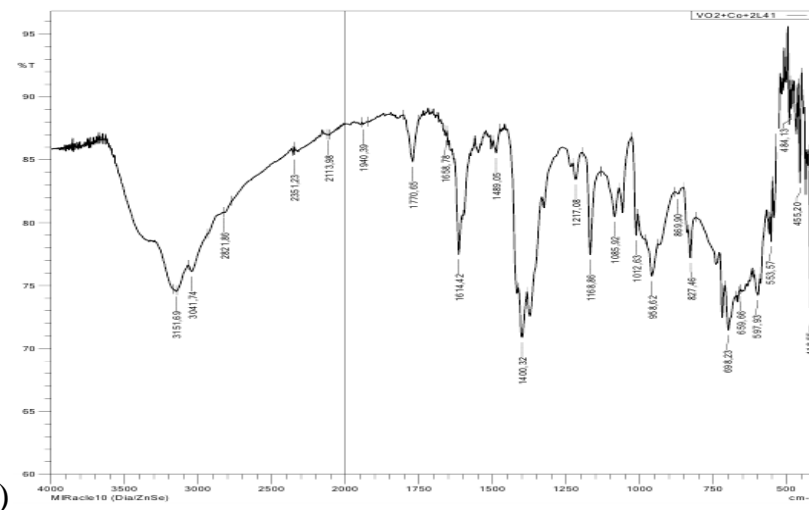
3.8-Rasm.a)L^1; b) [Co(L^1)$_2$(H$_2$O)$_2$]; v) [V$_4$O$_{12}$](L^1+H$^+$)$_4$; g) [Co$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O larning IQ-spektrlari.

L^1 bilan sintez qilingan gomo- va geterometalli kompleks birikmalarining IQ-spektrlaridagi asosiy tebranish chastotalari (sm^{-1})

Birikma	ν_{as} (C=N)	ν_s (C=N)	(S-H)	ν(C-O-C)	ν(OH)	ν(V=O)	ν(V-O)	ν(M-N) ν(M-O)
L^1	1595	1616	2358	1421	-	-	-	-
$[Co(L^1)_2(H_2O)_2]$	1562	1630	-	1384	3243	-	-	501 462(M-S) -
$[Cu(L^1)_2(H_2O)_2]$	1553	1642	-	1392	3275	-	-	510 458(M-S) -
$[Ni(L^1)_2(H_2O)_2]$	1556	1637	-	1369	3266	-	-	506 467(M-S) -
$[Zn(L^1)_2(H_2O)_2]$	1555	1621	-	1390	3254	-	-	511 479(M-S) -
$[V_4O_{12}(L^1)_4]$	1595	1630	2360	1367	-	825	690	410 547
$[Cu_2V_4O_{12}(L^1)_4]\cdot2H_2O$	1592	1614	2368	1400	3122	958	698	418 597
$[Ni_2V_4O_{12}(L^1)_4]\cdot2H_2O$	1548	1635	2380	1402	3151	985	682	418 601
$[Co_2V_4O_{12}(L^1)_4]\cdot2H_2O$	1500	1616	2369	1371	3115	956	692	426 599
$[Zn_2V_4O_{12}(L^1)_4]\cdot2H_2O$	1544	1614	2393	1415	3130	958	692	410 599
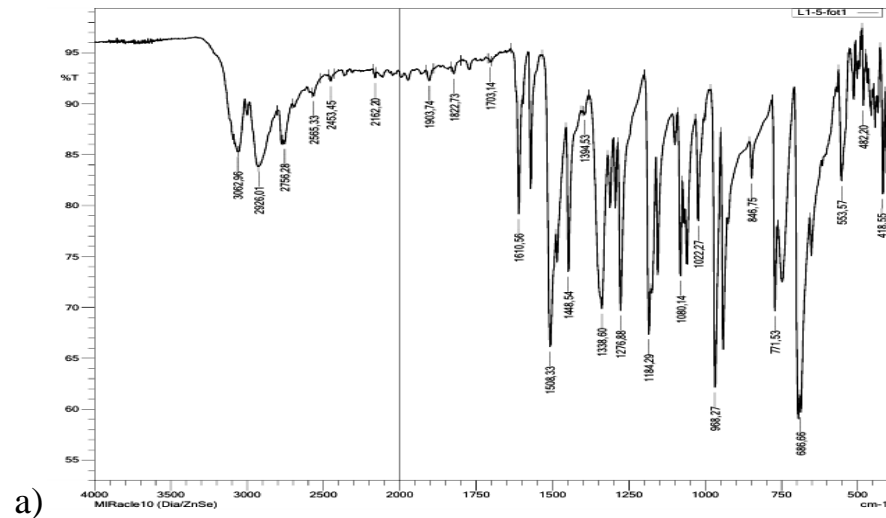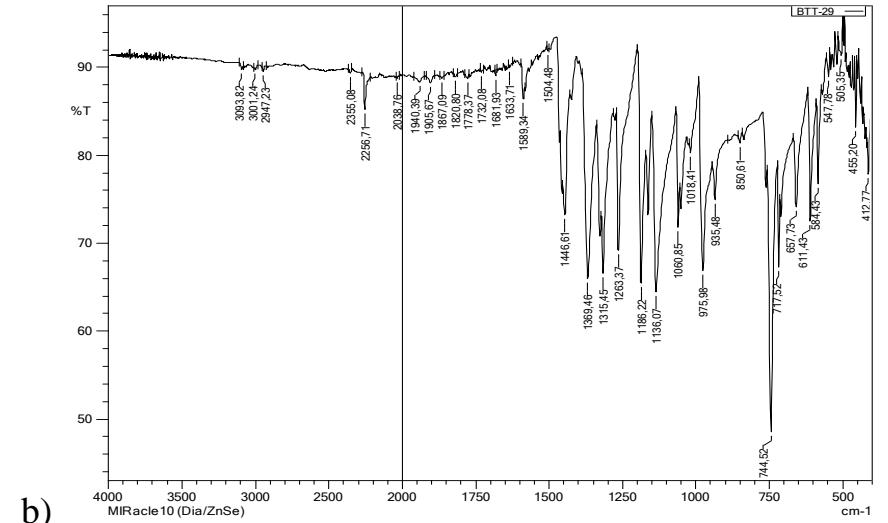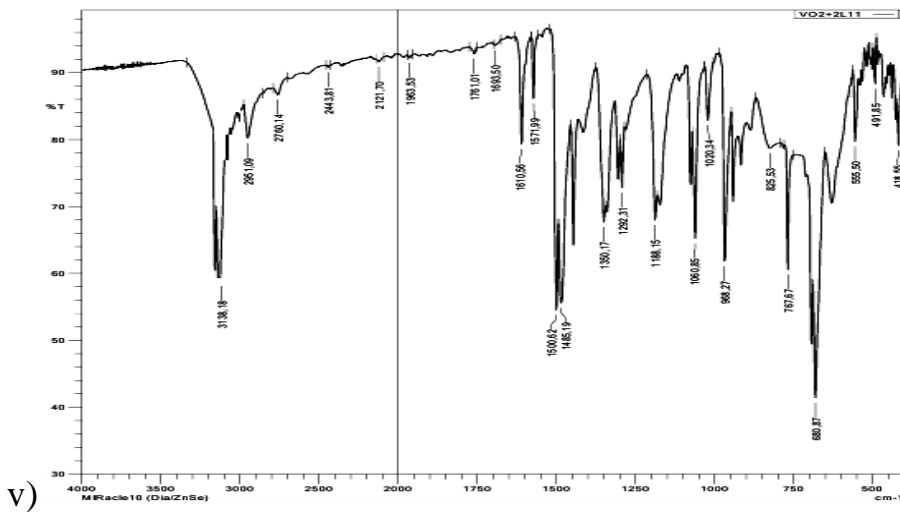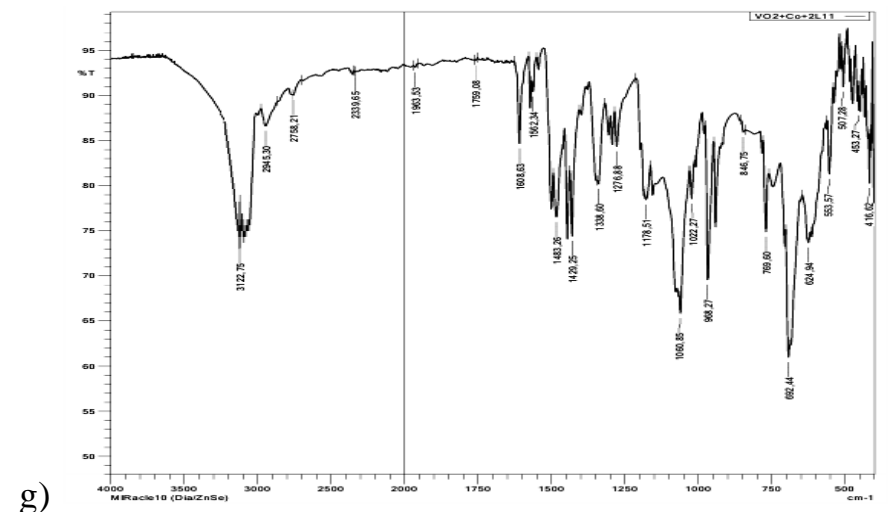
3.9-Rasm. a)L^2; b) [Co(L^2)$_2$]; v) [V$_4$O$_{12}$](L^2+H$^+$)$_4$; g) [Co$_2$V$_4$O$_{12}$ (L^2)$_4$]·2H$_2$O larning IQ-spektrlari

L^2 bilan sintez qilingan kompleks birikmalarning IQ-spektrlaridagi asosiy tebranish chastotalari (sm^{-1})

Birikma	ν_s (C=N)	ν_{as} (C=N)	ν(C-O-C)	ν(OH)	ν(V=O)	ν(V-O)	ν(M-N)	ν(M-S)	ν(M-O)
L^2	1595	1610	1338	-	-	-	-	-	-
[Co(L^2)$_2$]	1582	1617	1301	-	-	-	ν(M-N)584	ν(M-S)455	-
[Cu(L^2)$_2$]	1564	1604	1284	-	-	-	ν(M-N)569	ν(M-S)424	-
[Ni(L^2)$_2$]	1566	1616	1322	-	-	-	ν(M-N)560	ν(M-S)450	-
[Zn(L^2)$_2$]	1580	1605	1331	-	-	-	ν(M-N)583	ν(M-S)425	-
[V$_4$O$_{12}$](L^2+H$^+$)$_4$	1571	1600	1350	-	955	680	-	-	-
[Co$_2$V$_4$O$_{12}$(L^2)$_4$]·2H$_2$O	1592	1608	1339	3122	968	624	ν(M-N) 562	-	ν(M-O)533
[Cu$_2$V$_4$O$_{12}$(L^2)$_4$]·2H$_2$O	1587	1606	1340	3157	956	692	ν(M-N) 581	-	ν(M-O)526
[Ni$_2$V$_4$O$_{12}$(L^2)$_4$]·2H$_2$O	1573	1610	1350	3138	968	628	ν(M-N) 567	-	ν(M-O)515
[Zn$_2$V$_4$O$_{12}$(L^2)$_4$]·2H$_2$O	1571	1610	1341	3155	960	650	ν(M-N) 577	-	ν(M-O)520
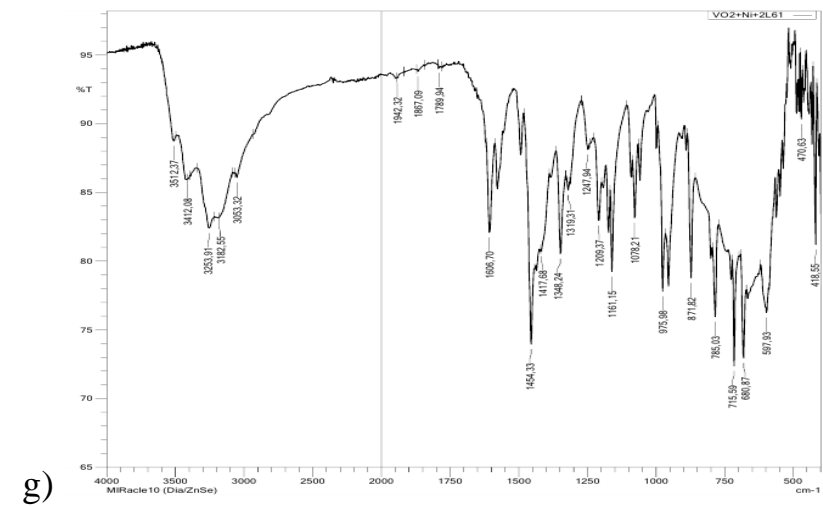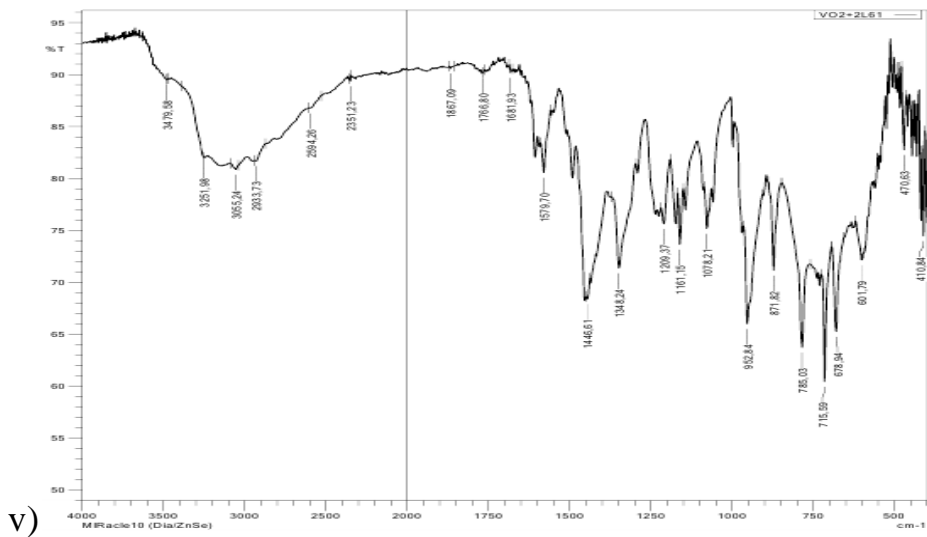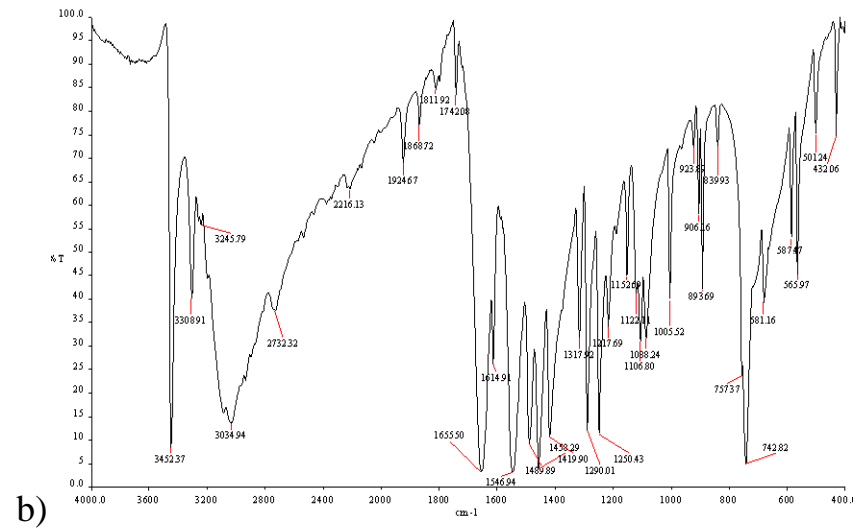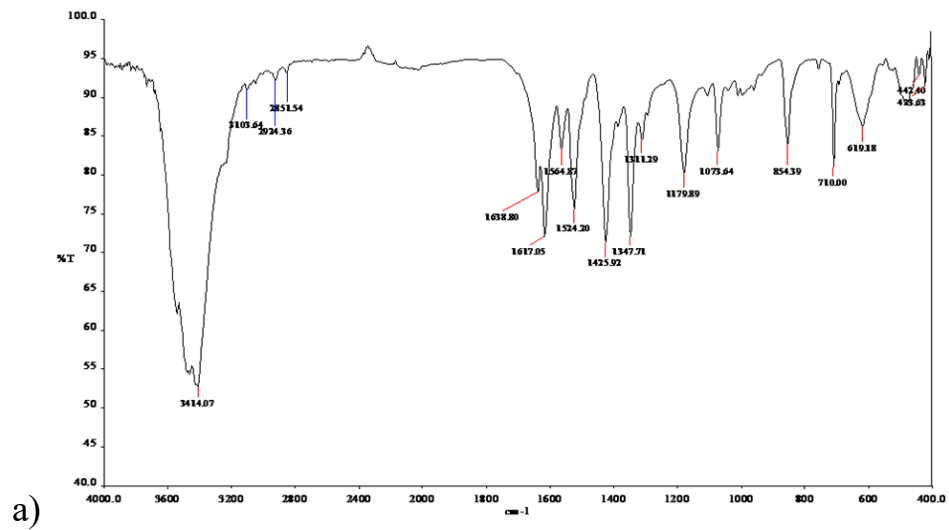
3.10-Rasm. a) L^3; b) [Co(L^3)$_2$(H$_2$O)$_2$]; v)[V$_4$O$_{12}$](L^3+H$^+$)$_2$; g)[Co$_2$V$_4$O$_{12}$(L^3)$_2$]·2H$_2$O larning IQ-spektrlari.

L^3 bilan sintez qilingan kompleks birikmalarning IQ-spektrlaridagi asosiy tebranish chastotalari (sm^{-1})

Birikma	ν(C-O-C)	ν_{as} (COO) ν_s (COO)	ν_{as} (CN) ν_s (CN)	ν(OH)	ν(V=O)	ν(V-O)	ν(M-O)	$\Delta=\nu_{as}$ (COO)-ν_s (COO)
L^3	1294	1564 1425	1638 1617	-	-	-	-	139
$[Co(L^3)_2(H_2O)_2]$	1290	1546 1317	1742 1655	3452	-	-	565	229
$[Cu(L^3)_2(H_2O)_2]$	1299	1532 1322	1699 1656	3369	-	-	507	210
$[Ni(L^3)_2(H_2O)_2]$	1302	1566 1331	1707 1647	3560	-	-	518	235
$[Zn(L^3)_2(H_2O)_2]$	1307	1538 1337	1677 1619	3494	-	-	560	201
$[V_4O_{12}](L^3+H^+)_4$	1298	1579 1446	1766 1681	-	952	678	470	133
$[Co_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	1301	1568 1431	1740 1687	3255	954	682	598	137
$[Cu_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	1310	1565 1421	1755 1693	3165	945	679	599	144
$[Ni_2V_4O_{12}(L^3)_2] \cdot 2H_2O$	1312	1592 1412	1789 1742	3287	975	680	597	171
$[Zn_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	1319	1564 1408	1656 1616	3251	968	677	593	156
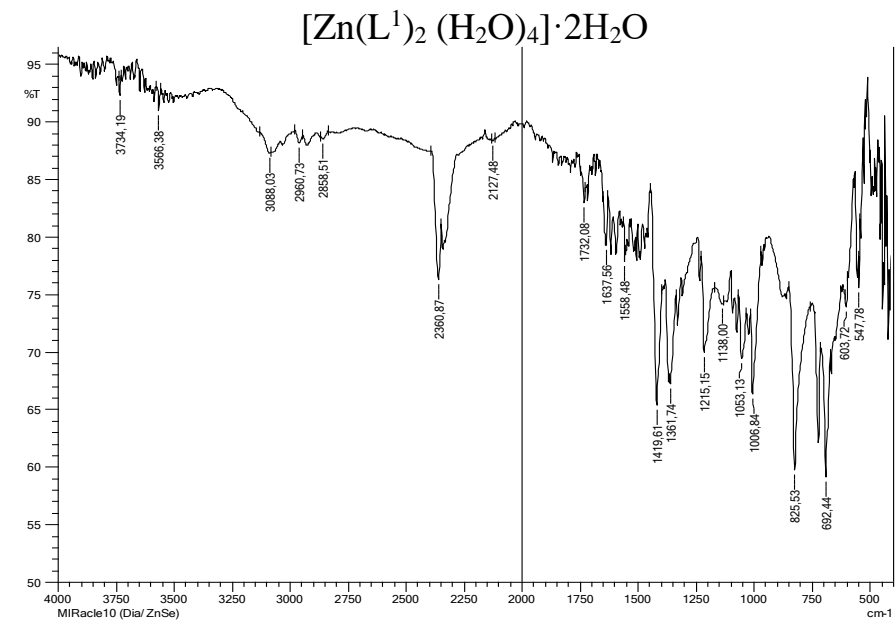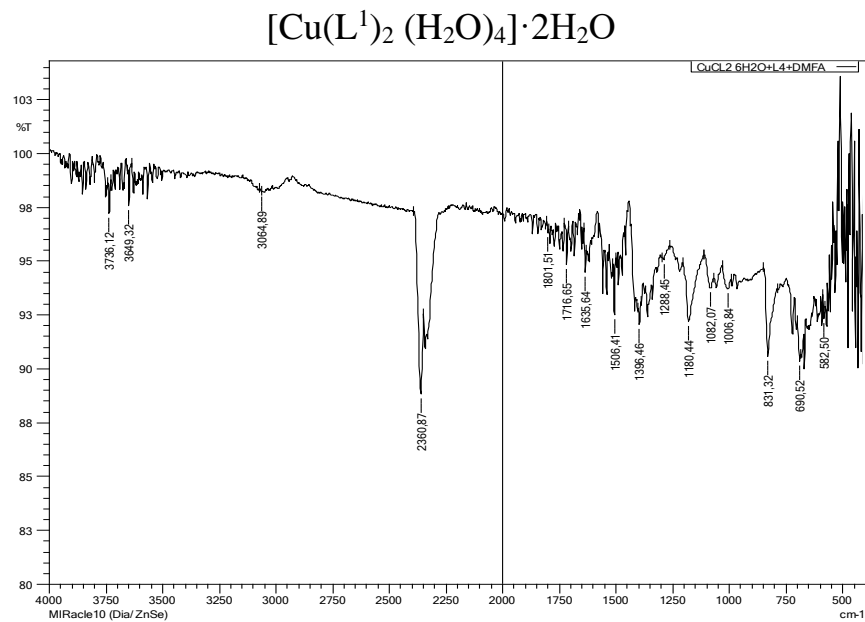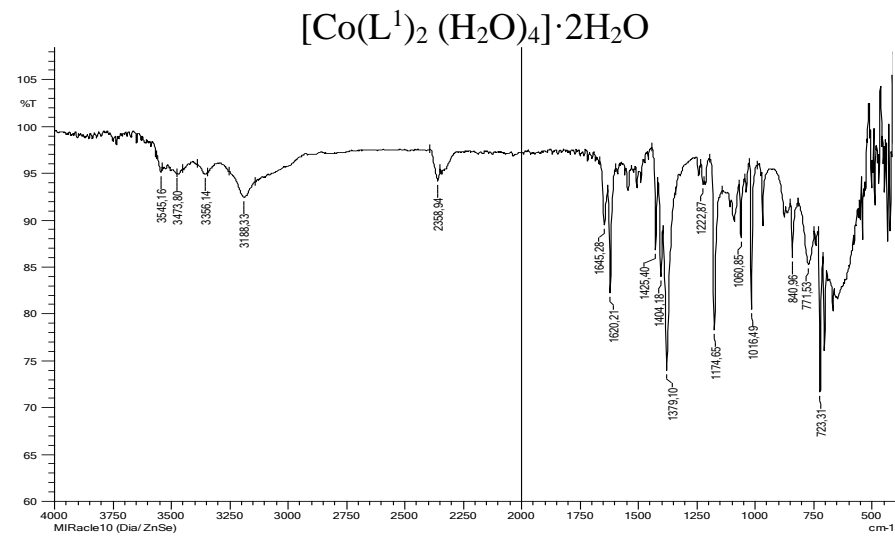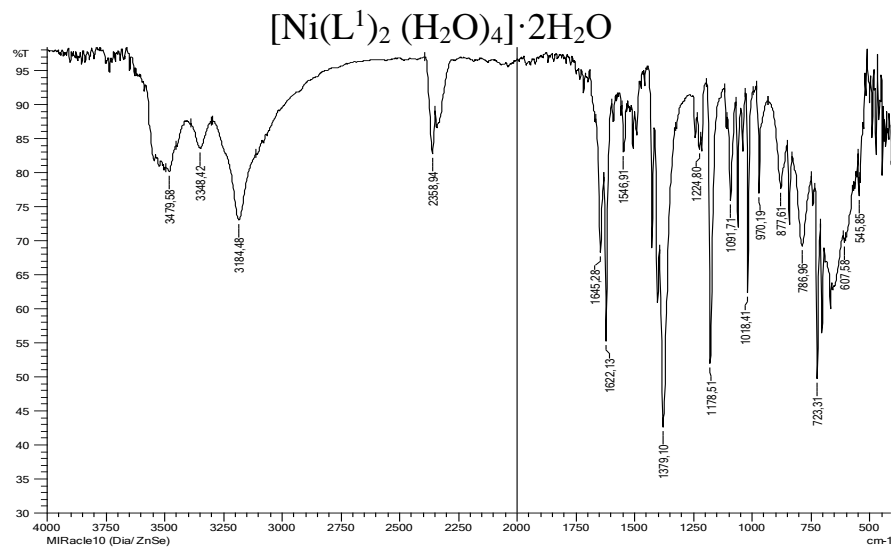
$[Ni(L^1)_2 (H_2O)_4]\cdot2H_2O$

$[Co(L^1)_2 (H_2O)_4]\cdot2H_2O$

$[Cu(L^1)_2 (H_2O)_4]\cdot2H_2O$

$[Zn(L^1)_2 (H_2O)_4]\cdot2H_2O$

3.11-Rasm. L^1 ning MCl_2 ishtirokidagi kompleks birikmalari IQ spektrlari

{[Ni(L^1)$_4$(H$_2$O)$_2$]}

{[Co(L^1)$_4$(H$_2$O)$_2$]}

{[Zn(L^1)$_4$(H$_2$O)$_2$]}

{[Cu(L^1)$_4$(H$_2$O)$_2$]}
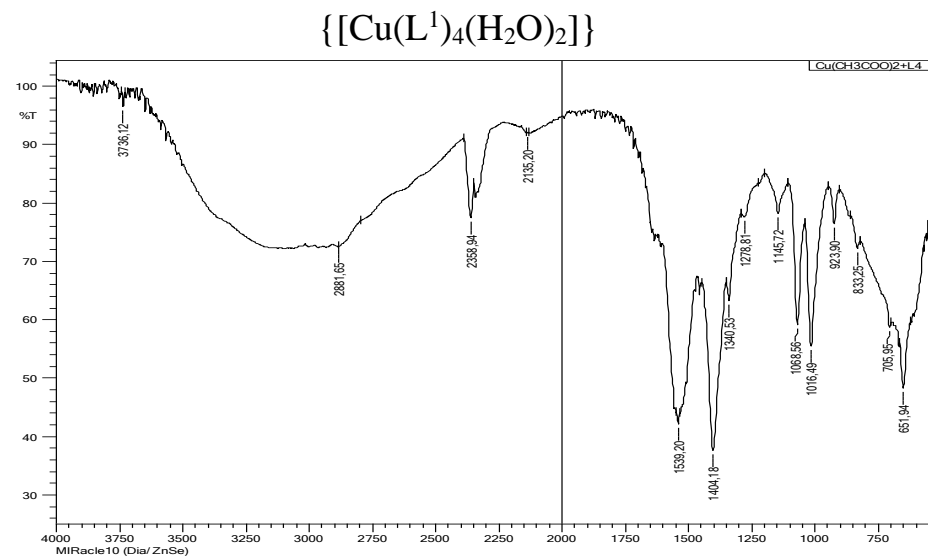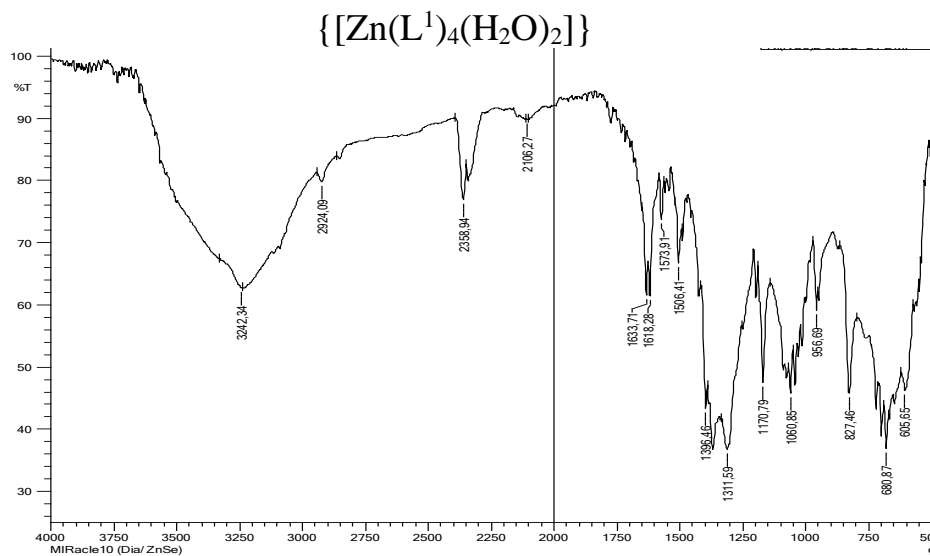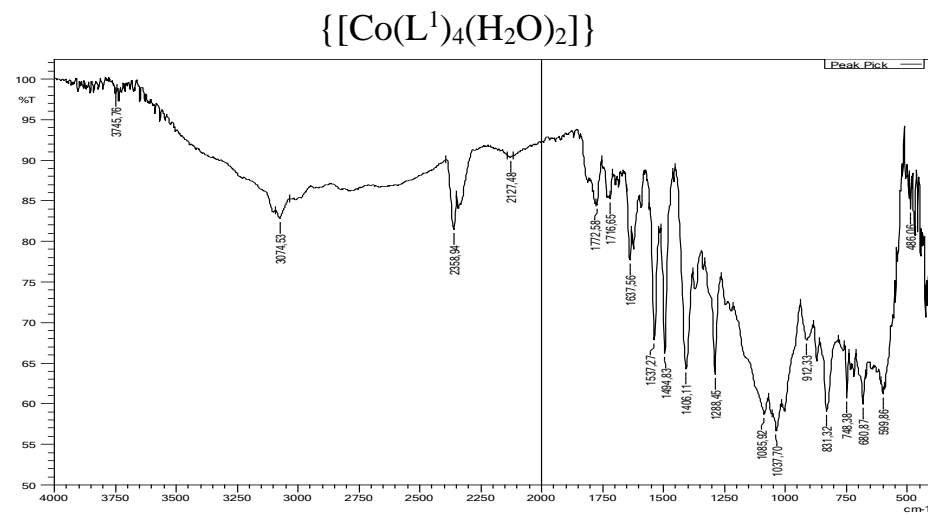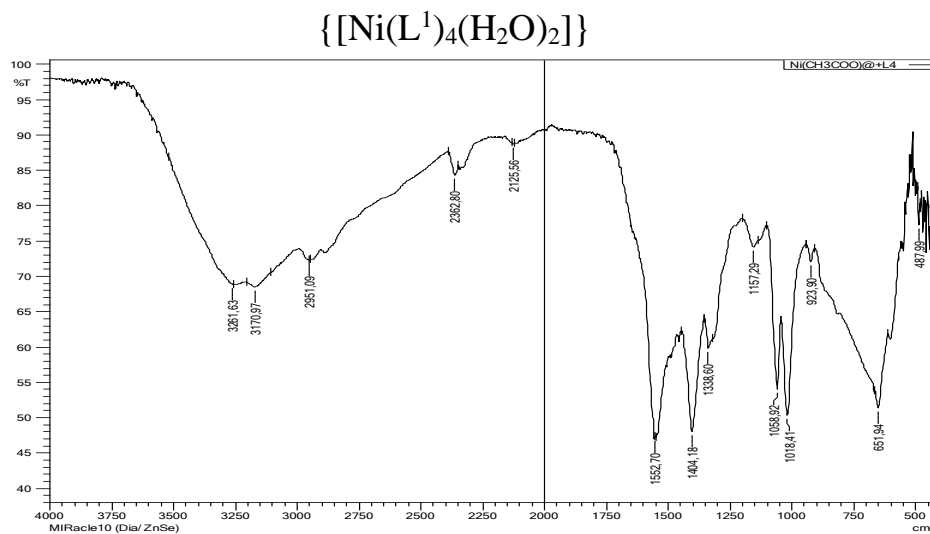
3.12-Rasm. L^1 ning M(OAc)$_2$ ishtirokidagi kompleks birikmalari IQ spektrlari

$[V_4O_{12}](L^1+H^+)_4$

$[Ni_2V_4O_{12}(L^1)_4]$

$[Zn_2V_4O_{12}(L^1)_4]$

$[Co_2V_4O_{12}(L^1)_4]$
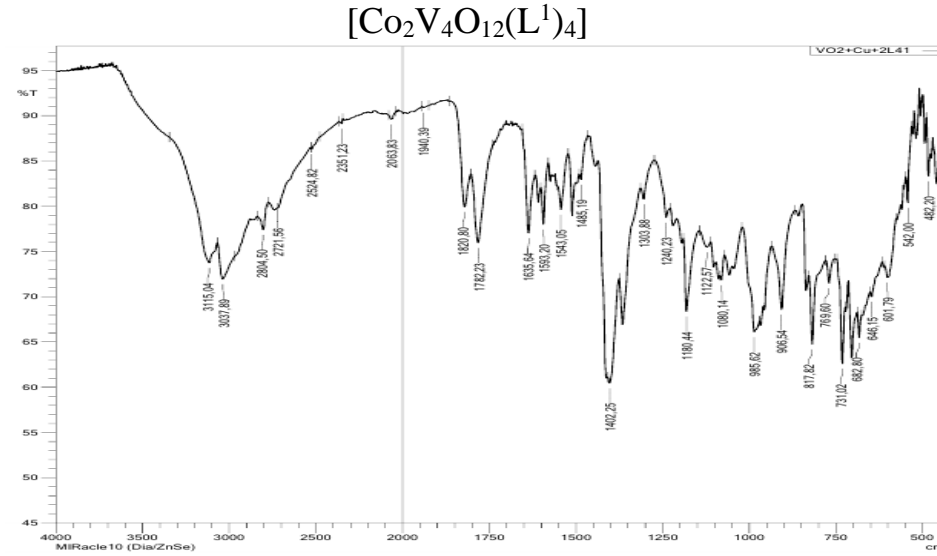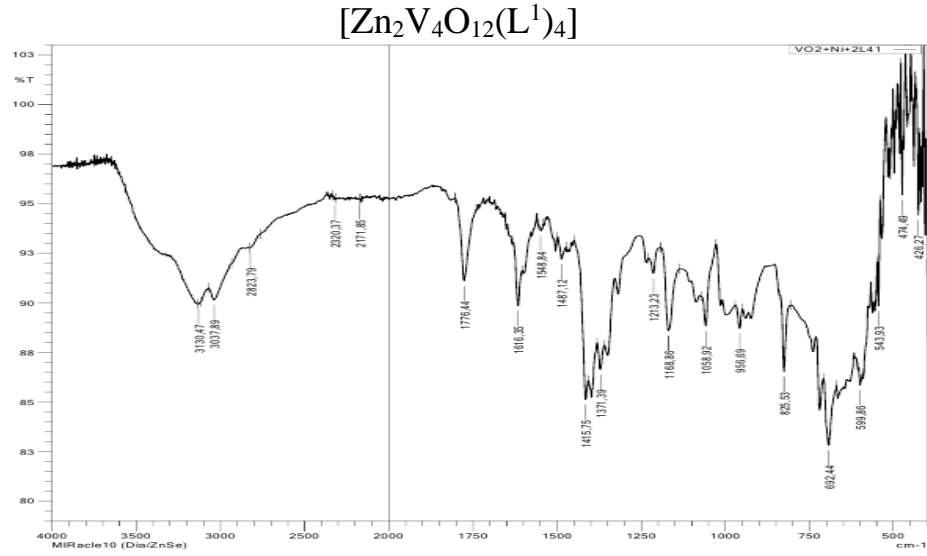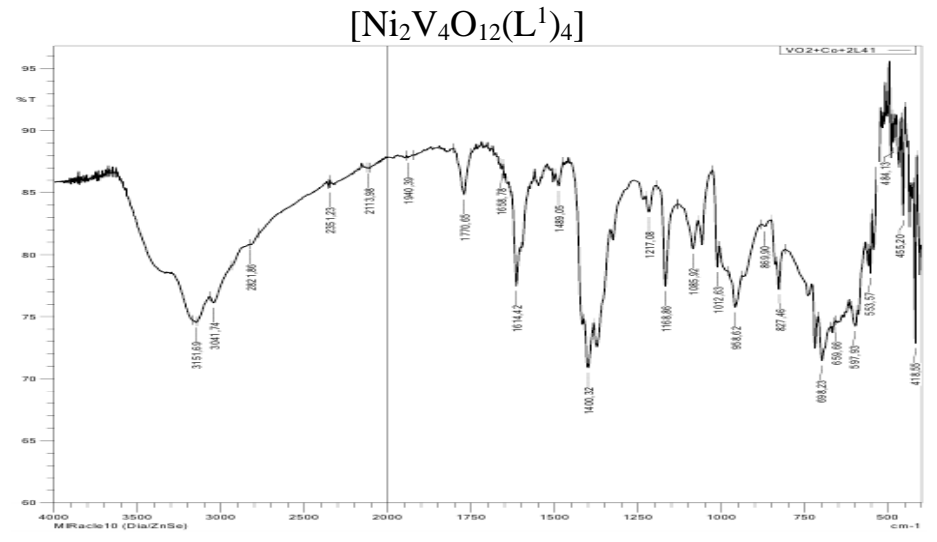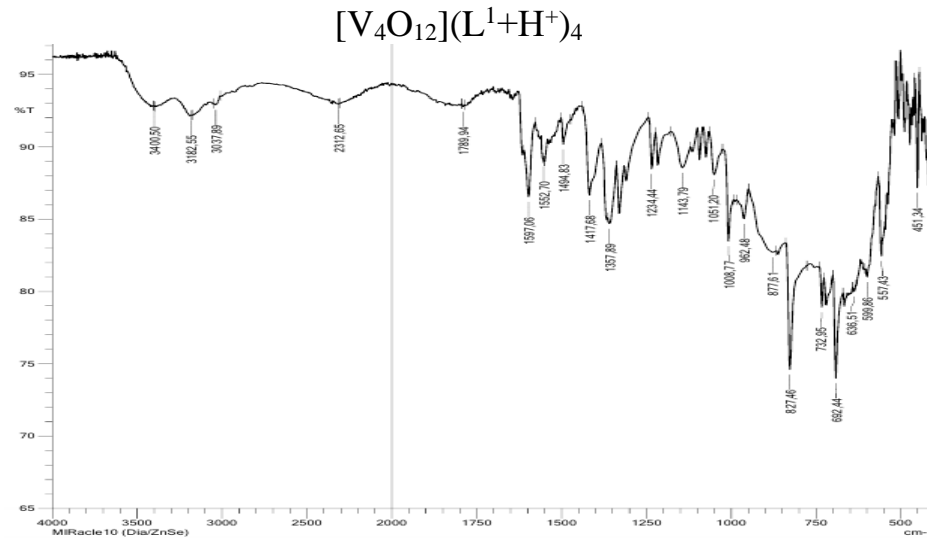
3.13-Rasm. L^1 ning MCl_2 ishtirokidagi geterometalli kompleks birikmalari IQ spektrlari

3.14-Rasm. L^2 ningг MCl$_2$ ishtirokidagi kompleks birikmalari IQ spektrlari

$[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O$

$[Co_2V_4O_{12}(L^2)_4]\cdot 2H_2O$

$[Zn_2V_4O_{12}(L^2)_4]\cdot 2H_2O$

$[Cu_2V_4O_{12}(L^2)_4]\cdot 2H_2O$
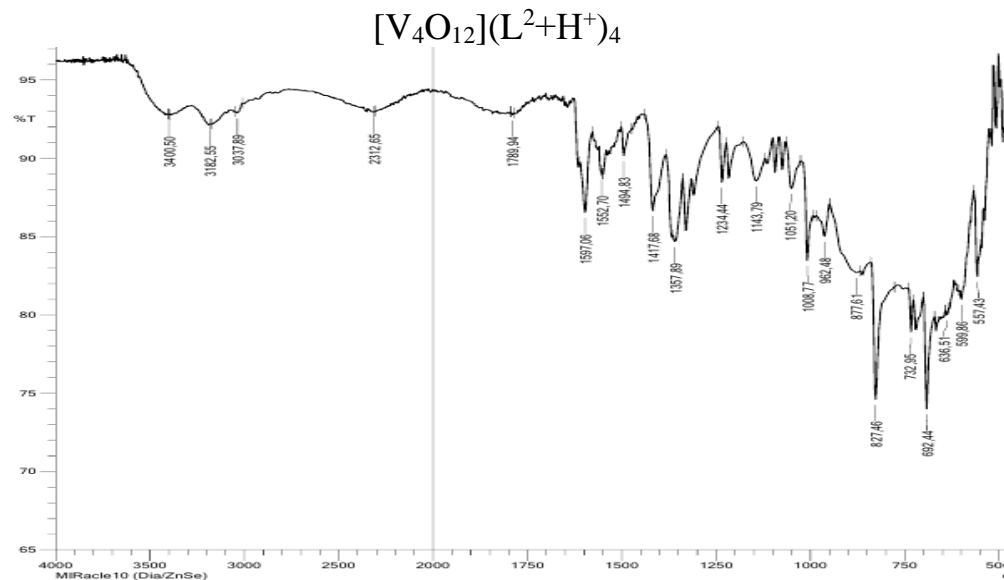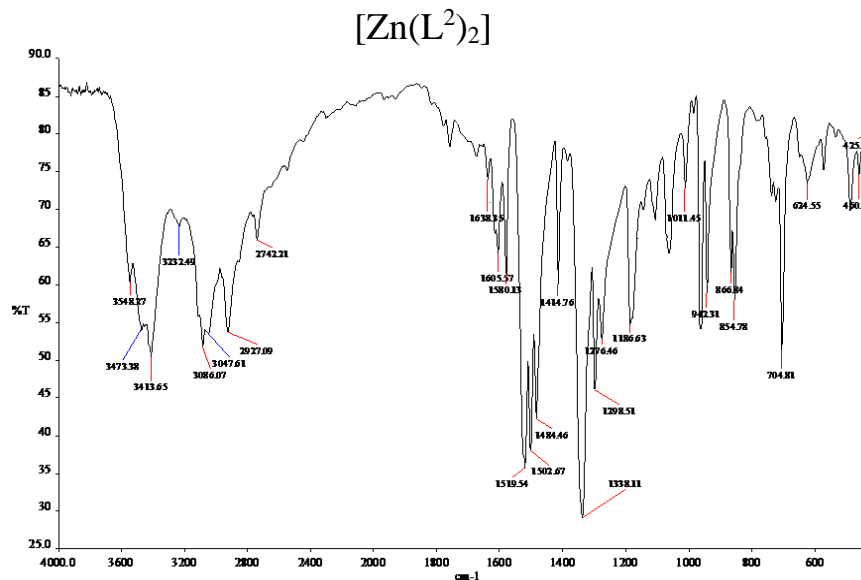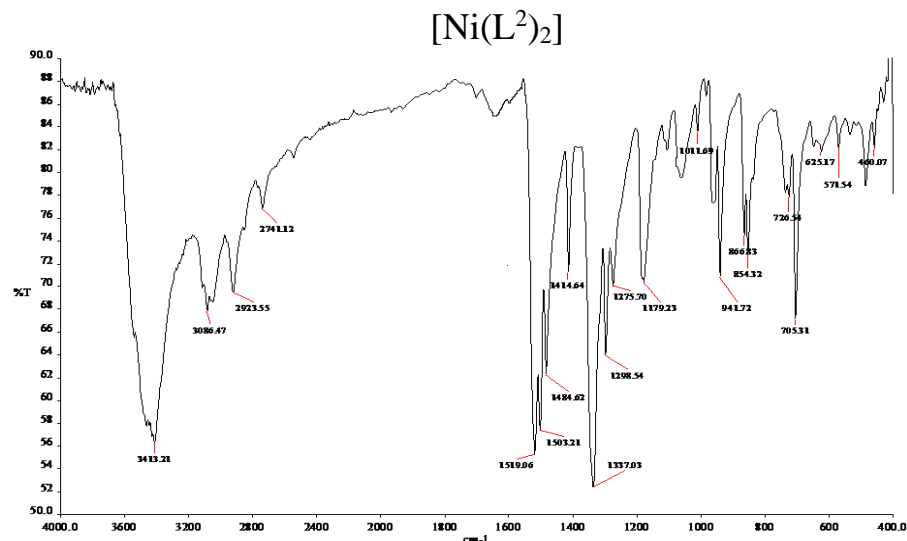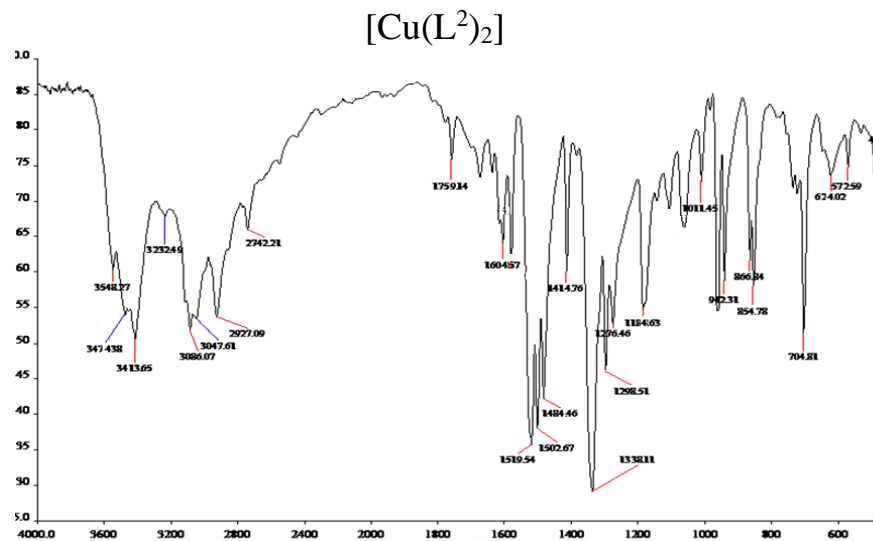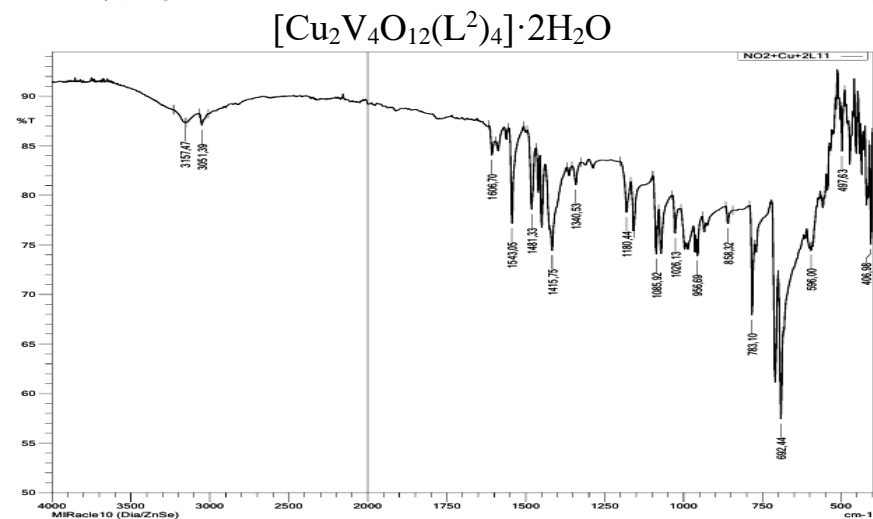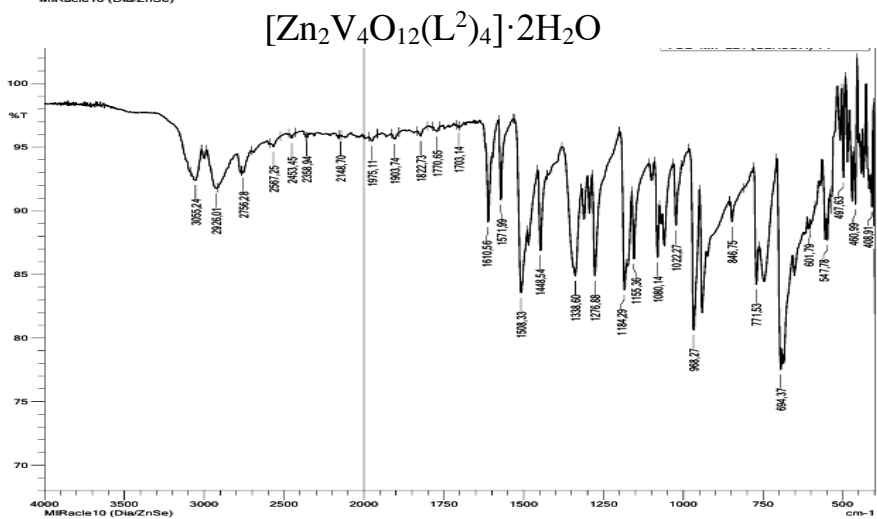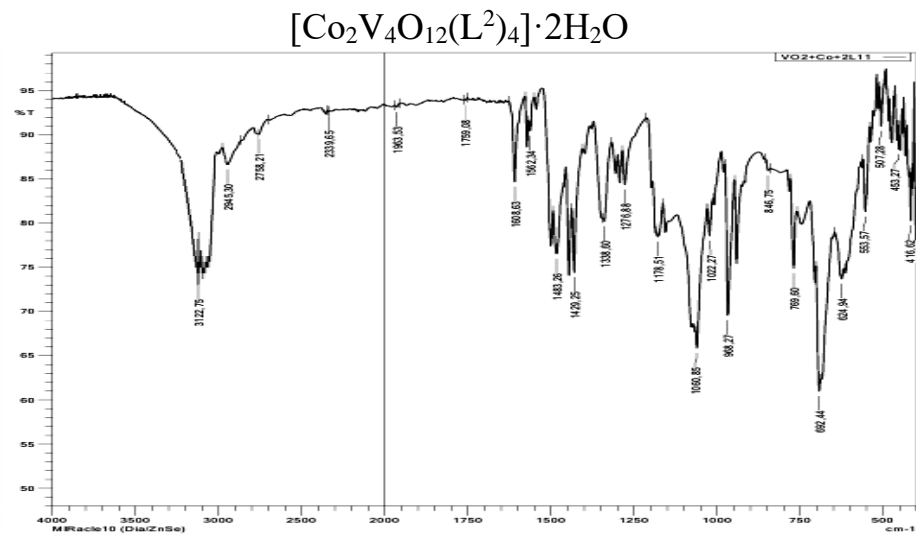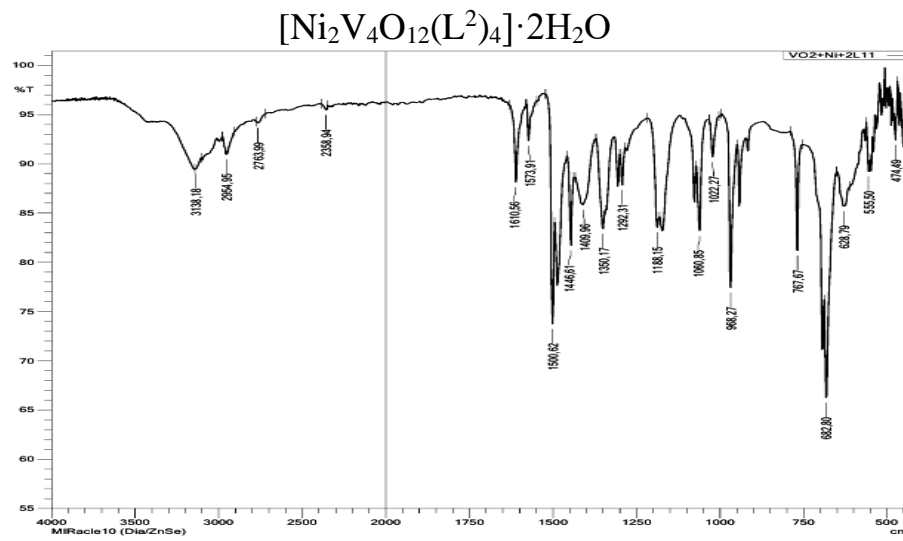
3.15-Rasm. L^2 ning MCl_2 ishtirokidagi geterometalli kompleks birikmalari IQ spektrlari

88

$[V_4O_{12}](L^3+H)^+{}_2$

$[Co_2V_4O_{12}(L^3)_2] \cdot 2H_2O$

$[Zn_2V_4O_{12}(L^3)_2] \cdot 2H_2O$

$[Cu_2V_4O_{12}(L^3)_2] \cdot 2H_2O$
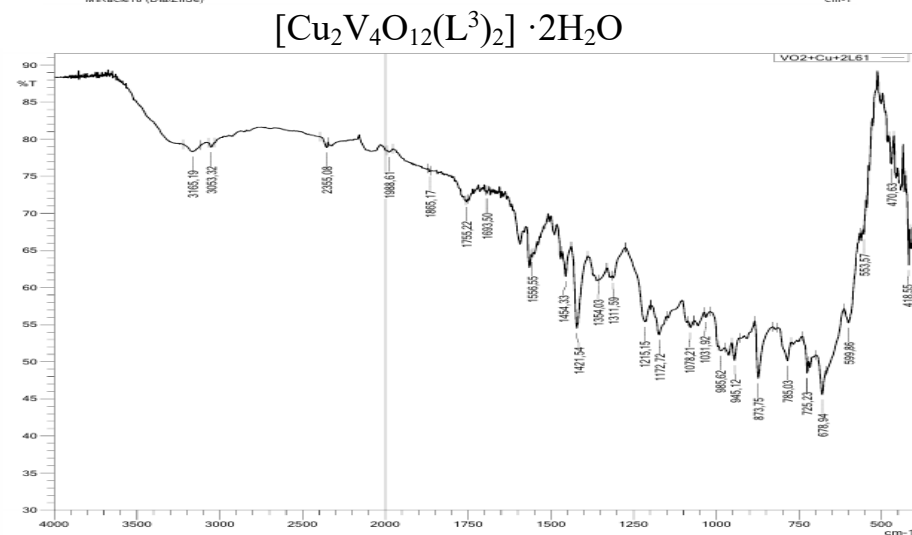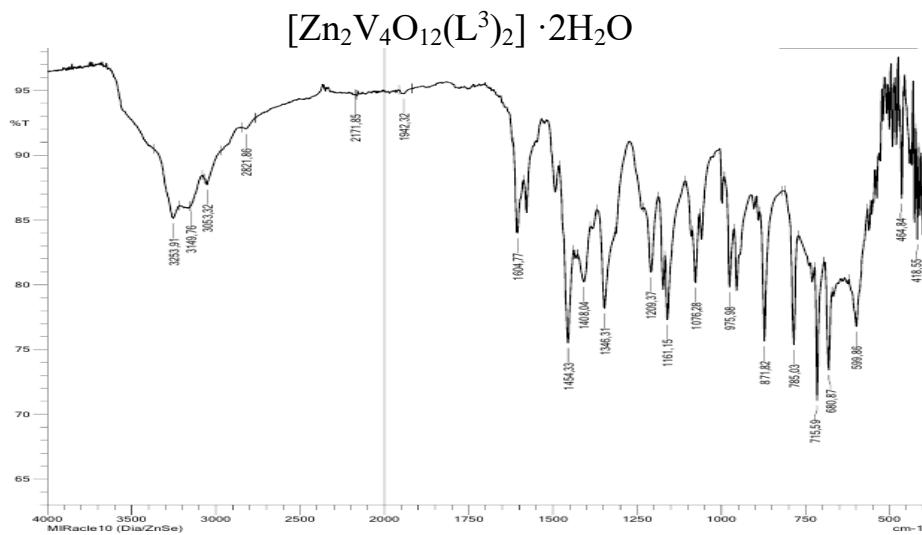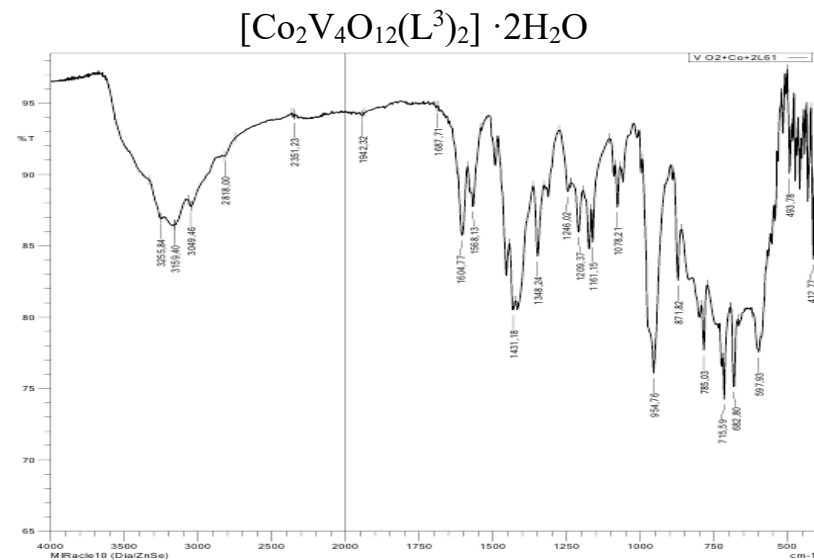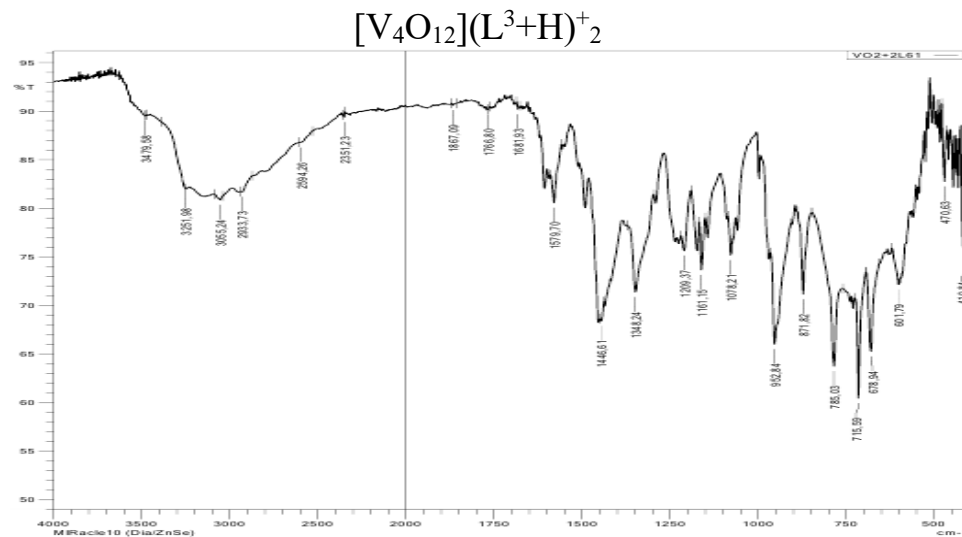
3.16-Rasm. L^3 ning MCl_2 ishtirokidagi geterometalli kompleks birikmalari IQ spektrlari

3.3-§. Sintez qilingan koordinatsion birikmalarning diffuz qaytarilish elektron spetrlari tahlili

Kompleks birikmalarning geometriyasini aniqlashda, markaziy atomning koordinatsion sonini topishda diffuz qaytarilishni elektron spektrlari tahlili muhim ma'lumotlar beradi [135]. Ushbu taxlil usuli UB-sohada 200-800 nm to'lqin uzunligida, to'lqinlar ta'sirida markaziy atomda turli elektron o'tishlar sodir bo'lishi orqali o'lchanadi. Bunda nafaqat markaziy atomning tabiati, balki uni atrofidagi ligand tabiati ham katta ahamiyatga ega bo'ladi.

Sintez qilingan komplekslarda ligandlar tabiatining elektron o'tishlarga ta'sirini o'rganish va Co^{2+}, Ni^{2+}, Cu^{2+} va VO_2^+ ionlarining koordinatsion sonini hamda fazoviy joylashishini aniqlash uchun komplekslarning diffuz qaytarish elektron spektrlari olindi. Bunda nafaqat markaziy atomning tabiati, balki uni atrofidagi ligand tabiati ham katta ahamiyatga ega bo'ladi. $[V_4O_{12}](L^1+H^+)_4$ tarkibli kompleksda vanadiy VO_2^+ (vanadil) holatda uchta o'tish: $^2E{\rightarrow}^2B_2$ (I-335 nm=29850 sm^{-1}), $^2B_1{\rightarrow}^2B_2$ (II-384 nm=26041 sm^{-1}) va $^2A_1{\rightarrow}^2B_2$ (III-402 nm=24875 sm^{-1}) orbitallarda kuzatildi. $[Co(L^2)_2]$ Kompleksda kobaltning tetraedrik yuqori spinli koordinatsion birikmalarida quyidagi uchta o'tishlar kuzatilishi mumkin: $^4T_{1g}(F){\rightarrow}$ $^4T_{2g}$(I-701 nm=14624 sm^{-1}), $^4T_{1g}(F){\rightarrow}$ $^4A_{2g}$ (II-793 nm=12610 sm^{-1}) va $^4T_{2g}(F){\rightarrow}$ $^4T_{1g}(P)$ (III-520 nm=19230 sm^{-1}) (4-rasm, a). $[Ni(L^3)_2(H_2O)_2]$ kompleksda markaziy atomga xos bo'lgan I-o'tish $^1E_{2g}(F){\rightarrow}$ $^3T_{1g}$(819 nm=12210 sm^{-1}), II-o'tish $^1E_{2g}{\rightarrow}$ $^3A_{2g}$ (P)(758 nm=13192 sm^{-1}), III-o'tish $^3T_{2g}{\rightarrow}$ $^3A_{2g}$ (455 nm=21978 sm^{-1}) oralig'ida kuzatildi. Bu nikelli kompleks birikmaning oktaedrik tuzilishda ekanligidan dalolat berdi. Geterometalli tarkibi $[Cu_2V_4O_{12}(L^3)_4]{\cdot}H_2O$ bo'lgan kompleks birikmaning diffuz qaytarilish spektrlari tahlil qilinganda Cu^{2+} ioniga xos bo'lgan 2ta o'tish : $^2E_{2g}{\rightarrow}$ $^2T_{2g}$(758 nm=12992 sm^{-1}) va $^2B_2{\rightarrow}$ ^2E (665 nm=15037 sm^{-1}), vanadil (VO_2^+) uchun $^2E{\rightarrow}^2B_2$ (312 nm=32015 sm^{-1}), $^2B_1{\rightarrow}^2B_2$ (349 nm=28653 sm^{-1}) hamda $^2A_1{\rightarrow}^2B_2$ (390 nm=25641 sm^{-1}) o'tishlar mavjudligi aniqlandi (4-rasm, b). Bunda strukturaning aksial siqilishi kuzatiladi, bunda Cu^{2+} va VO_2^+ ioni siqilgan tetraedrik tuzilishda ekanligi aniqlandi. Quyidagi 3.17-rasmda kompleks birikmalar tarkibidagi asosiy o'tishlarini hisoblash natijalari (sm^{-1}) keltirildi.
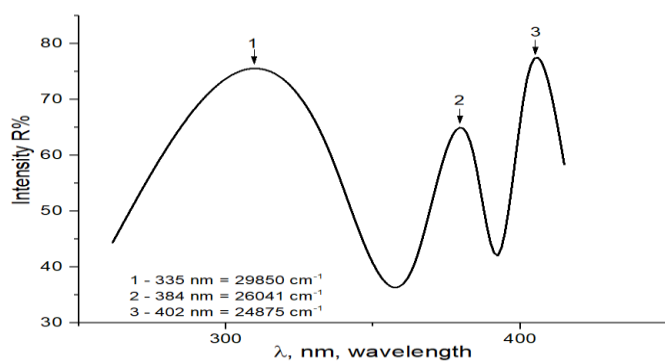
a) $[V_4O_{12}](L^1+H^+)_4$
I-o'tish $^2E\rightarrow^2B_2$ (30000 sm^{-1})
335 nm=29850 sm^{-1}
II-o'tish $^2B_1\rightarrow^2B_2$ (28000 sm^{-1})
384 nm=26041 sm^{-1}
III-o'tish $^2A_1\rightarrow^2B_2$ (25000 sm^{-1})
402 nm=24875 sm^{-1}
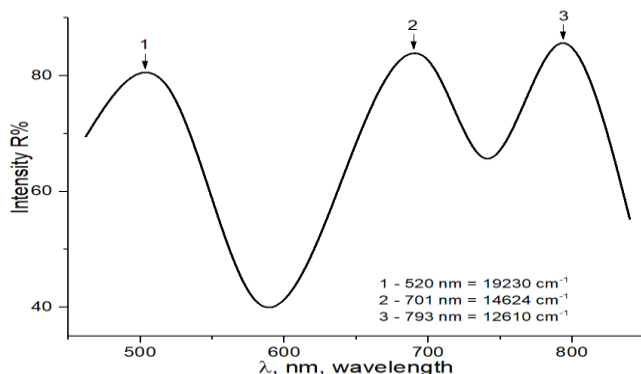
b) $[Co(L^2)_2]$
I-o'tish: $^4T_{1g}(F)\rightarrow^4T_{2g}$(14000 sm^{-1})
I-701 nm=14624 sm^{-1}
II-o'tish: $^4T_{1g}(F)\rightarrow^4A_{2g}$ (12000 sm^{-1})
793 nm=12610 sm^{-1}
III-o'tish: $^4T_{2g}(F)\rightarrow^4T_{1g}(P)$(19000 sm^{-1})
520 nm=19230 sm^{-1}
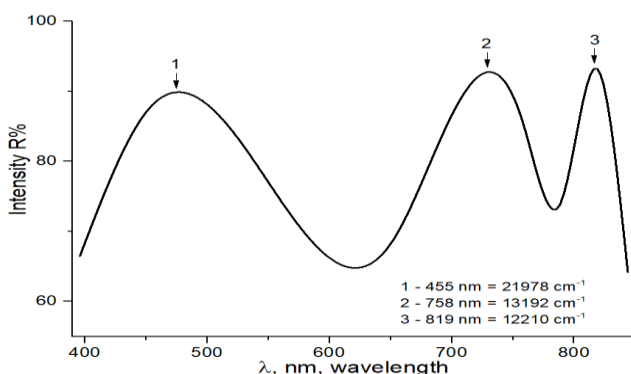
v) $[Ni(L^3)_2(H_2O)_2]$
I-o'tish: $^1E_{2g}(F)\rightarrow^3T_{1g}$(8000-13000 sm^{-1})
819 nm=12210 sm^{-1}
II-o'tish:$^1E_{2g}\rightarrow^3A_{2g}(P)$(13000-17000 sm^{-1})
758 nm=13192 sm^{-1}
III-o'tish: $^3T_{2g}\rightarrow^3A_{2g}$ (19000-27000 sm^{-1})
455 nm=21978 sm^{-1}
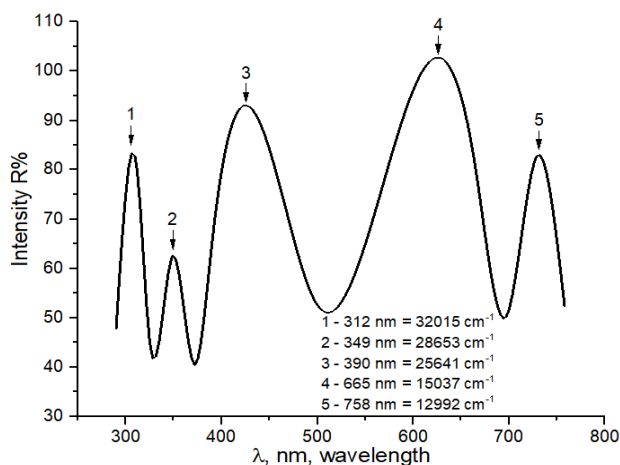
g) $[Cu_2V_4O_{12}(L^3)_4]\cdot2H_2O$
Cu^{2+} uchun
I-o'tish: $^2E_{2g}\rightarrow^2T_{2g}$(10000-13000 sm^{-1})
758 nm=12992 sm^{-1}
II-o'tish: $^2B_2\rightarrow^2E$ (13000-15000 sm^{-1})
665 nm=15037 sm^{-1}
VO_2^+ uchun
I-o'tish: $^2E\rightarrow^2B_2$ (30000 sm^{-1})
312 nm=32015 sm^{-1}
II-o'tish: $^2B_1\rightarrow^2B_2$ (28000 sm^{-1})
349 nm=28653 sm^{-1}
III-o'tish $^2A_1\rightarrow^2B_2$ (25000 sm^{-1})
390 nm=25641 sm^{-1}

3.17-Rasm. a) $[V_4O_{12}](L^1+H^+)_4$; b) $[Co(L^2)_2]$; v) $[Ni(L^3)_2(H_2O)_2]$;

g)$[Cu_2V_4O_{12}(L^3)_4]\cdot2H_2O$ komplekslarning DQES lari

3.4-§. Sintez qilingan kompleks birikmalarining rentgenfazaviy tahlili tadqiqoti

Sintez qilingan gomo- va geterometalli kompleks birikmalarning individualligini, o'ziga xos kristall panjaraga ega ekanligini, boshlang'ich va sintez qilingan moddalar rentgenogrammalaridagi tekisliklar orasidagi masofalari va ularning sezgirliklarini solishtirish maqsadida rentgenfazaviy tahlildan foydalanildi.

Kompleks birikmalarning rentgenogrammalari 3.18-3.20 rasmlarda, difraktogrammaning hisoblash natijalari 3.9-3.11 jadvallarda keltirilgan.
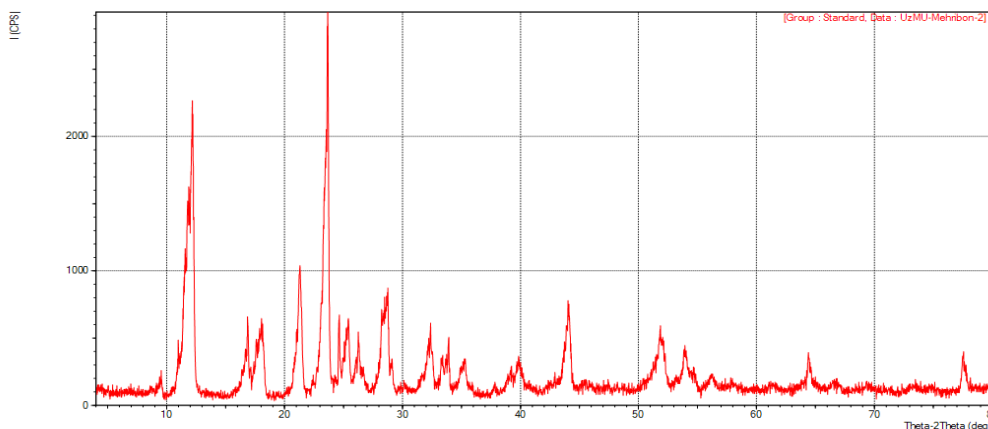
3.18-Rasm. L^1 ning rengenogrammasi.
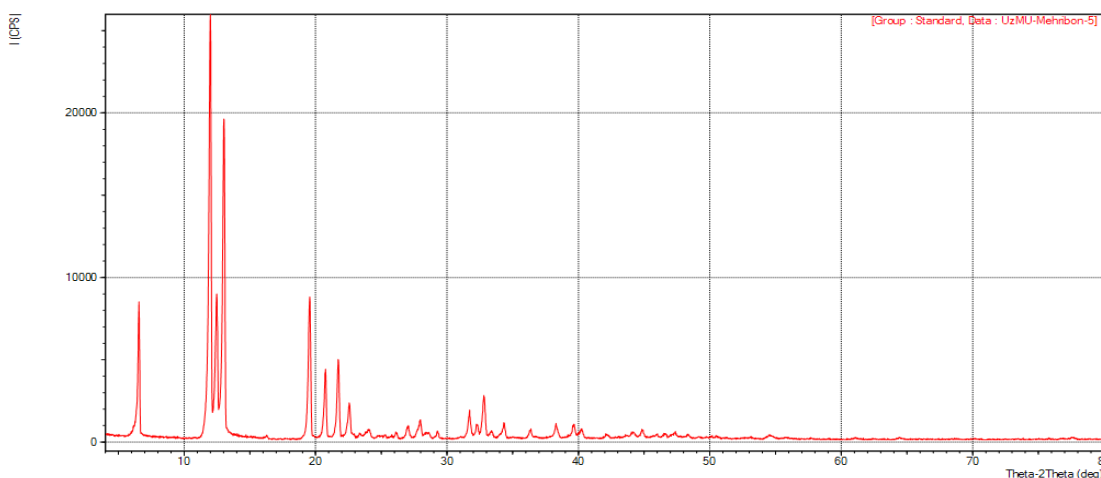
3.19-Rasm. $[Co(L^1)_2(H_2O)_2]$ ning rentgenogrammasi

L^1 ning rentgenogrammasidagi muhim ko'rsatkichlari

Burchak; [2θ]	Balandligi [cts]	Tekisliklar orasidagi masofa; [Å]	Intensivlik I (%)	Uch kengligi
9.4800	467	9.32180	5	0.2800
11.0400	1353	8.00784	11	0.4320
11.6200	6339	7.60941	43	0.5428
12.1600	7143	7.27268	84	0.3212
16.3400	534	5.42042	5	0.2400
16.7883	1806	5.27668	18	0.4433
17.5800	1436	5.04079	14	0.4200
18.0000	2253	4.92411	21	0.5040
20.7800	763	4.27120	8	0.2400
21.2582	3642	4.17619	38	0.4005
23.5217	11937	3.77918	100	0.4603
24.6112	852	3.61430	14	0.2358
25.2662	2132	3.52206	19	0.4725
26.2185	1167	3.39626	12	0.3571
26.6800	316	3.33855	4	0.1900
27.7800	299	3.20880	3	0.2400
28.3200	2268	3.14883	24	0.4756
28.6400	2067	3.11437	30	0.3534
29.0400	667	3.07238	10	0.2700
31.5800	362	2.83082	4	0.2600
32.2600	2042	2.77268	16	0.5360
33.3200	578	2.68686	9	0.2800
33.7571	962	2.65306	11	0.4208
35.1125	1187	2.55369	9	0.5450
38.8200	500	2.31791	4	0.1734
39.2000	0	2.29631	6	0.0000
39.8216	1637	2.26188	9	0.5767
42.8400	262	2.10925	3	0.1466
43.6400	960	2.07242	11	0.2960
43.9793	2400	2.05721	26	0.4653
51.3200	1017	1.77886	6	0.4800
51.8583	2172	1.76165	16	0.6567
53.9150	1432	1.69921	12	0.3900
54.7200	404	1.67610	5	0.2266
56.1500	476	1.63675	4	0.3800
63.8500	273	1.45667	3	0.2200
64.4008	953	1.44554	12	0.2717
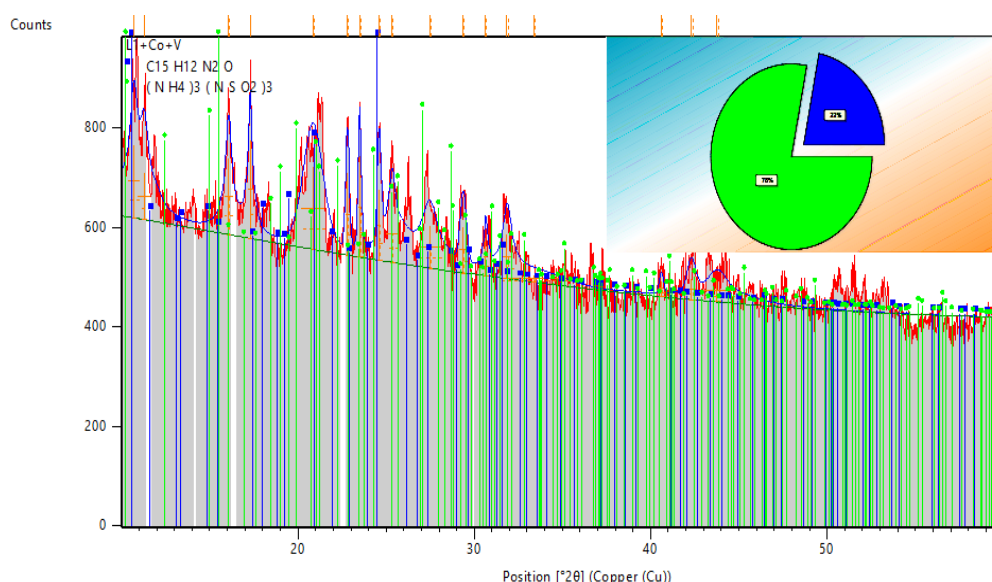
3.20-Rasm. $[Co_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ ning rentgenogrammasi

Burchak; [2θ]	Balandlik [cts]	Tekisliklar orasidagi masofa; [Å]	Intensivlik I (%)	Uch kengligi
6.5395	1477	13.50528	29	0.1623
11.9614	5055	7.39298	100	0.1974
12.4478	1646	7.10517	33	0.2150
13.0009	3837	6.80411	76	0.2058
19.5228	1745	4.54332	35	0.1791
20.7190	832	4.28364	16	0.1887
21.6982	961	4.09249	19	0.2051
22.5348	410	3.94241	8	0.2600
27.9100	220	3.19415	4	0.2013
31.6784	312	2.82225	6	0.2006
32.2661	166	2.77217	3	0.2239
34.3032	523	2.72995	10	0.1992
38.2746	189	2.61206	4	0.2077
39.6120	177	2.27337	4	0.2219

Burchak; [2θ]	Balandlik [cts]	Tekisliklar orasidagi masofa; [Å]	Intensivlik I (%)	Uch kengligi
10.7010	148.19	8.26077	73.01	0.7633
10.7276	74.09	8.26077	36.51	0.7633
11.2876	95.67	7.83275	47.14	0.8827
11.3157	47.84	7.83275	23.57	0.8827
16.0651	153.65	5.51254	75.70	0.5901
16.1053	76.82	5.51254	37.85	0.5901

17.2919	195.96	5.12411	96.55	0.3286
17.3352	97.98	5.12411	48.28	0.3286
20.8475	166.94	4.25752	82.25	1.6109
20.8998	83.47	4.25752	41.13	1.6109
22.7903	164.80	3.89878	81.20	0.2899
22.8477	82.40	3.89878	40.60	0.2899
23.4847	202.96	3.78505	100.00	0.2278
23.5439	101.48	3.78505	50.00	0.2278
24.5908	141.57	3.61724	69.75	0.2888
24.6529	70.78	3.61724	34.88	0.2888
25.3215	116.54	3.51449	57.42	0.7808
25.3855	58.27	3.51449	28.71	0.7808
27.4604	85.01	3.24541	41.89	1.5039
27.5300	42.51	3.24541	20.94	1.5039
29.3547	94.70	3.04015	46.66	0.4816
29.4292	47.35	3.04015	23.33	0.4816
30.6312	78.70	2.91630	38.78	0.2090
30.7092	39.35	2.91630	19.39	0.2090
31.8480	90.36	2.80760	44.52	0.7381
31.9292	45.18	2.80760	22.26	0.7381
33.3920	14.86	2.68123	7.32	4.4824
33.4774	7.43	2.68123	3.66	4.4824
40.5834	31.96	2.22116	15.75	0.2978
40.6887	15.98	2.22116	7.87	0.2978
42.2769	42.63	2.13603	21.00	0.6495
42.3870	21.31	2.13603	10.50	0.6495
43.7525	44.34	2.06734	21.85	2.1753
43.8669	22.17	2.06734	10.92	2.1753

Ligand va sintez qilingan gomo- va geterometalli kompleks birikmalarning rentgenogrammalarini solishtirilganda ular bir-biridan tubdan farq qilishi aniqlandi. Difraktogrammaning tahlilidagi hisoblash natijalari asosida olingan tahlil qiymatlari sintez qilingan gomo- va geterometalli kompleks birikmalarning individual ekanligini koʻrsatdi. Rentgenfazaviy tahlilda bir va aralash metalli komplekslar birikmalar oʻzaro izostruktur emasligi isbotlandi [136].

3.5-§. Geterometalli koordinatsion birikma rentgenfazaviy tahlil natijalarini Fullprof dasturi yordamida qayta ishlashdan olingan natijalarning strukturaviy tahlili

Sintez qilingan geterometalli kompleks birikmalarning tuzilishini isbotlash uchun O'zR FA Yadro fizikasi ilmiy tadqiqot institutida rentgen nurlari sochilishiga asoslanib ishlaydigan Malvern Pananalytical kompaniyasining Empyrean rusumli zamonaviy difraktometrida strukturaviy tahlil olib borildi. Ushbu qurilma o'zining texnik ko'rsatkichlari, tadqiqotlar o'tkazish imkoniyatlari, qo'shimcha asbob-uskunalari, zamonaviy dasturlari, difraksiya natijalari asosida to'laqonli strukturalar bazasi mavjudligi bilan dunyodagi stabil, ishonchli ishlaydigan yetakchi qurilmalardan hisoblanadi. Boshqa difraktometrlardan farqli o'laroq, bu difraktometr kichik va keng sochilish burchaklaridan tashqari o'ta kichik sochilish burchaklarida ham tadqiqotlar o'tkazishga imkon beradi. Turli material, birikma hamda har xil o'lcham va holatdagi namunalarning strukturasini, tarkib-tuzilish hamda ularning xossalari orasidagi bog'liqlikni aniqlash asosida ularning xossalarini yaxshilashga imkonyatlar yaratib beradi [137].

Difraktogramma natijalarini Fullprof dasturi orqali qayta ishlashdan olingan kristallografik xarakteristikalar va rentgenostrukturaviy tahlil natijalari 3.12-3.15-jadvallar va 3.21-3.22 rasmlarda keltirilgan.

3.12-Jadval

$[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O$ kompleksining kristallografik ma'lumotlari va struktura detallari

Parametrlar	Ko'rsatkich	Parametrlar	Ko'rsatkich
Formula	$Ni_2V_4O_{16}C_{32}H_{24}N_8S_4$	Z	8
Molyar massa	1220	μ (CuK$_\alpha$), mm^{-1}	1.929
Singoniya	ortorombik	T, °K	298
Fazoviy guruh	P n/a 21	Kristal o'lchami	54 nm
a, Å	27.701870	Nur sindirish ko'rsatkichi	6,2175
b, Å	29.338186	R$_{int}$	0,673
c, Å	27.275402	$F^2 \geq 2\sigma(F^2)$ kriteriy	0,071
α, β, γ, deg	90, 90, 90	Parametr	1,01
V, Å^3	22409.297825	Muvofiqlik mezonlari (F^2)	0,210

θ°, grad	min: 0094	R₁, ωR₂ (I>2σ(I))	298
	max: 49.986877		

Difraksion intensivliklarning kengligi yordamida rentgen nurlarining kogerent tarqalish mintaqalari (KTM) o'lchamlarini tahmin qilish mumkin, bu esa kristallarning o'rtacha o'lchamlariga to'g'ri keladi. Buning uchun odatda Debay-Sherrer formulasidan foydalaniladi:

$$D = \frac{k\lambda}{\beta_S \cos\theta} \qquad (3.1)$$

Bu yerda, k – zarra shaklini hisobga olish uchun tuzatish koeffitsienti (k ~ 0,9), λ – nurlanish to'lqin uzunligi (masalan, Cu anod uchun 0,15406 nm), θ – difraksiya refleksi uchun Bragg burchagi, β_S–maksimal yarmining to'lqin kengligi (radianlarda) [138].

3.13-Jadval

Rentgen nurlarining kogerent tarqalish mintaqalari o'lchamlari

2θ°	FWHM°	β_S, rad	D, nm
9.20616	0.09763	0.00170	81.68
10.66235	0.08667	0.00151	91.82
21.47379	0.16324	0.00285	49.52
25.38050	0.34147	0.00596	23.84
32.50150	0.35496	0.00619	23.34

a)   b)

3.21-Rasm. $[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O\cdot$kompleksining:
a)elementar yacheykasi b) upakovkalangan strukturaviy tuzilishi.
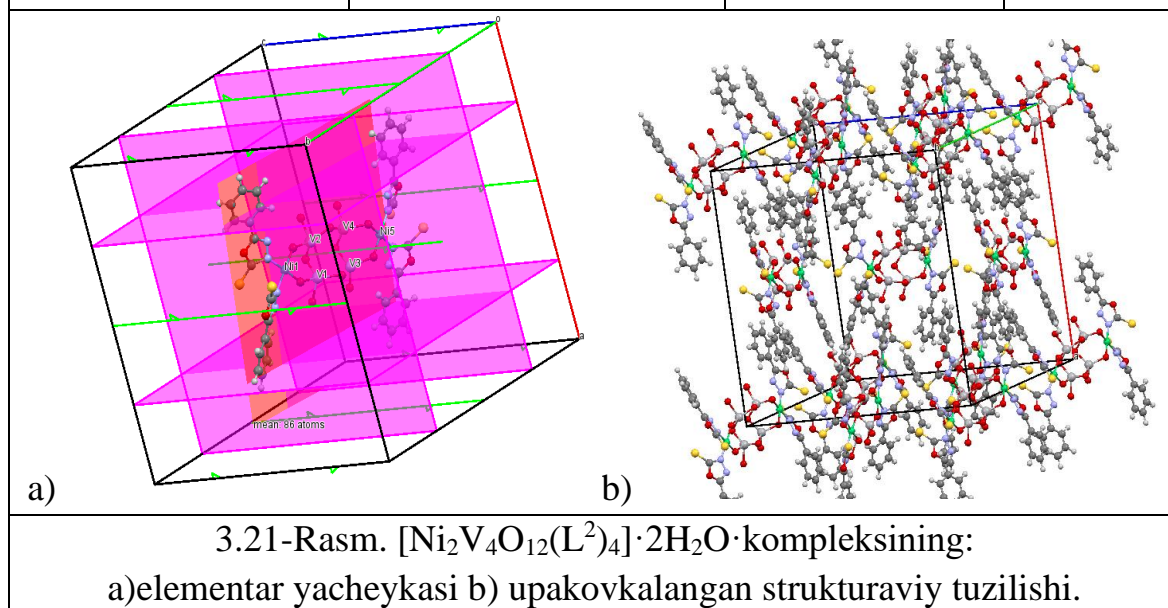
Molekulalarning bog' uzunliklari

Бог	Å	Бог	Å
Ni1-N1	2.164	O8-V4	2.412
Ni1-N3	2.260	V3-O10	2.135
Ni1-O3	2.099	V3-O11	2.0905
Ni1-O4	2.112	V3-O13	2.401
O1-C1	1.4997	V4-O11	2.0994
O1-C3	1.4823	V4-O12	2.130
N1-N2	1.488	V4-O14	2.360
N1-C3	1.625	O13-Ni5	2.124
N2-C1	1.480	O14-Ni5	2.095
C1-C2	1.6429	Ni5-N5	2.242
C2-C4	1.5586	Ni5-N6	2.245
C2-C5	1.609	N5-N7	1.5033
C3-S1	1.9560	N5-C17	1.654
C4-H1	1.220	N6-N8	1.5179
C4-C6	1.5208	N6-C19	1.624
C5-H2	1.2060	N7-C18	1.4503
C5-C7	1.5288	N8-C20	1.494
C6-C8	1.588	C17-O15	1.4970
C6-H19	1.2126	C17-S3	2.001
C7-H3	1.229	C18-O15	1.535
C7-C8	1.557	C18-C30	1.700
C8-H20	1.1837	C19-O16	1.4972
O2-C9	1.4807	C19-S4	1.9474
O2-C11	1.4761	C20-O16	1.5136
N3-N4	1.5080	C20-C24	1.722
N3-C11	1.649	C21-C22	1.5690
N4-C9	1.484	C21-C30	1.6002
C9-C10	1.649	C21-H9	1.251
C10-C12	1.5479	C22-C32	1.613
C10-C13	1.614	C22-H10	1.2098
C11-S2	1.9624	C23-C31	1.5374
C12-H4	1.2156	C23-C32	1.5387
C12-C14	1.522	C23-H12	1.253
C13-H5	1.2040	C24-C25	1.650
C13-C15	1.533	C24-C26	1.609
C14-H6	1.1969	C25-C29	1.554
C14-C16	1.574	C25-H14	1.235
C15-H7	1.2270	C26-C27	1.532
C15-C16	1.5455	C26-H18	1.229
C16-H8	1.1795	C27-C28	1.574

O3-V1	2.431	C27-H17	1.2252
O4-V2	2.444	C28-C29	1.580
V1-O5	2.431	C28-H16	1.1896
V1-O6	2.0936	C29-H15	1.242
V1-O9	2.137	C30-C31	1.625
V2-O6	2.0861	C31-H13	1.1981
V2-O7	2.120	C32-H11	1.1990
V2-O8	2.411		

3.15-Jadval

Molekuladagi atomlar orasidagi valent burchaklar

Burchak	ω, grad	Burchak	ω, grad
N1-Ni1-N3	84.93	V1-O6-V2	94.52
N1-Ni1-O3	91.44	V2-O8-V4	139.63
N1-Ni1-O4	178.84	O10-V3-O11	111.85
N3-Ni1-O3	176.35	O10-V3-O13	94.53
N3-Ni1-O4	96.15	O11-V3-O13	102.02
O3-Ni1-O4	87.48	O8-V4-O11	108.69
C1-O1-C3	102.21	O8-V4-O12	97.85
Ni1-N1-N2	123.70	O8-V4-O14	135.09
Ni1-N1-C3	133.84	O11-V4-O12	115.22
N2-N1-C3	102.45	O11-V4-O14	107.57
N1-N2-C1	108.67	O12-V4-O14	89.83
O1-C1-N2	114.48	V3-O11-V4	98.65
O1-C1-C2	120.85	V3-O13-Ni5	133.01
N2-C1-C2	124.54	V4-O14-Ni5	128.74
C1-C2-C4	117.25	O13-Ni5-O14	83.76
C1-C2-C5	122.71	O13-Ni5-N5	92.35
C4-C2-C5	119.94	O13-Ni5-N6	174.51
O1-C3-N1	112.11	O14-Ni5-N5	175.78
O1-C3-S1	118.88	O14-Ni5-N6	93.10
N1-C3-S1	128.87	N5-Ni5-N6	90.65
C2-C4-H1	121.55	Ni5-N5-N7	116.39
C2-C4-C6	119.54	Ni5-N5-C17	141.62
H1-C4-C6	118.87	N7-N5-C17	101.05
C2-C5-H2	123.71	Ni5-N6-N8	124.24
C2-C5-C7	120.55	Ni5-N6-C19	134.83
H2-C5-C7	115.71	N8-N6-C19	100.70
C4-C6-C8	120.01	N5-N7-C18	111.88
C4-C6-H19	116.40	N6-N8-C20	110.55
C8-C6-H19	123.57	N5-C17-O15	111.07
C5-C7-C8	118.28	N5-C17-S3	130.41
H3-C7-C8	121.34	O15-C17-S3	118.35

C6-C8-C7	121.57	N7-C18-O15	112.57
C6-C8-H20	121.21	N7-C18-C30	118.49
C7-C8-H20	117.22	O15-C18-C30	128.60
C9-O2-C11	102.75	C17-O15-C18	103.26
Ni1-N3-N4	127.00	N6-C19-O16	112.84
Ni1-N3-C11	133.08	N6-C19-S4	126.76
N4-N3-C11	99.81	O16-C19-S4	119.25
N3-N4-C9	110.00	N8-C20-O16	112.30
O2-C9-N4	114.21	N8-C20-C24	126.32
O2-C9-C10	118.95	O16-C20-C24	120.83
N4-C9-C10	126.84	C19-O16-C20	102.90
C9-C10-C12	117.56	C22-C21-C30	117.68
C9-C10-C13	122.96	C30-C21-H9	125.03
C12-C10-C13	119.48	C21-C22-C32	121.59
O2-C11-N3	113.04	C21-C22-H10	118.70
O2-C11-S2	114.82	C32-C22-H10	119.71
N3-C11-S2	131.56	C31-C23-C32	117.42
C10-C12-H4	121.29	C31-C23-H12	121.25
C10-C12-C14	119.43	C32-C23-H12	121.32
H4-C12-C14	119.28	C20-C24-C25	124.13
C10-C13-H5	123.96	C20-C24-C26	118.50
C10-C13-C15	120.76	C25-C24-C26	117.23
C12-C14-H6	117.79	C24-C25-H14	125.92
C12-C14-C16	120.69	C29-C25-H14	113.36
H6-C14-C16	121.52	C24-C26-C27	121.01
C13-C15-H7	121.23	C24-C26-H18	125.27
C13-C15-C16	118.09	C27-C26-H18	113.66
H7-C15-C16	120.68	C26-C27-C28	120.44
C14-C16-C15	121.55	C26-C27-H17	118.70
C14-C16-H8	119.93	C28-C27-H17	120.85
C15-C16-H8	118.52	C27-C28-C29	121.73
Ni1-O3-V1	142.24	C27-C28-H16	116.87
Ni1-O4-V2	133.13	C29-C28-H16	121.41
O3-V1-O5	154.34	C25-C29-C28	118.84
O3-V1-O6	98.21	C25-C29-H15	120.39
O3-V1-O9	84.62	C28-C29-H15	120.76
O5-V1-O6	101.90	C18-C30-C21	127.40
O5-V1-O9	100.07	C18-C30-C31	114.76
O6-V1-O9	116.95	C21-C30-C31	117.78
O4-V2-O6	103.70	C23-C31-C30	124.09
O4-V2-O7	84.23	C23-C31-H13	114.30
O4-V2-O8	157.50	C30-C31-H13	121.57
O6-V2-O7	127.26	C22-C32-C23	121.40

| O6-V2-O8 | 98.74 | C22-C32-H11 | 122.95 |
| O7-V2-O8 | 83.58 | C23-C32-H11 | 115.65 |

$[Ni_2V_4O_{12}(L^2)_4] \cdot 2H_2O$ geterometalli kompleksning strukturaviy tuzilishini rentgen difraktogrammasi eksperimentda kuzatilgan spektrini hisoblangan spektr bilan taqqoslash diagrammasi taqqoslanganda, kuzatilgan spektrini hisoblangan spektr bilan moslik darajasidagi chetlanish 6,2175 ga teng.
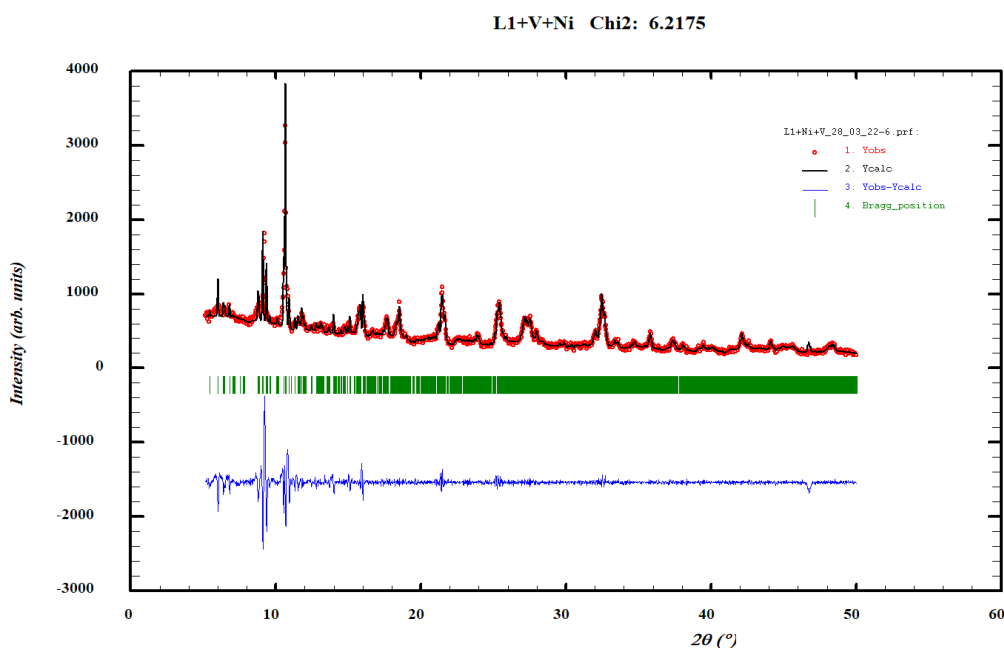
3.22-Rasm. $[Ni_2V_4O_{12}(L^2)_4] \cdot 2H_2O$ strukturaviy tuzilishining rentgen difraktogrammasi. I –eksperementda kuzatilgan spektrini (−) hisoblangan spektr (−) bilan taqqoslash, II – Bragg reflekslari ($\vdots$), III – kuzatilgan spektr va hisoblangan spektr o'rtasidagi farq ($\sqrt{}$).

Olingan natijalarga ko'ra aralash metalli kompleksda vanadiy kislorod bog'lari mavjud bo'lib, ular o'zaro ma'lum izchillikda birikkan va nikel ioni bilan ham bog'lanish hosil qilgan. Ligand Ni^{2+} ioniga oksadiazol halqasidagi azot atomi orqali bog'langanligidan dalolat beradi

3.6-§. YuESX-mass spektrometriya usuli yordamida $[V_4O_{12}](L^1+H^+)_4$ kompleksini o'rganish

Komplekslarning nisbiy molekulyar massalari va komplekslarning miqdor ko'rsatkichlarini aniqlash uchun namunalar YuESX-mass (ESI-mass)

spektrometriya tahlili yordamida o'rganildi va [139] adabiyot yordamida tahlil qilindi.
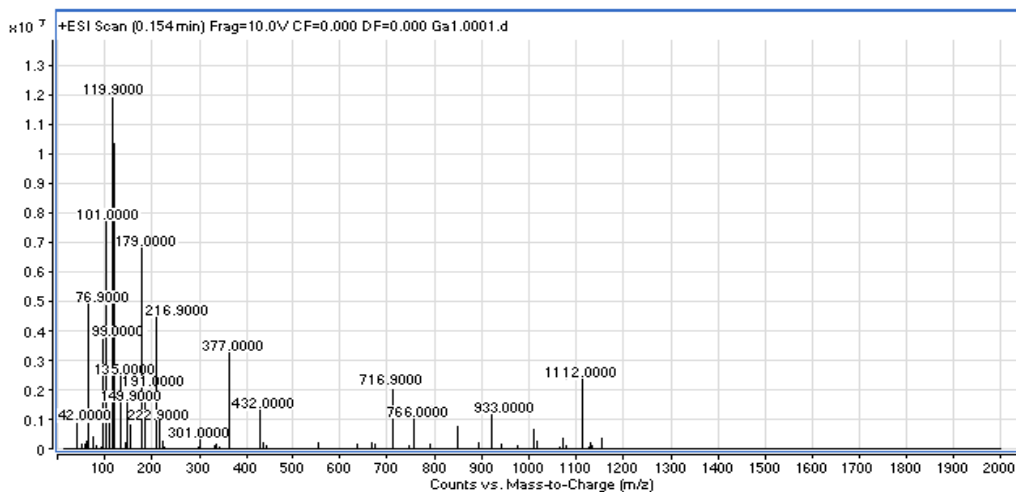
3.23-Rasm. L^1 asosidagi vanadiyli kompleksining elektr maydonida sachratib ionlantirish sharoitida olingan mass-spektri, erituvchi – metanol.

$[V_4O_{12}](L^1+H^+)_4$ kompleksning ESI-MS spektrida to'rtta turdagi kompleks ionlari: $[[V_4O_{12}](L^1+H^+)_3]^-$, $[[V_4O_{12}](L^1+H^+)_2]^{2-}$, $[[V_4O_{12}](L^1+H^+)]^{3-}$, $[[V_4O_{12}]\cdot2H_2O]^{4-}$ va $[L^1]^+$. Tarkibi $[V_4O_{12}](L^1+H^+)_4$ kompleksning fragmentatsiyalanishida $[L^1]^+$ ning bosqichli yo'qotilishi natijasida noturg'un $[[V_4O_{12}](L^1+H^+)_3]^-$ m/z=933, $[[V_4O_{12}](L^1+H^+)_2]^{2-}$ m/z=377, $[[V_4O_{12}](L^1+H^+)]^{3-}$ m/z=191 kompleks ionlari hosil bo'lgan. Spektrda ligandning $[L^1]^+$ protonlangan molekulasi m/z=179,0 sohada namoyon bo'lgan. Kompleks $[V_4O_{12}]^{4-}$ m/z=99,0 ionigacha fragmentatsiyalangan. m/z=135 sohadagi pik siklovanadat ioniga $[[V_4O_{12}]\cdot2H_2O]^{4-}$ gidratlanish ro'y berganligini kuzatishimiz mumkin. Kompleks molekulasi quyidagi sxemada keltirilgan tartibda parchalanadi (sxema).
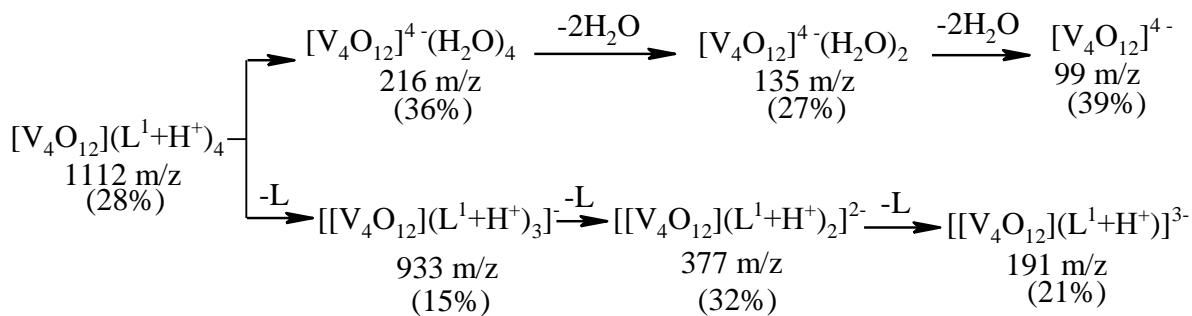
Sxema. $[V_4O_{12}](L^1+H^+)_4$ kompleksining fragmentatsiyasi

3.7-§. Oksadiazoltion hosilalari asosida gomo- va geterometalli kompleks birikmalarini termik tahlil usuli bilan o'rganish

Kompleks birikmalarning termik barqarorligini va tarkibida suv molekulalari mavjudligini aniqlash maqsadida derivatografiya natijalari tahlil qilindi. Ligandlar L^1, L^2 va L^3 hamda ular asosida sintez qilingan kompleks birikmalarning termik xossalari differensial termik taxlili yordamida o'rganildi [140-142].

Bir vaqtning o'zida o'rganilayotgan birikmalarning termogravigrammalarida turli xil jarayonga mos keladigan endo- va ekzo- effektlar, namuna massasining parchalanish tezligi, komplekslarning parchalanish massasining o'zgarishi va termik barqarorlikning harorat ortib borishi bilan o'zgarishi aniqlanadi. Shunday qilib, termik analiz natijasida kompleksning parchalanishini va suyuqlanishini, ligandning termik barqarorligi va kompleksning oxirgi mahsulotlari aniqlanadi.

Kompleks birikmalarning derivatogrammalari va olingan natijalar 3.24-3.28 rasmlarda, 3.16-3.17 jadvalda keltirilgan.

L^1 termogrammasi (3.25-(a)rasm) tahlil qilinganda 256,8°C-265°C harorat oralig'ida TG egri chizig'ining massa yo'qotilishi 23% ni tashkil qiladi, qizdirish egri chizig'ida 263,5°C da bitta endotermik effektni va 267,2°C da bitta ekzotermik effektni ko'rsatdi. 267,2°C da ekzotermik effektni tabiati ligandning kuchli parchalanishiga to'g'ri keladi. Keyingi termik effektlarning bosqichma-bosqich parchalanish, yonish jarayonlari bilan bog'liqligi kuzatildi va o'rganilayotgan birikma termolizining yakuniy mahsuloti aniqlandi. TG egri chizig'iga ko'ra 256,8-360°C harorat oralig'ida umumiy massa yo'qotish 83% ni tashkil qiladi [140-142].

L^1 asosida sintez qilingan komplekslarning derivatogrammalari (3.25-(b), (c), (d) rasmlar) tahlil qilinganda barcha namunalar ~ 400°C da parchalanadi. Cu(II) va Ni(II) komplekslarining xloridlari termogrammasidagi 50-150°C oralig'ida past haroratli massa yo'qotish qayd etilgan. 150-200°C oralig'ida yana massa yo'qotilishi kuzatildi. Ushbu ma'lumotlar komplekslarning IQ-spektrlari tahlili natijasida taklif qilingan koordinatsion va kristalizatsion suv molekulalarining mavjudligini aniq ravshan ko'rsatdi. O'z navbatida, Cu (II) nitrat kompleksining

termogrammasida 130°C gacha massa yo'qotish kuzatilmadi, bu ham kompleksning IQ-spektrida kristallogidrat holatdagi suv yo'qligi haqidagi natijani tasdiqladi.

3.16-Jadval

Kompleks birikmalarning termik analiz natijalari

Birikma	Fragment	Piroliz oralig'i (^{0}C)	Piroliz ko'rsatkich (^{0}C) (ДТА)	Issiqlik effekti	Massa yo'qotilishi mg/%
L^1	NCO	240-265	263,5	endoterm	1,173/23
	Py+CNS	265-300	267,2	ekzoterm	3/60
	Py+CNS	300-370		-	0,85/17
$[NiL^1(H_2O)_4] \cdot 2H_2O$	2 H_2O	43-67	55,07	endoterm	0,246/6,86
	4 H_2O	95-143	123,08	endoterm	0,468/13
	2NCS	143-260			0,576/16
	Ni+Py+ NCO	350-420	400	ekzoterm	1,11/30,84
	Ni+Py+ NCO	420-600		-	0,8/22,2
$[CuL^1(H_2O)_4]$	2 H_2O	78-108	100	endoterm	0,34/7,35
	4 H_2O	108-184	150	endoterm	0,41/8,91
	2NCS	184-222	203	ekzoterm	0,62/14,13
	Cu+Py NCO	266-304	278	endoterm	1,43/31
	Cu+Py NCO	400-475	450	endoterm	0,6/13
$[Cu(L^1)_2(H_2O)_2]$	2 H_2O	100-215		-	1,2/14,6
	2 NCO	215-264	232	endoterm	1,43/17
	Cu+Py+ NCS	365-390	377	endoterm	3,07/36,5

L^1 asosida olingan gomometalli kompleks birikmalarda 200-220°C harorat oralig'ida maksimal massa yo'qotilishini mavjudligini ko'rsatdi, bu esa piridin, -NCS va - NCO fragmentlarinnig yo'qotilishiga to'g'ri keladi. Tahlil o'rganilayotgan koordinatsion birikmalar tadqiqoti doirasida to'liq bo'lmagan pirolizni ko'rsatadi, bu termik parchalanish mahsulotlarining yonishi va metall oksidlarining hosil bo'lishi bilan bog'liq, shu sababli pirolizning yakuniy mahsulotini aniqlab bo'lmadi.

Metall atsetatlarining L^1 asosida olingan gomometalli kompleks birikmalari gelga o'xshash mahsulot hosil qilganligi sababli termogravimetrik analiz usuli bilan tahlil qilib bo'lmadi.

Sintez qilingan gomo- va geterometalli kompleks birikmalarning termik xossalarini taqqoslanganda, $[CuL^1_2(H_2O)_2]$ kompleks birikmaning termogravigrammasida (3.24-(b)rasm) 100°C gacha bo'lgan haroratda massa yo'qotilishi kuzatilmaydi, bu kristalizatsion suv molekulasi mavjud emasligidan dalolat beradi, kristalizatsion suv molekulasi yo'qligini IK spektr natijasi ham tasdiqlaydi. 100-200°C harorat oralig'ida ~8% massa yo'qotilishi bilan endotermik effekt kuzatildi, bu ikki molekula koordinatsion suvning yo'qotilishiga to'g'ri keladi. Kompleks birikmalarda 200-500°C harorat oralig'ida maksimal massa yo'qotilishi kuzatildi, bu piridin, -NCS va -NCO fragmentlarining yo'qotilishiga to'g'ri keladi.

3.17-Jadval

L^1 ning gomo- va geterometalli kompleks birikmalarininig termik tahlil natijalari

Birikma	Fragment	Piroliz ko'rsatkichi (^0C)	Piroliz piki	Issiqlik effeki
L^1	NCO	240-265	263,5	endoterm
	Py+CNS	265-300	267,2	ekzoterm
	Py+CNS	300-370	-	-
$[CuL^1_2 (H_2O)_2]$	2 H_2O	125-215	-	endoterm
	2 NCO	215-264	232	endoterm
	Cu+Py+ NCS	365-390	377	endoterm
$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$	$2H_2O$	50-110	-	endoterm
	4Py+4NCO	110-250	225	ekzoterm
	V_4O_{12}	250-400	320	ekzoterm
	Cu+2NCS	450-525	500	endoterm

$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ tarkibli geterometalli kompleks birikmaning termogravigrammalarida 110°C gacha bo'lgan sohada, ikki molekula kristalizatsion suvning massa yo'qotilishiga to'g'ri keladigan ~3% bo'lgan endoeffekt kuzatildi. 110-400°C harorat oralig'ida, organik radikallar va tetraoksovanadatga to'g'ri keladigan ~66% massa yo'qotilishi bilan birga ikkita ketma-ket ekzotermik effekt

kuzatiladi. Keyingi piroliz choʻqqisi ~500°C da 16% massa yoʻqotilishi bilan boradi, bu Cu+2NCS fragmentiga toʻgʻri keladi. Oʻrganilayotgan kompleks birikmalar tadqiqot doirasida toʻliq boʻlmagan pirolizni koʻrsatdi, bu termal parchalanishining mahsulotlarining yonishi va metall oksidlarining hosil boʻlishi bilan bogʻliq, shuning uchun pirolizning yakuniy bosqichini aniqlab boʻlmadi. L^1 va [CuL$^1_2$ (H$_2$O)$_2$], [Cu$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O larning parchalanish mahsulotlari 3.17-jadvalda keltirilgan (3.24-(s)rasm).

a) L^1
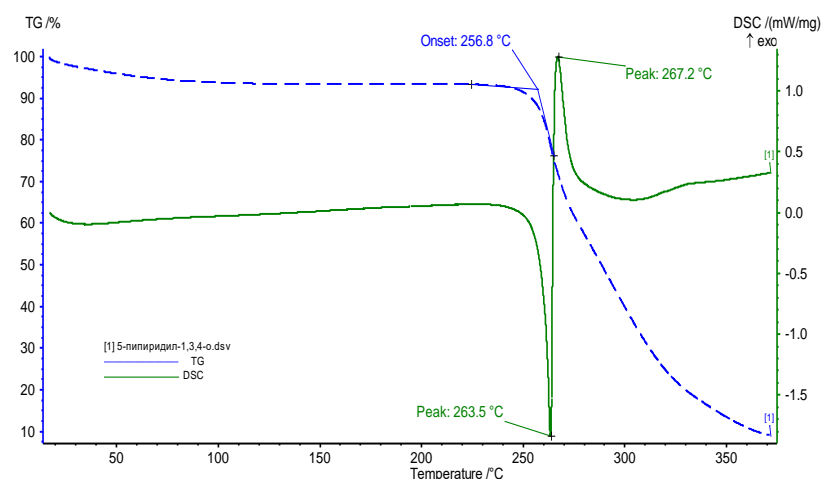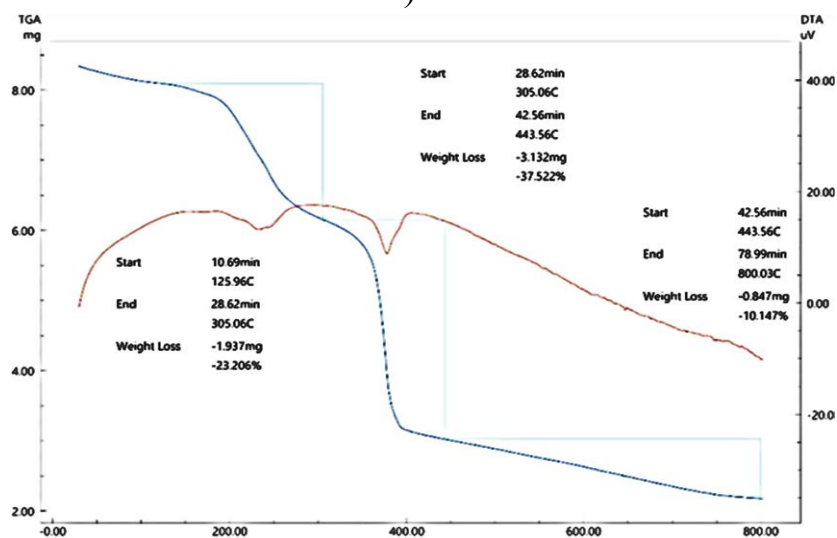
b) [CuL$^1_2$ (H$_2$O)$_2$]
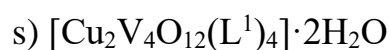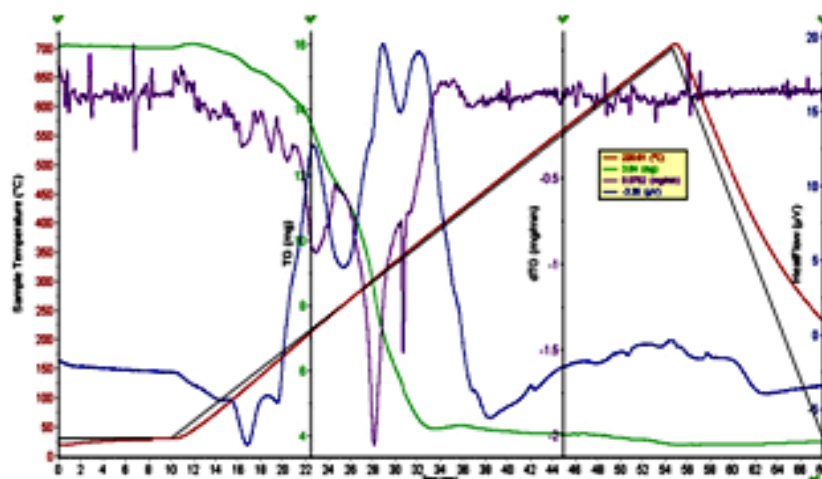
s) $[Cu_2V_4O_{12}(L^1)_4]\cdot2H_2O$

3.24-Rasm. a) L^1; b) $[CuL^1_2(H_2O)_2]$; s) $[Cu_2V_4O_{12}(L^1)_4]\cdot2H_2O$ larning termogrammalari

Ligandlar va barcha metall komplekslarining termik analiz natijalari tahlil qilinib, biz termik barqarorlik haqida umumiy xulosaga kelindi. Organik geterohalqali ligandlar $L^3<L^2<L^1$ qatori bo'yicha termik barqarorligi ortib boradi.
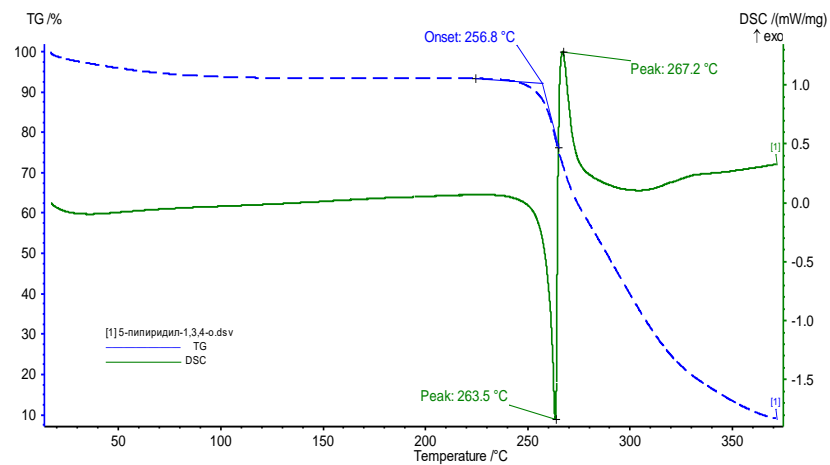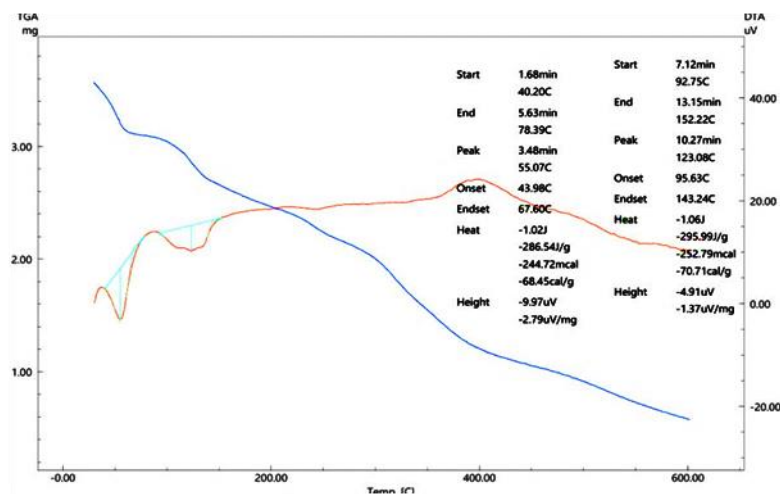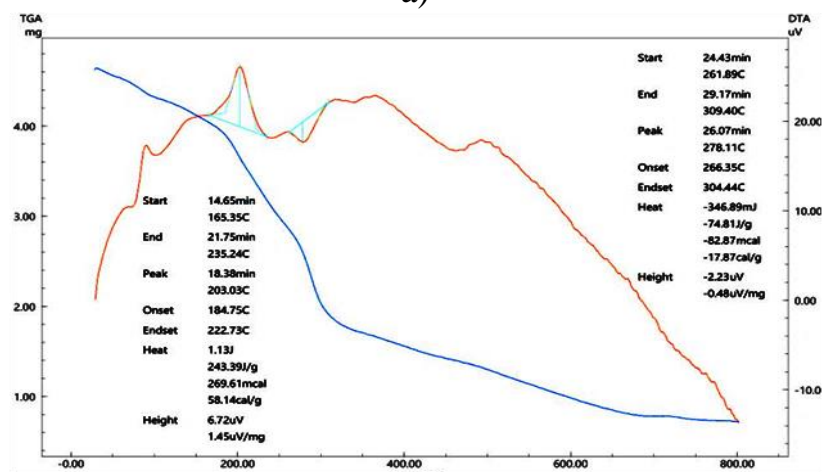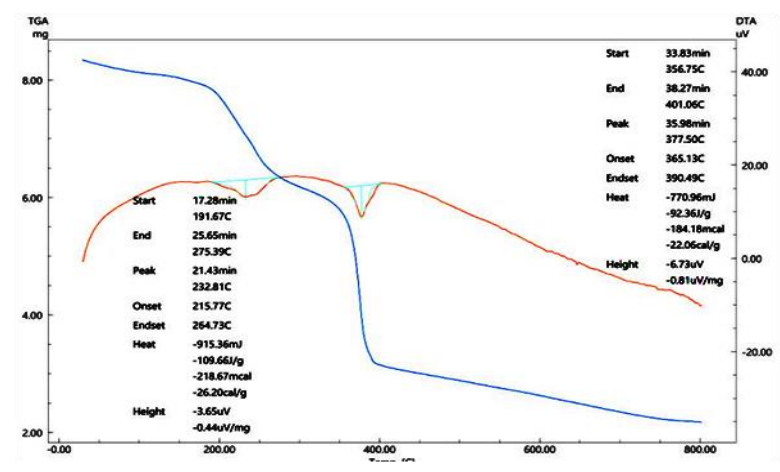
3.25-Rasm. a) L^1; b) $[NiL^1(H_2O)_4] \cdot 2H_2O$; c) $[CuL^1(H_2O)_4] \cdot 2H_2O$; d) $[CuL^1(H_2O)_2]$ derivatogrammalari; 1-Temperatura egri chizig'i; 2- differensial termogravimetrik tahlil egri chizig'i (DTGA); 3- differensial termogravimetrik tahlil egri chizig'ining hosilasi (DTGP);

L^1 – 5-piridil-1,3,4-oksadiazol-2(3H)-tion

$[Cu(L^1)_2(H_2O)_2]$

$[V_4O_{12}](L^1+H)^+_4$

$[Cu_2V_4O_{12}(L^1)_4]\cdot 2H_2O$
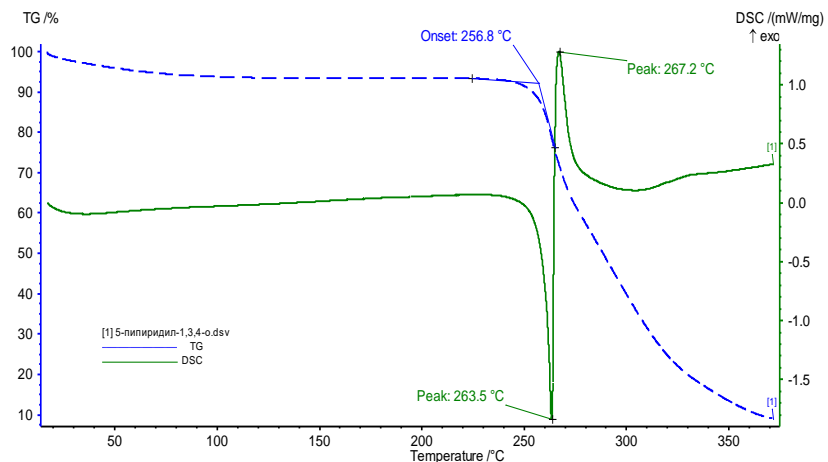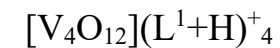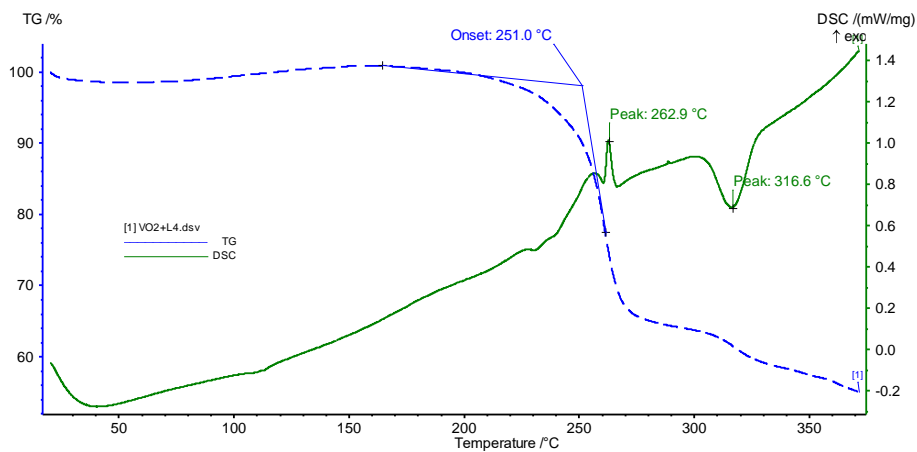
3.26-Rasm. L^1 va uning asosida olingan metallokomplekslarninng termogrammalari

L^2 – 5-fenil-1,3,4-oksadiazol-2(3H)-tion

$[Ni(L^2)_2]$

$[V_4O_{12}](L^2+H)^+_4$

$[Ni_2V_4O_{12}(L^2)_4]\cdot 2H_2O$

3.27-Rasm. L^2 va uning asosida olingan metallokomplekslarninng termogrammalari

L³-2-karboksimetiltio-5-fenil-1,3,4-oksadiazol

[Co(L³)₂(H₂O)₂]

[V₄O₁₂](L³+H)⁺₄

[Co₂V₄O₁₂(L³)₂]·2H₂O

3.28-Rasm. L³ va uning asosida olingan metallokomplekslarninng termogrammalari

Gomo- va geterometalli kompleks birikmalarning termik hossalari o'rganilganda, gomometalli kompleks birikmaning termik barqarorligi yuqoriligi geterometalli kompleks birikmanikidan yuqoriligi $[Cu_2V_4O_{12}(L^1)_4] \cdot 2H_2O < [CuL^1_2(H_2O)_2]$ aniqlandi. Komplekslarning termogrammalari 3.29 -3.31 rasmlarda keltirilgan va bu holat gomo-, geterometalli kompleks birikmalarni kvant-kimyoviy hisoblash orqali olingan MO natijalari yordamida isbotlandi. Geterometalli komplekslarda d-orbitallarning qoplanishi natijasidagi $|HOMO-LUMO|=\Delta$ ayirmaning farqi $\Delta \leq 2$ ($[Ni(L^3)_2(H_2O)_2]$, $\Delta = |-6.28-(-4.86)| = 1.42$) ga, gomometalli kompleksda $\Delta \leq 5$ ($[Ni_2V_4O_{12}(L^1)_4] \cdot 2H_2O$, $\Delta = |-6.34-(-1.77)| = 4.57$) ga nisbatan kichik bo'lishi bilan izohlandi.
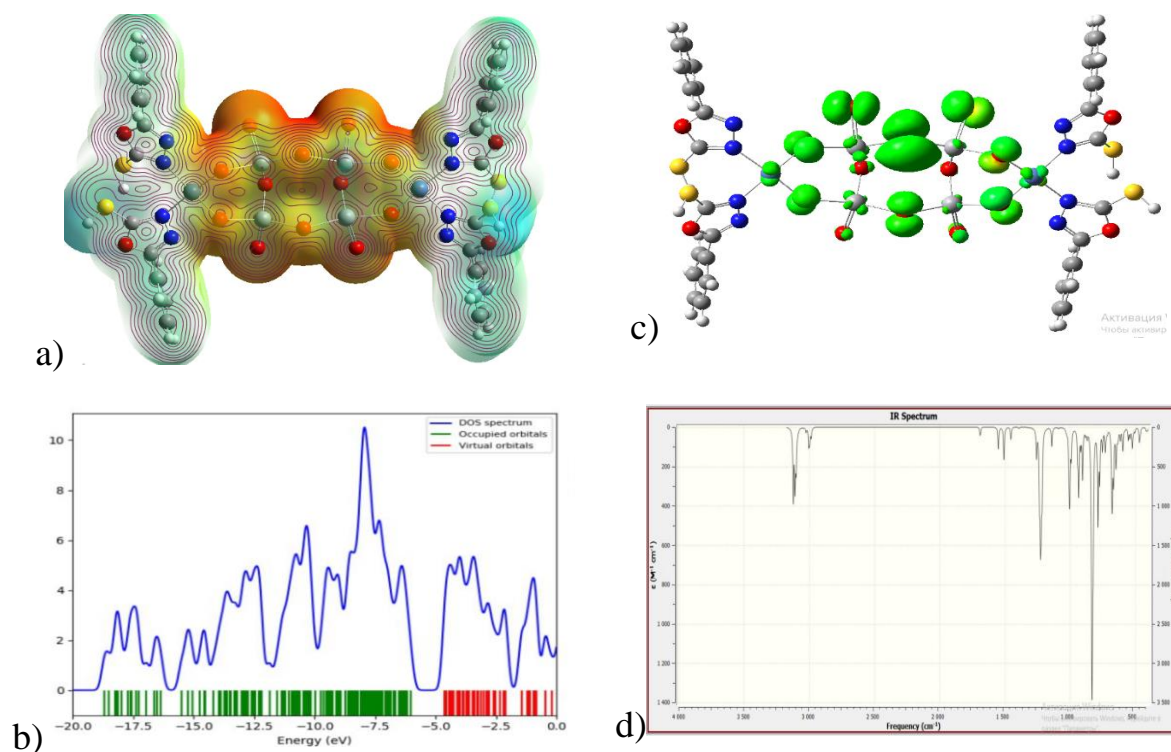
3.29-Rasm. $[Ni_2V_4O_{12}(L^2)_4] \cdot 2H_2O$ ning a)MO qavatlarning umumiy zichligi va zichlik spektri (b); c)HOMO, LUMO orbitallar; d)IQ spektri
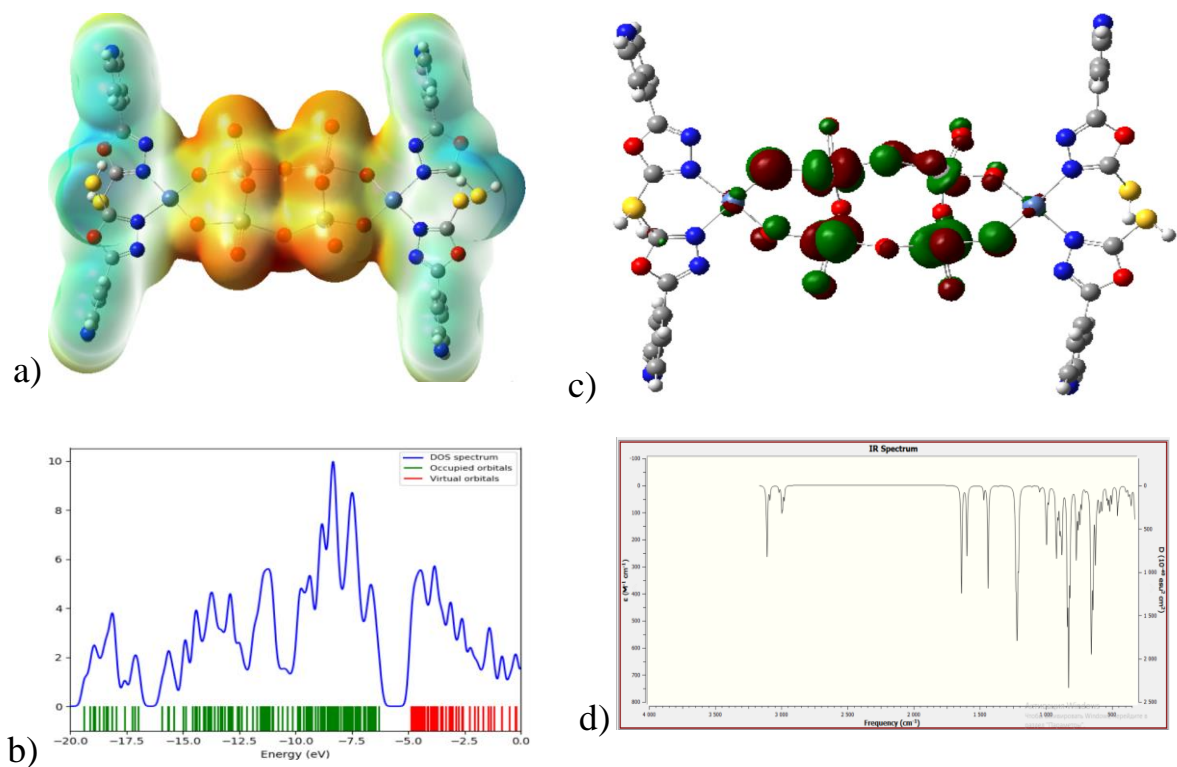
3.30-Rasm. $[Ni_2V_4O_{12}(L^1)_4] \cdot 2H_2O$ ning a)MO qavatlarning umumiy zichligi va zichlik spektri (b); c)HOMO, LUMO orbitallar; d)IQ spektri
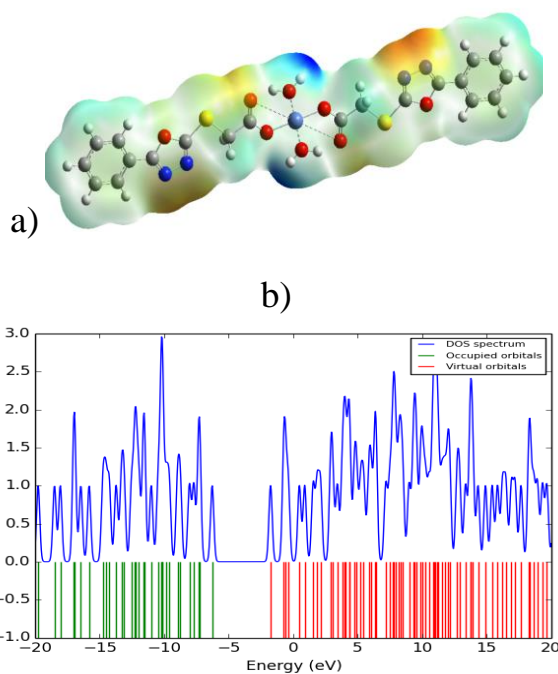
3.31-Rasm. $[Ni(L^3)_2(H_2O)_2]$ ning a)MO qavatlarning umumiy zichligi va zichlik spektri (b); c)HOMO, LUMO orbitallar; d)IQ spektri

Gomo- va geterometalli kompleks birikmalarning termodinamik parametrlari

Xarakteristika	Gomometalli	Geterometalli
	$[Ni(L^3)_2(H_2O)_2]$	$[Ni_2V_4O_{12}(L^1)_4] \cdot 2H_2O$
Ichki energiya (E, kkal/mol)	231.48	314.8
Dipol momenti (Debye)	0.05	9.19
Qutblanganlik (a.u)	355.9	1232
Entalpiya (H, kkal/mol)	315.38	231.54
Entropiya (S, kkal/mol *K)	0.346	0.399
Gibbs energiyasi (G, kkal/mol)	212.19	112.59
Issiqlik sig'imi (Cv, kal/mol *K)	235.5	135.7

3.8-§. Sintez qilingan kompleks birikmalarning rentgenstruktur tahlili

Rentgen strukturaviy tahlil (XDR,shuningdek: rentgen nurlanishini tahlil qilish) – moddaning tuzilishini o‘rganish uchun diffraksiya usullaridan biri hisoblanadi. Bu usul uch o‘lchamli kristall panjara ustidagi rentgen nurlarining difraksiyasi hodisasiga asoslangan. RSA usuli elementar yacheykaning fazoviy guruhini, uning o‘lchamlari va shaklini o‘z ichiga olgan moddaning atom tuzilishini, shuningdek, kristallning simmetriya guruhini aniqlashga imkon beradi. Bugungi kunga kelib rentgen nurlari diffraksion tahlili oddiyligi, universalligi (har qanday monokristallni o‘rganish uchun qo‘llanilishi mumkin) va nisbatan arzonligi tufayli moddaning tuzilishini aniqlashning eng keng tarqalgan usuli hisoblanadi [143].

L^2 ning Zn^{2+} ioni bilan sintez qilingan gomometalli kompleksining tarkibi $[Zn(L^2)_2]$ ligi EA natijasi yordamida aniqlandi. Ushbu kompleks birikmaning tuzilishini chuqurroq tahlil qilish uchun rentgenstruktur tahlil o‘tkazildi (3.32-rasm).

a)   b)
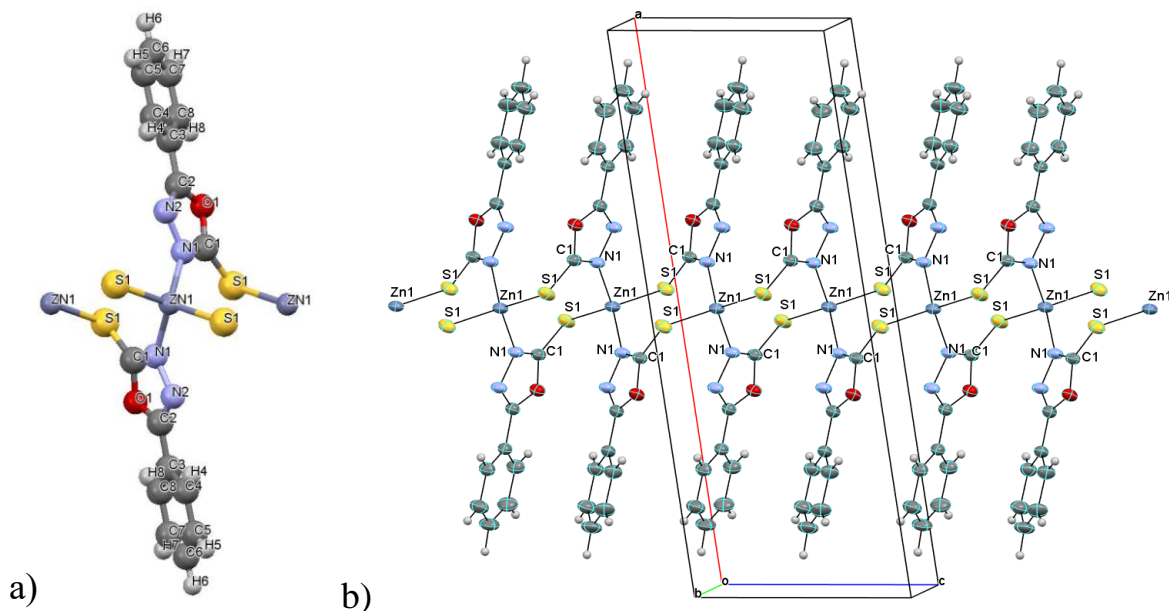
3.32-Rasm. Molekula tuzilishi (a) va uning kristall yacheyka tuzilishi (b)

Kristallografik ma'lumotlari: $[Zn(L^2)_2]_n$, $M=[420]_n$ g·mol^{-1}, monoklin singoniyali tiniq novot rang kristallar, fozoviy guruhi C2∕c (№15), a=20.4198(3), b=11.3243(2), c=7.4005(1) Å, α=90º, β=98,3067(14)º, γ=90º, V=1693.35(4)Å^3, Z=8, D_{cal}=1.2982 g∕sm^3 (3.14-jadval). Kristallda o‘qli diedrik simmetriya

ko'rinishida birgina ikkinchi darajali simmetriya o'qi – 2 bo'ladi. Shu bilan bog'liq ravishda simmetriya o'qiga tik yo'nalgan monoedr, bundan tashqari, pinakoid bilan diedr ishtirok etadi.

Ushbu 3.32-rasmda $[Zn(L^2)_2]_n$ kompleksning kristall tuzilishida markaziy Zn atomi ikkita oltingugurt va ikkita azot atomi orqali bog'lanib, jami to'rtta kristallografik jihatdan mustaqil ligandlar tomonidan muvofiqlashtirilib, $[\theta 2\theta]$ yo'nalishi bo'ylab zigzag zanjirlarini hosil qiladi. Zn1- N1 va Zn1- S1 mos ravishda 2.018Å, 2.3370Å ga teng. Bunday holda tetraedrik poliedr hosil qiluvchi atomlarning valent burchagi, N1- Zn1- N1 (111.37°), S1- Zn1- S1(100,46°) va N1- Zn1- S1(108,50°) bu ko'rsatkichlar haqiqiy tetraedr burchaklaridan bir oz farq qiladi. Ligand tarkibidagi N1va S1 atomlarining yuqori elektrodonorlikni namoyon qilib, ikkita Zn ioni bilan sakkiz a'zoli [Zn-S-C-N-Zn-S-C-N] o'rindiqsimon halqa hosil qiladi.

3.18-Jadval

$[Zn(L^2)_2]_n$ kompleksning kristallografik tahlil natijasining asosiy parametrlari

Parametrlar	Ko'rsatkich	Parametrlar	Ko'rsatkich
Molekular formula	$[Zn(C_8H_6N_2OS)_2]_n$	O'lchash intervali (θ, grad)	0.615
M_r	$[420]_n$	h, k, l o'tishlar	0.099, 1.000
a, Å	20.4198(3)	T_{min}, T_{max}	0.039, 0.744
b, Å	11.3243(2)	μ_{exp} (мм$^{-1}$)(MoKα)	3.99135
c, Å	7.4005(1)	Umumiy aks ettirish	7033
α, °	90	Mustaqil aks ettirish	1536
β, °	98.3067(14)	Aks ettirish soni (I>2σ(I))	1634
γ, °	90	R_{int}	0.028
V, Å^3	1693.35(4)	Aniqlangan parametrlar	115
ρ(his.), г/см^3	1.2982	Kuzatilgan aks ettirishlar [$F^2 \geq 2\sigma(F^2)$]	1634
Z	8	R_1, wR_2 (I>2σ(I))	0.026, 0.073
Fazoviy guruh	C 2/c (15)	Muvofiqlik sifati	1.096
Singoniya	Monoklin	$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, -0.30
Kristal o'lchami (mm)	0.098×0.056×0.026	T, K	253

Ligand molekulasining fenil (C3–C8) va oksadiazol (C1/O1/C2/N2/N1) halqalarining oʻrtacha tekisliklari orasidagi ikki yoqli burchak 13,42 (8)° ga teng. Ligandning oksadiazol-tiol fragmentining konformatsiyasi tahminan tekis (standart ogʻish 0,006 Å), O1 atomi uchun eng kichik kvadratlar tekisligidan maksimal ogʻish 0,009 Å ga teng. Ikki qoʻshni mustaqil oksadiazol tiollari (C1/O1/C2/N2/N1/S1) fragmentlari tekisliklari orasidagi ikki yoqli burchak 64,10° ga teng boʻlib, strukturadagi valent va torsion burchaklar 3.19-3.16 jadvallarda keltirilgan.

3.19-Jadval

$[Zn(L^2)_2]_n$ strukturadagi valent burchak kattaliklari

Burchak	ω,-grad	Burchak	ω,-grad	Burchak	ω,-grad
N1-Zn1-N1	111.37(2)	H4-C4-C5	119.94(2)	C2-C3-C4	118.63(2)
N1- Zn1-S1	113.83(2)	C3-C8-H8	120.15(2)	C2-C3-C8	121.46(2)
N1- Zn1-S1	108.49(4)	C3-C8-C7	119.69(2)	C4-C3-C8	119.91(2)
N1- Zn1-S1	113.83(2)	H8-C8-C7	120.15(2)	S1-C1-O1	120.27(2)
S1- Zn1-S1	100.46(2)	C4-C5-H5	120.18(2)	S1-C1-N1	129.90(2)
C1-S1- Zn1	102.39(2)	C4-C5-C6	119.65(2)	O1-C1-N1	109.81(2)
C2-O1-C1	103.92(2)	H5-C5-C6	120.18(2)	C3-C4-H4	119.94(2)
Zn1-N1-N2	119.57(2)	C8-C7-H7	119.90(2)	C3-C4-C5	120.12(2)
Zn1N1-C1	131.79(2)	C8-C7-C6	120.19(2)	H4-C4-C5	119.94(2)
N2-N1-C1	108.59(2)	H7-C7-C6	119.90(2)	C3-C8-H8	120.15(2)
N1-N2-C2	105.03(2)	C5-C6-C7	120.42(2)	C3-C8-C7	119.69(2)
O1-C2-N2	112.62(2)	C5-C6-H6	119.79(2)	H8-C8-C7	120.15(2)
O1-C2-C3	119.66(2)	C7-C6-H6	119.79(2)	C4-C5-H5	120.18(2)
N2-C2-C3	127.72(2)	C1-S1-ZN1	102.39(2)	C4-C5-C6	119.65(2)
C2-C3-C4	118.63(2)	C2-O1-C1	103.92(2)	H5-C5-C6	120.18(2)
C2-C3-C8	121.46(2)	Zn1-N1-N2	119.57(2)	C8-C7-H7	119.90(2)
C4-C3-C8	119.91(2)	Zn1-N1-C1	131.79(2)	C8-C7-C6	120.19(2)
S1-C1-O1	120.27(2)	N2-N1-C1	108.59(2)	H7-C7-C6	119.90(2)
S1-C1-N1	129.90(2)	N1-N2-C2	105.03(2)	C5-C6-C7	120.42(2)
O1-C1-N1	109.81(2)	O1-C2-N2	112.62(2)	C5-C6-H6	119.79(2)
C3-C4-H4	119.94(2)	O1-C2-C3	119.66(2)	C7-C6-H6	119.79(2)
C3-C4-C5	120.12(2)	N2-C2-C3	127.72(2)		

$[Zn(L^2)_2]_n$ strukturadagi torsion burchak kattaliklari

A1	A2	A3	A4	Torsion	A1	A2	A3	A4	Torsion
N1	Zn1	N1	N2	-136.1	H6	C6	C7	C8	177(2)
N1	Zn1	N1	C1	40.9	C6	C7	C8	C3	-0.5(3)
S1	Zn1	N1	N2	100.9	C6	C7	C8	H8	-179(2)
S1	Zn1	N1	C1	-82.1	H7	C7	C8	C3	180(2)
S1	Zn1	N1	N2	-10.0	H7	C7	C8	H8	1(3)
S1	Zn1	N1	C1	166.9	Zn1	S1	C1	O1	-116.5
N1	Zn1	N1	N2	-136.1	Zn1	S1	C1	N1	65.3
N1	Zn1	N1	C1	40.9	C2	O1	C1	S1	179.8(1)
S1	Zn1	N1	N2	-10.0	C2	O1	C1	N1	-1.7(2)
S1	Zn1	N1	C1	166.9	C1	O1	C2	N2	1.2(2)
S1	Zn1	N1	N2	100.9	C1	O1	C2	C3	-178.4(1)
S1	Zn1	N1	C1	-82.1	Zn1	N1	N2	C2	176.9
Zn1	S1	C1	O1	-116.5	C1	N1	N2	C2	-0.7(2)
Zn1	S1	C1	N1	65.3	Zn1	N1	C1	S1	2.7
C2	O1	C1	S1	179.8(1)	Zn1	N1	C1	O1	-175.7
C2	O1	C1	N1	-1.7(2)	N2	N1	C1	S1	179.9(1)
C1	O1	C2	N2	1.2(2)	N2	N1	C1	O1	1.5(2)
C1	O1	C2	C3	-178.4(1)	N1	N2	C2	O1	-0.4(2)
Zn1	N1	N2	C2	176.9	N1	N2	C2	C3	179.2(2)
C1	N1	N2	C2	-0.7(2)	O1	C2	C3	C4	-13.2(2)
Zn1	N1	C1	S1	2.7	O1	C2	C3	C8	166.6(2)
Zn1	N1	C1	O1	-175.7	N2	C2	C3	C4	167.3(2)
N2	N1	C1	S1	179.9(1)	N2	C2	C3	C8	-12.9(3)
N2	N1	C1	O1	1.5(2)	C2	C3	C4	H4	1(2)
N1	N2	C2	O1	-0.4(2)	C2	C3	C4	C5	-179.3(2)
N1	N2	C2	C3	179.2(2)	C8	C3	C4	H4	-179(2)
O1	C2	C3	C4	-13.2(2)	C8	C3	C4	C5	0.9(3)
O1	C2	C3	C8	166.6(2)	C2	C3	C8	C7	179.7(2)
N2	C2	C3	C4	167.3(2)	C2	C3	C8	H8	-1(2)
N2	C2	C3	C8	-12.9(3)	C4	C3	C8	C7	-0.6(3)
C2	C3	C4	H4	1(2)	C4	C3	C8	H8	178(2)
C2	C3	C4	C5	-179.3(2)	C3	C4	C5	H5	-178(2)
C8	C3	C4	H4	-179(2)	C3	C4	C5	C6	-0.2(3)
C8	C3	C4	C5	0.9(3)	H4	C4	C5	H5	2(3)
C2	C3	C8	C7	179.7(2)	H4	C4	C5	C6	180(2)
C2	C3	C8	H8	-1(2)	C4	C5	C6	H6	-177(2)
C4	C3	C8	C7	-0.6(3)	C4	C5	C6	C7	-0.9(3)
C4	C3	C8	H8	178(2)	H5	C5	C6	H6	1(3)
C3	C4	C5	H5	-178(2)	H5	C5	C6	C7	177(2)
C3	C4	C5	C6	-0.2(3)	C5	C6	C7	H7	-179(2)
H4	C4	C5	H5	2(3)	C5	C6	C7	C8	1.2(3)
H4	C4	C5	C6	180(2)	H6	C6	C7	H7	-3(3)

C4	C5	C6	H6	-177(2)	H6	C6	C7	C8	177(2)
C4	C5	C6	C7	-0.9(3)	C6	C7	C8	C3	-0.5(3)
H5	C5	C6	H6	1(3)	C6	C7	C8	H8	-179(2)
H5	C5	C6	C7	177(2)	H7	C7	C8	C3	180(2)
C5	C6	C7	H7	-179(2)	H7	C7	C8	H8	1(3)
C5	C6	C7	C8	1.2(3)					
H6	C6	C7	H7	-3(3)					

Supramolekulyar xususiyatlari. Polimer kompleksning monomeri sifatida $[Zn(L^2)_2]_n$ birligi berilgan. Polimer zanjir c oʻqiga parallel. Kristallda bir birining oʻrtasida tutilgan polimer zanjirlar C6-H6…S1 orasida molekulalararo vodorod bogʻlanish uchraydi, bu esa a va b oʻqlari boʻylab tarmoqlanishni hosil qiladi (3.33-rasm). Vodorod bogʻlanishdan tashqari fenil halqasining C3...C8 atomlari orasida polimer ichidagi π kontaktlari (3.399Å) va polimerlararo zanjir (3.326Å) mavjud.
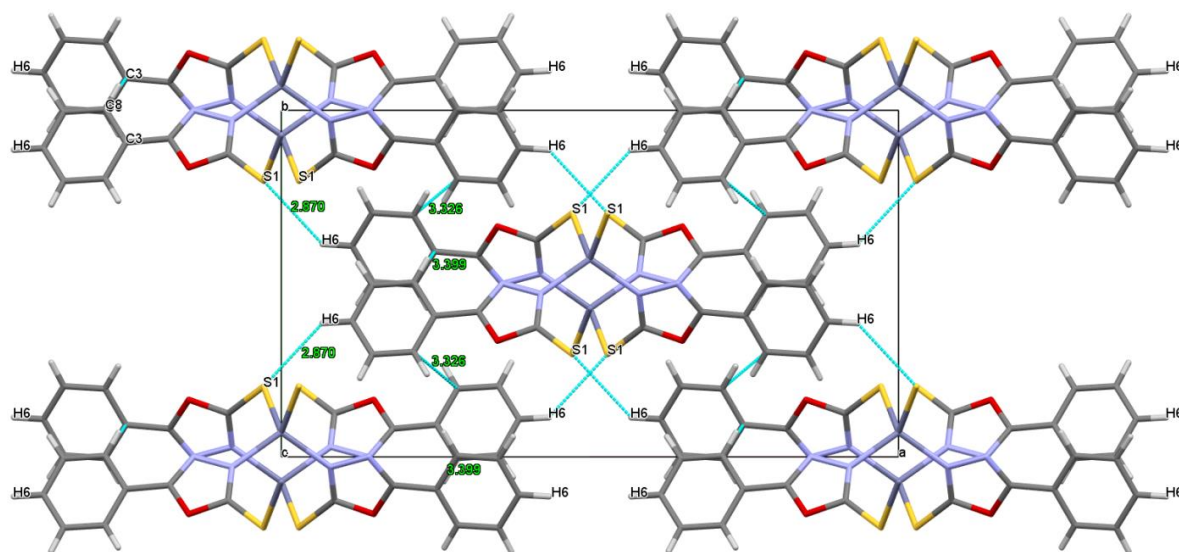
3.33-Rasm. $[Zn(L^2)_2]_n$ c oʻqda joylashuvi.

3.21-Jadval

$[Zn(L^2)_2]_n$ strukturadagi vodorod bogʻ geometriyasi

D-H…A	A atomning joylashuvi	Masofa, Å			Burchak AHD, grad
		D…A	D…H	H…A	
C6-H6…S1	-1/2+x,-1/2+y,z	3.608	0.997	2.860	132.2(2)

Vodorod bog'lar geometriyasiga qaraydigan bo'lsak, bir ligandning fenil halqasidagi C6-H6 va ikkinchi ligandning 1,3,4-oksadiazol halqasiga birikkan tiol guruhining oltingugurti S1 orasida (C6-H6…S1) molekulalararo vodorod bog'lanish mavjud (3.21-3.22 jadvallar).

3.22-Jadval

$[Zn(L^2)_2]_n$ strukturadagi bog' uzunliklari

Боғ		d, Å	Боғ		d, Å	Боғ		d, Å
Zn1	N1	2.018	N2	C2	1.285(2)	C6	H6	1.00(3)
Zn1	N1	2.018	C2	C3	1.460(2)	C6	C7	1.384(3)
Zn1	S1	2.3370	C3	C4	1.388(3)	C7	H7	0.91(2)
Zn1	S1	2.3370	C3	C8	1.385(3)	C7	C8	1.380(3)
S1	C1	1.706(2)	C4	H4	0.92(2)	C8	H8	0.89(2)
S1	Zn1	2.3370	C4	C5	1.382(3)	S1	C1	1.706(2)
O1	C1	1.363(2)	C5	H5	0.89(3)	S1	Zn1	2.3370
O1	C2	1.371(2)	C5	C6	1.377(3)	O1	C1	1.363(2)
N1	N2	1.406(2)	C6	H6	1.00(3)	O1	C2	1.371(2)
N1	C1	1.299(2)	C6	C7	1.384(3)	N1	N2	1.406(2)
N2	C2	1.285(2)	C7	H7	0.91(2)	N1	C1	1.299(2)
C2	C3	1.460(2)	C7	C8	1.380(3)	N2	C2	1.285(2)
C3	C4	1.388(3)	C8	H8	0.89(2)	C2	C3	1.460(2)
C3	C8	1.385(3)	S1	C1	1.706(2)	C3	C4	1.388(3)
C4	H4	0.92(2)	S1	Zn1	2.3370	C3	C8	1.385(3)
C4	C5	1.382(3)	O1	C1	1.363(2)	C4	H4	0.92(2)
C5	H5	0.89(3)	O1	C2	1.371(2)	C4	C5	1.382(3)
C5	C6	1.377(3)	N1	N2	1.406(2)	C5	H5	0.89(3)
C6	H6	1.00(3)	N1	C1	1.299(2)	C5	C6	1.377(3)
C6	C7	1.384(3)	N2	C2	1.285(2)	C6	H6	1.00(3)
C7	H7	0.91(2)	C2	C3	1.460(2)	C6	C7	1.384(3)
C7	C8	1.380(3)	C3	C4	1.388(3)	C7	H7	0.91(2)
C8	H8	0.89(2)	C3	C8	1.385(3)	C7	C8	1.380(3)
S1	C1	1.706(2)	C4	H4	0.92(2)	C8	H8	0.89(2)
S1	Zn1	2.3370	C4	C5	1.382(3)	Zn1	N1	2.018
O1	C1	1.363(2)	C5	H5	0.89(3)	Zn1	N1	2.018
O1	C2	1.371(2)	C5	C6	1.377(3)	Zn1	S1	2.3370
N1	N2	1.406(2)	C6	H6	1.00(3)	Zn1	S1	2.3370
N1	C1	1.299(2)	C6	C7	1.384(3)	S1	C1	1.706(2)
N2	C2	1.285(2)	C7	H7	0.91(2)	S1	Zn1	2.3370
C2	C3	1.460(2)	C7	C8	1.380(3)	O1	C1	1.363(2)
C3	C4	1.388(3)	C8	H8	0.89(2)	O1	C2	1.371(2)
C3	C8	1.385(3)	Zn1	N1	2.018	N1	N2	1.406(2)
C4	H4	0.92(2)	Zn1	N1	2.018	N1	C1	1.299(2)

C4	C5	1.382(3)	Zn1	S1	2.3370	N2	C2	1.285(2)
C5	H5	0.89(3)	Zn1	S1	2.3370	C2	C3	1.460(2)
C5	C6	1.377(3)	S1	C1	1.706(2)	C3	C4	1.388(3)
C6	H6	1.00(3)	S1	Zn1	2.3370	C3	C8	1.385(3)
C6	C7	1.384(3)	O1	C1	1.363(2)	C4	H4	0.92(2)
C7	H7	0.91(2)	O1	C2	1.371(2)	C4	C5	1.382(3)
C7	C8	1.380(3)	N1	N2	1.406(2)	C5	H5	0.89(3)
C8	H8	0.89(2)	N1	C1	1.299(2)	C5	C6	1.377(3)
Zn1	N1	2.018	N2	C2	1.285(2)	C6	H6	1.00(3)
Zn1	N1	2.018	C2	C3	1.460(2)	C6	C7	1.384(3)
Zn1	S1	2.3370	C3	C4	1.388(3)	C7	H7	0.91(2)
S1	C1	1.706(2)	C3	C8	1.385(3)	C7	C8	1.380(3)
O1	C1	1.363(2)	C4	H4	0.92(2)	C8	H8	0.89(2)
O1	C2	1.371(2)	C4	C5	1.382(3)	S1	C1	1.706(2)
N1	N2	1.406(2)	C5	H5	0.89(3)	S1	Zn1	2.3370
N1	C1	1.299(2)	C5	C6	1.377(3)	O1	C1	1.363(2)

Rentgenstruktur tahlil natijalari CIF fayl ko'rinishida Kembridj kristallografik ma'lumotlar bazasiga (CCDC reference: 2184492, https://doi.org/10.1107/S2056989022006922) joylandi.

3.9-§. [(ZnL$^2_2$)$_n$] kompleks birikmaning Hirshfeld sirt tahlili

Hirshfeld sirt tahlili molekulyar kristallarning molekulalararo o'zaro ta'siri haqidagi qo'shimcha ma'lumotlarni olish uchun qo'llaniladigan kuchli tahlil usuli hisoblanadi. Ushbu tahlil usuli molekulyar kristallardagi sirtning o'lchami, shakli, molekulalararo yaqin kontaktlarning sifati, miqdorini o'rganish va vizualizatsiya qilish imkonini beradi [144]. Hirshfeld yuza tahlili Crystal Explorer17 dasturida amalga oshirildi.

Hirshfeld yuzasi d_{norm} va turli o'zaro ta'sirlarni ifodalovchi mos ranglar 3.34–rasm (a) da ko'rsatilgan. Ushbu polimer kompleksining Hirshfeld yuzasini hisoblash uchun monomer birligi sifatida ZnL$^2_2$ molekulyar fragmentida olib borildi
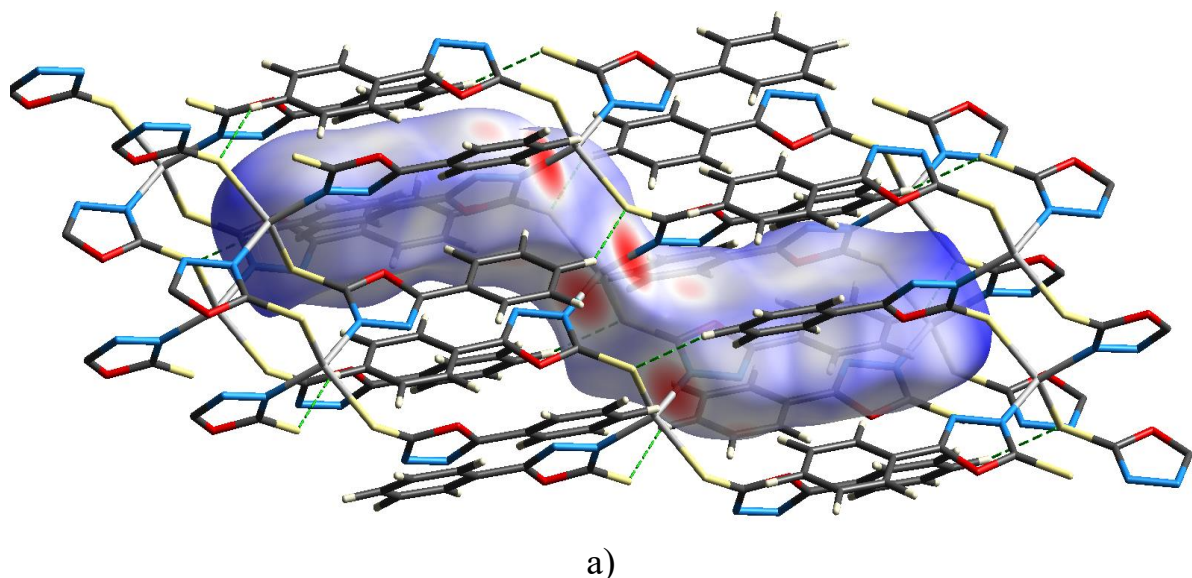
a)
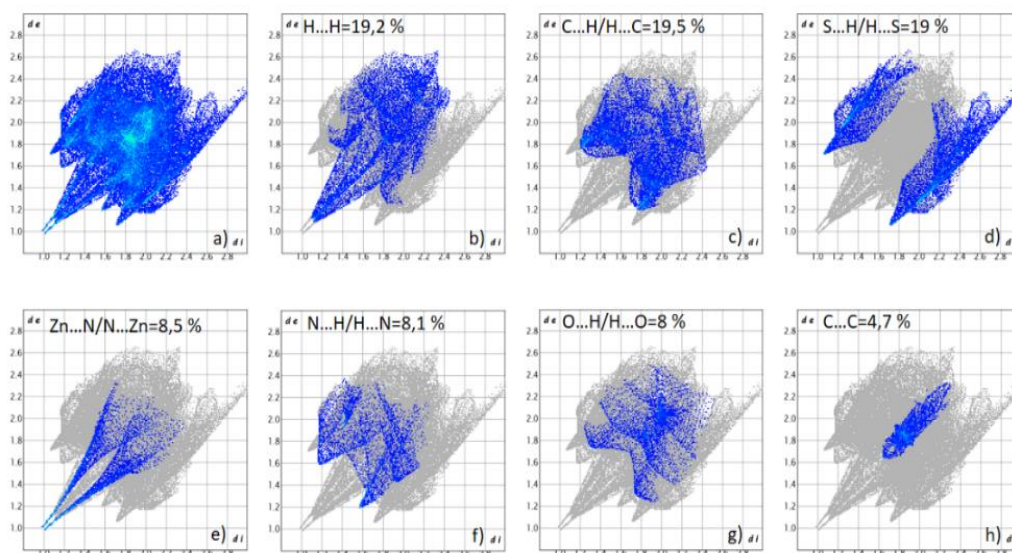
b)

3.34-Rasm. a) d$_{norm}$ Hirshfeld sirt yuzasi va molekulalarning o'zaro elektrostatik ta'sirlari; b) molekulyar kristallardagi sirtning molekulalararo yaqin kontaktlarning sifati va miqdori.

Sirtdagi katta qizil nuqtalar Zn … N o'zaro ta'sirlarga to'g'ri keladi. Hirshfeld yuzasida eng katta ulush (19,2%), (19,5%) va (19%) mos ravishda H...H, C…H/H…C va S…H/H…S kontaktlarning mavjudligini ko'rsatdi. N...H/H…N (8.1 %), O...H/H…O (8 %) va C…C (4.7 %) zaif kontaktlar ham kuzatildi. Ushbu o'zaro ta'sirlar kristall taxlamining umumiy barqarorlashuvida hal qiluvchi rol o'ynadi (3.34-rasm (b)).

3.10-§. Koordinatsion birikmalarni barqarorlik konstantasini Babko usulida aniqlash

Ko'pchilik koordinatsion birikmalarning eritmada barqarorligini aniqlash va ularni qo'llash imkoniyatlarini belgilovchi eng muhim xususiyatlaridan biri bu ularning barqarorlik konstantalari hisoblanadi [145]. Eritmada ko'p funksional ligandlar bilan oraliq metall ionlarining koordinatsiyalanish jarayonini o'rganish metall ionlarini bog'lanishining selektivligi va turli ligand markazlarining raqobatli koordinatsiyasi haqida ma'lumot berishi adabiyotlardan ma'lum. Eritma holatida 5-(4-piridil)-1,3,4-oksadiazol-2(3H)-tion (L^1), 5-fenil-1,3,4-oksadiazol-2(3H)-tion (L^2) va 2-karboksimetiltio-5-fenil-1,3,4-oksadiazol (L^3) bilan oraliq metall ionlarining kompleks hosil qilish jarayonlari amalda o'rganilmagan.

Ushbu tadqiqot ishida Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} va V^{5+} ionlari komplekslarining spirtli eritmadagi barqarorlik konstantalari fotometrik usulda, Babkoning suyultirish usuli bilan hisoblandi. O'rganilayotgan komplekslar uchun ekvimolyar konsentratsiyali metall va ligand eritmalaridan foydalanildi.

Aniqlash usuli: sig'imi 25 ml bo'lgan o'lchov kolbalariga optimal pH =6-8 li universal bufer eritmalaridan 10 ml quyildi; stexiometrik nisbatda reaksiyaga kirishuvchi komponentlar (M:L=1:2; M:V:L =1:2:2) va ularning hajmi distillangan suv bilan kolbaning belgisigacha keltirildi. Eritmalar aralashtirildi va optik zichlik UV/VIS spektrofotometrda o'lchandi. Solishtirma eritma sifatida metall ionlari bo'lmagan va boshqa komponentlar bo'lgan eritmadan foydalanildi. So'ngra komplekslarning eritmalari distillangan suv bilan 2 marta suyultirilib optik zichlik qayta o'lchandi. O'lchash asosida olingan natijalar 3.18-jadvalda keltirilgan. Olingan natijalardan kompleks birikmalarning barqarorlik konstantasi (K$_{bar}$) 3.1-3.3-formulalar bo'yicha hisoblanadi:

$$\Delta = \frac{A - pA_p}{A} \quad (3.1) \qquad \alpha = \frac{\Delta}{\sqrt{2}-1} \quad (3.2) \qquad \beta_{\text{к}} = \frac{1-\alpha}{\alpha^2 C_{\text{м}}} \quad (3.3)$$

Δ-dissotsilanish tufayli nur yutulish asosiy qonuniyatidan chetlanish; A va A$_p$-dastlabki va suyultirilgan eritmalarning optik zichliklari; suyultirishdan

oldingi va keyingi optik zichlik; α-kompleksning dissotsilanish darajasi; r-suyultirish darajasi (r=2);

C_M-eritma suyultirilgandan keyin metall ionlarining konsentratsiyasi (C_2).

3.22-jadval ma'lumotlaridan ko'rinib turibdiki, Babko usuli bilan hisoblangan, etil spirt eritmasida hosil qilingan komplekslarning barqarorlik konstantalari qiymatlari qoniqarli bo'lib, eritmadagi metall xloridlari ligand bilan M:L 1:2; M:V:L 1:2:2 nisbatda hosil bo'ladi:

a)   b)
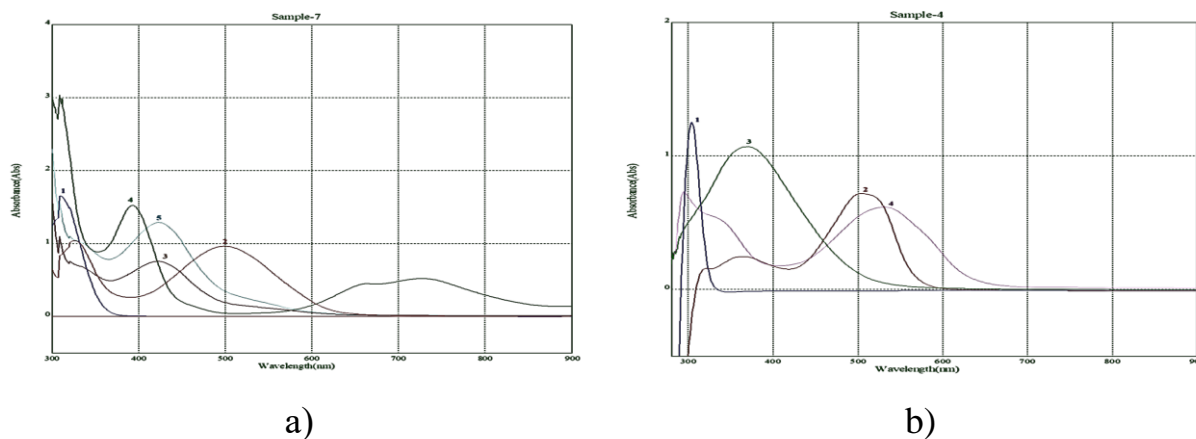
3.35- Rasm. a) L^1-1; [Co(L^1)$_2$(H$_2$O)$_2$]-2; [Cu(L^1)$_2$(H$_2$O)$_2$]-3; [Ni(L^1)$_2$(H$_2$O)$_2$]-4; [Zn(L^1)$_2$(H$_2$O)$_2$]-5 va b) L^1-1; [Co(L^1)$_2$(H$_2$O)$_2$]-2; [V$_4$O$_{12}$](L^1 +H$^+$)$_4$ -3; [Co$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O-4 larning nur yutilish spetrlari

Natijalarga ko'ra barqarorlik konstantasi qiymatlarini taqqoslash shuni ko'rsatdiki, Cu^{2+} va Zn^{2+} komplekslari uchun bu qiymatlar boshqa metall komplekslariga qaraganda yuqoriligi aniqlandi (3.35-rasm.(a)
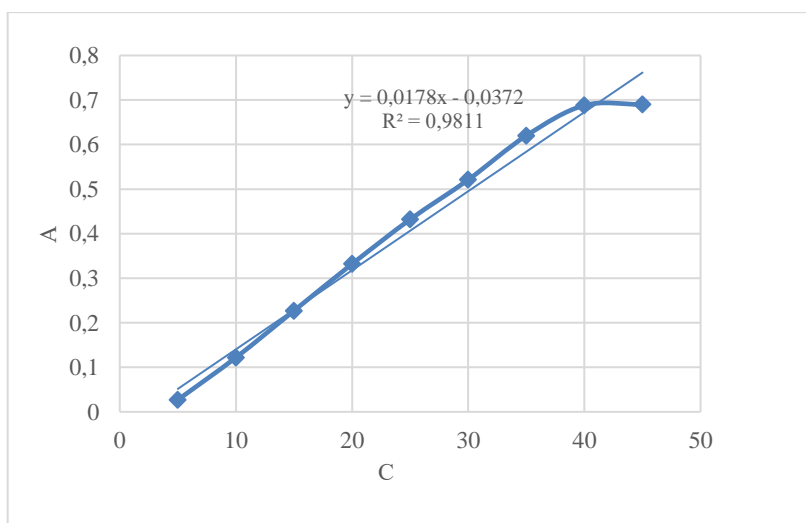
3.36-Rasm. $[Co_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ kompleksini Lambert Buger-Ber qonuniga bo'ysunish grafigi.

Ushbu olingan natijalar Lambert Buger-Ber qonuniga muvofiqligi aniqlandi, ushbu qonun faqat past konsentratsiyali eritmalar uchun amal qiladi (3.36-rasm). Bunda eritmaning nur yutilish intensivligi, konsentratsiyaga to'g'ri proporsional ravishda o'zgarishi kuzatildi [146- 147].

Gomo- va geterometalli kompleks birikmalarning barqarorligi taqqoslanganda gomometalli kompleks birikmalarning barqarorligi nisbatan yuqoriligi aniqlandi, bu geterometalli kompleks birikmalarning quyi gidratlanish energiyasiga ega bo'lishi hamda geterometalli kompleksning markaziy qismida zaryadlangan $[V_4O_{12}]^{4-}$ siklning mavjudligi bilan izohlandi. kompleks tarkibida $[V_4O_{12}]^{4-}$ ning mavjudligi Gibbs energiyasining kamayishiga olib keladi, bu esa erituvchida kompleksning gidratlanishini oshishi hisobiga bo'lishi ko'rsatildi.

Co^{2+}, Ni^{2+}, Cu^{2+} ,Zn^{2+} va V^{5+} ionlarini gomo- va geterometalli kompleks birikmalarining barqarorlik konstantalarini suyultirish usuli bilan aniqlash natijalari (Babko usuli)

№	Kompleks birikma	Rangi	λ_{max} nm	C_1 mol/l	A_1	C_2 mol/l	A_2	К$_{бар}$ ($\beta_к$)	К$_{бар}$ (lg$\beta_к$)
1	[Cu(L^1)$_2$(H$_2$O)$_2$]		484	$1,43 \cdot 10^{-4}$	0,450	$7,16 \cdot 10^{-5}$	0,182	$4,84 \cdot 10^7$	7,68
2	[Cu(L^3)$_2$(H$_2$O)$_2$]		480	$1,3 \cdot 10^{-4}$	0,498	$6,52 \cdot 10^{-5}$	0,118	$3,14 \cdot 10^7$	7,49
3	[Zn(L^3)$_2$(H$_2$O)$_2$]		349	$1,19 \cdot 10^{-4}$	0,478	$5,95 \cdot 10^{-5}$	0,194	$2,24 \cdot 10^7$	7,35
4	[Zn(L^1)$_2$(H$_2$O)$_2$]		344	$1,29 \cdot 10^{-4}$	0,389	$6,45 \cdot 10^{-5}$	0,136	$2,11 \cdot 10^7$	7,32
5	[Ni(L^1)$_2$(H$_2$O)$_2$]		611	$1,3 \cdot 10^{-4}$	0,342	$6,5 \cdot 10^{-5}$	0,124	$9,10 \cdot 10^6$	6,96
6	[Co(L^3)$_2$(H$_2$O)$_2$]		521	$1,31 \cdot 10^{-4}$	0,438	$6,54 \cdot 10^{-5}$	0,139	$8,86 \cdot 10^6$	6,94
7	[Ni(L^3)$_2$(H$_2$O)$_2$]		598	$5,48 \cdot 10^{-4}$	0,350	$2,74 \cdot 10^{-5}$	0,127	$7,56 \cdot 10^6$	6,87
8	[Co(L^1)$_2$(H$_2$O)$_2$]		503	$1,28 \cdot 10^{-4}$	0,324	$6,44 \cdot 10^{-5}$	0,129	$6,78 \cdot 10^6$	6,83
9	[Co(L^2)$_2$]		510	$2,82 \cdot 10^{-4}$	0,307	$1,41 \cdot 10^{-4}$	0,109	$6,40 \cdot 10^6$	6,80
10	[V$_4$O$_{12}$](L^1 +H$^+$)$_4$		374	$3,49 \cdot 10^{-4}$	0,383	$1,74 \cdot 10^{-4}$	0,142	$5,84 \cdot 10^6$	6,78
11	[V$_4$O$_{12}$](L^2 +H$^+$)$_4$		382	$1,44 \cdot 10^{-4}$	0,381	$7,19 \cdot 10^{-5}$	0,193	$5,77 \cdot 10^6$	6,76
12	[V$_4$O$_{12}$](L^3+H$^+$)$_4$		388	$3,24 \cdot 10^{-4}$	0,302	$1,56 \cdot 10^{-4}$	0,111	$4,74 \cdot 10^6$	6,65
13	[Cu$_2$V$_4$O$_{12}$(L^1)$_4$] ·2H$_2$O		490	$3,8 \cdot 10^{-4}$	0,314	$1,9 \cdot 10^{-4}$	0,101	$3,95 \cdot 10^6$	6,60
14	[Co$_2$V$_4$O$_{12}$(L^1)$_4$] ·2H$_2$O		521	$3,53 \cdot 10^{-4}$	0,425	$1,75 \cdot 10^{-4}$	0,133	$2,99 \cdot 10^6$	6,47
15	[Co$_2$V$_4$O$_{12}$(L^3)$_4$]·2H$_2$O		508	$1,93 \cdot 10^{-4}$	0,324	$9,64 \cdot 10^{-5}$	0,116	$2,82 \cdot 10^6$	6,45
16	[Zn$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O		602	$3,0 \cdot 10^{-4}$	0,327	$1,83 \cdot 10^{-4}$	0,142	$3,52 \cdot 10^6$	6,39
17	[Ni$_2$V$_4$O$_{12}$(L^1)$_4$] ·2H$_2$O		591	$3,84 \cdot 10^{-4}$	0,408	$1,52 \cdot 10^{-4}$	0,128	$3,67 \cdot 10^6$	6,38
18	[Co$_2$V$_4$O$_{12}$(L^2)$_4$]·2H$_2$O		524	$3,54 \cdot 10^{-4}$	0,318	$1,76 \cdot 10^{-4}$	0,113	$1,67 \cdot 10^6$	6,23

3.11. Sintez qilingan kompleks birikmalarning biologik faolligini o'rganish

1,3,4-Oksadiazol hosilalari va ular asosida sintez qilingan bir va aralash metalli kompleks birikmalarning fitokimyoviy tekshiruvlari orqali antioksidantlik faollik aniqlandi, u bir nechta metodlarni qo'llash orqali baholandi [148- 149].

Tekshiriladigan moddalarning antioksidantlik faolligi adrenalinning *in vitro* autooksidlanish reaksiyasining ingibirlanishi bilan aniqlanadi hamda kislorodning erkin shaklini hosil bo'lishiga to'sqinlik qiladi.

Buning uchun 0,2 M li natriy karbonat bufer pH=10,65 (0,2 M li Na_2CO_3 0,2 M li $NaHCO_3$ buferi tayyorlanib 4 ml bufer ustiga 0,2 ml 0,1% li (5,46 ml M li adrenalin gidroxlorid (epinefrin) solinib, aralashtiriladi hamda Agilent Technologies Cary 60 UV-Vis spetrofotometrda tekshirildi. Eritma 347 nm 30 sek da 10 min ichida 1 sm li kyuvetada tekshiriladi (D_1). 4 ml Na_2CO_3 buferi 0,2 ml 0,1 % li adrenalin gidroxlorid aralashtiriladi va to'lqin uzunligida o'lchandi (D_2). Antioksidantlik faollik (AF) quyidagi formula orqali aniqlanadi.

$$A\Phi = \frac{(D_1 - D_2)}{D_2} \cdot 100$$

AF 10% dan yuqori ko'rsatgichni namoyon qilsa, preparatning antioksidantlik faolligi yuqoriligidan dalolat beradi.

Ishlatilgan reaktivlar va laboratoriya jihozlari: 0,1% (56 mkl) adrenalin, Na_2CO_3.

Nazorat	**Tajriba**
2 ml bufer	2 ml bufer
55,55≈56 mkl adrenalin	56 mkl adrenalin
-	30 mkl antioksidant

Bu tekshirishlarni quyidagi reja asosida amalga oshirildi:

1. Har bir modda (preparatni) eruvchanligini, va ularning (100%, 75%, 50%, 25%, 10%) li eritmalarini tayyorlash.

2. Har bir moddaning qanday diapozonda (pik) berishini nm da o'lchash 200-1000 (800) nm uzinlikda o'lchash va ularni tahlil qilish.

3. Har bir preparatning 5 xil konsentratsiyali eritmalarining antioksidantlik xususiyatlarini tekshirish.

4. Olib borilgan tadqiqot natijalarini hisoblash va jadval ko'rinishiga keltirish.

Sintez qilingan komplekslarning biologik faolligini o'rganish uchun quyidagi komplekslar tanlab olindi:

1.	Ligandlar: L^1 – 5-(4-piridin)-1,3,4-oksadiazol-2(3N)-tion; L^2 – 5-fenil-1,3,4-oksadiazol-2(3H)-tion; L^3 – 2-karboksimetiltio-5-fenil-1,3,4-oksadiazol;
2.	$[Co(L^1)_2(H_2O)_2]$
3.	$[Ni(L^1)_2(H_2O)_2]$
4.	$[Zn(L^1)_2(H_2O)_2]$
5.	$[Cu(L^1)_2(H_2O)_2]$
6.	$[V_4O_{12}](L^1+H^+)_4$
7.	$[Zn_2V_4O_{12}(L^1)_4]\cdot 2H_2O$
8.	$[Zn_2V_4O_{12}(L^2)_4]\cdot 2H_2O$
9.	$[Zn_2V_4O_{12}(L^3)_2]\cdot 2H_2O$

Har bir tuz 1mg (1000mkg) dan olinib 1ml H_2O da eritildi va proba 10 daqiqa ichida har 30 sekund davomida tekshirildi. Hamda o'rtacha ko'rsatkich chiqarildi va formulaga qo'yildi. Buning uchun har bir preparatni (kompleks birikmani) hisoblandi.

Tekshirish uchun moddadan 1mg (1000mkg) olinib 1ml suvda eritildi. Tayyor bo'lgan eritmani 100% lik desak. O'sha eritmadan 75%, 50%, 25% va 100% li eritmalar hosil qilandi.

Adabiyotdagi [148,149] ma'lumotlarga ko'ra xar bir moddani tekshirish uchun uni 1:80 (1 xajm antioksidant : 80 hajm H_2O) marta suyultirilishi lozim, chunki tekshiriladigan moddalar bu olingan miqdorda reaksion qobilyati optimal hisoblanadi. Bizga adrenalinning 0,1% li eritmasi kerak bo'ladi. Adrenalin oksidlanishi natijasida organizm uchun zarali hisoblangan adrenoxrom hosil bo'ladi.

адреналин → аденохром (4e, 4H⁺)
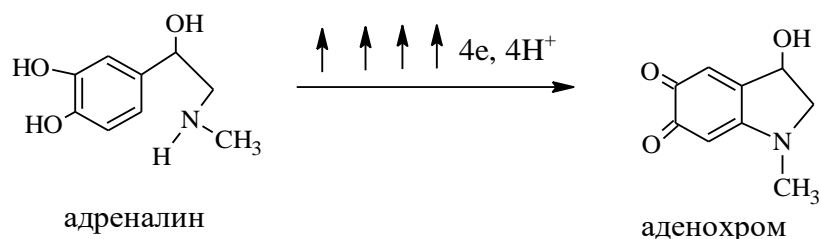
Ligandlar va ular asosida sintez qilingan gomo- va geterometalli kompleks birikmalarning antioksidantlik faolligi o'rganildi hamda antioksidantlik faolligi yuqori bo'lgan modda «Kversitin» bilan solishtirildi. Kversitin o'simlik flavonoidi bo'lib meva, sabzavot, barglarda bo'ladi. Qizil piyozda, sitrus mevalar, grechixa va asal tarkibida uchraydi. Kversitinning antioksidantlik faolligi α-tokoferol (vitamin E) dan ham yuqori hisoblanadi.Kversitin allergiyaga qarshi, yurak-tomir kasalliklarining oldini olish, saraton kasalliklari, virusga qarshi, immunitetni kuchaytiruvchi xossalarga ega [149-151].

(L1) 24,45; [Co(L1)2] 14,89; [Ni(L1)2] 19,05; [Cu(L1)2] 23,1; [Zn(L1)2] 24,2; [V4O12](L1+H... 29,5; Kversitin 35,7; Gliklozid 10

Adrenalinning autooksidlanishining ingibirlanishi (%)

(L1) 22,95; (L2) 21,72; (L3) 24,85; [V4O12](L1+H+)4 29,95; [Zn2V4O12(L1)4]·2H2O 30,30; [Zn2V4O12(L2)4]·2H2O 28,42; [Zn2V4O12(L3)2]·2H2O 31,3; Kversitin 35,7; Gliklozid 10

Adrenalinning autooksidlanishining ingibirlanishi (%)
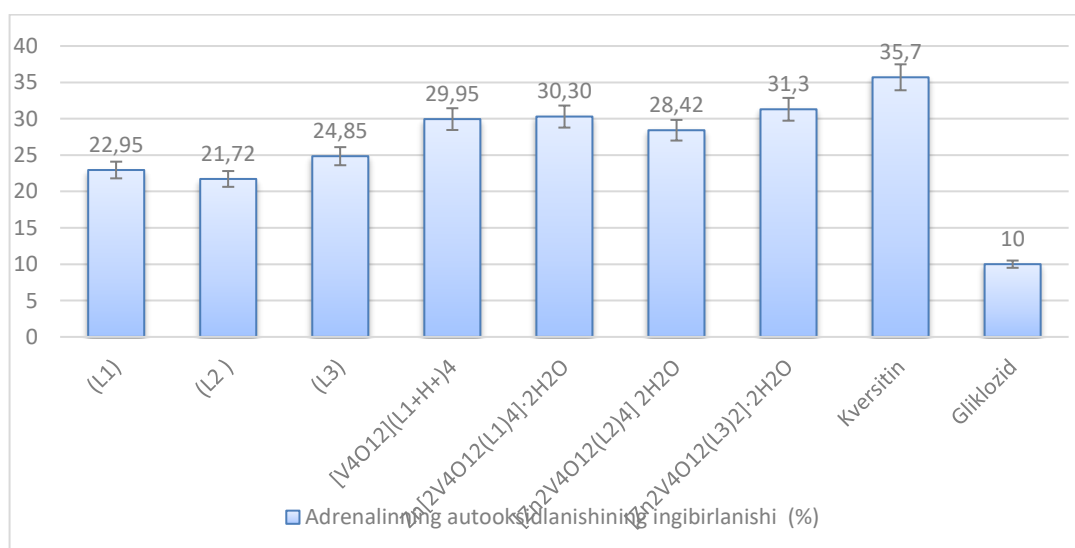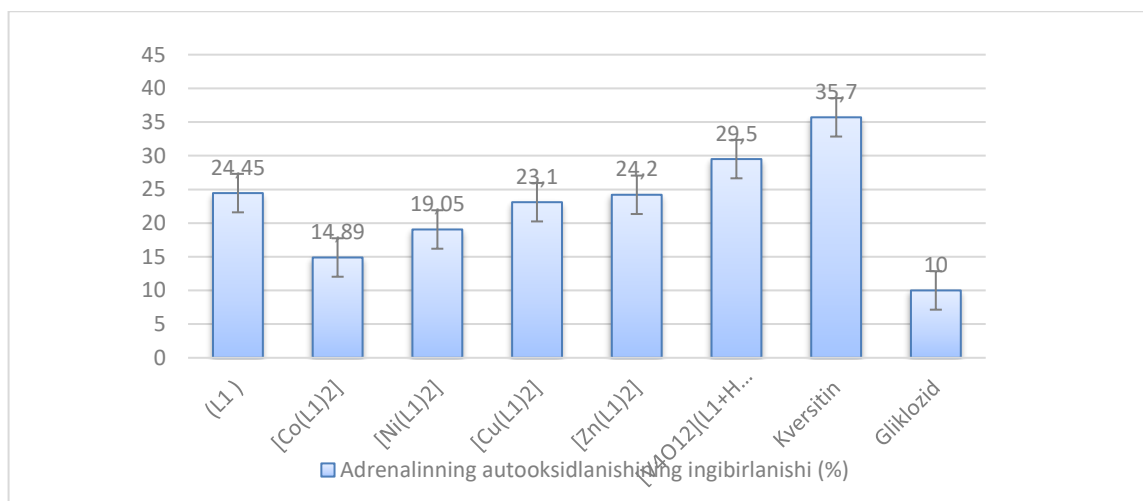
Yuqorida olib borilgan tadqiqot sintez qilingan komplekslarda antioksidantlik faolligi konsentratsiyaga bog'liq ravishda o'zgarishi 3.26-rasmda keltirilgan. Metall tabiatining antioksidantlik faolligiga ta'siri taqqoslanganda, ruxli (24,2%), vanadiyli (23,5%) va misli (23,1%) kompleks birikmaning antioksidantlik faolligi yuqoriligi aniqlandi (3.23-jadval).

a) X: 467.2657, Y: 0.1451673   Graph 1 - sample3

b) X: 481.8999, Y: 0.3832714   Graph 1 - sample1

c) X: 466.4955, Y: 0.4418216   Graph 1 - sample2

d) X: 452.6316, Y: 0.1685874   Graph 1 - sample4
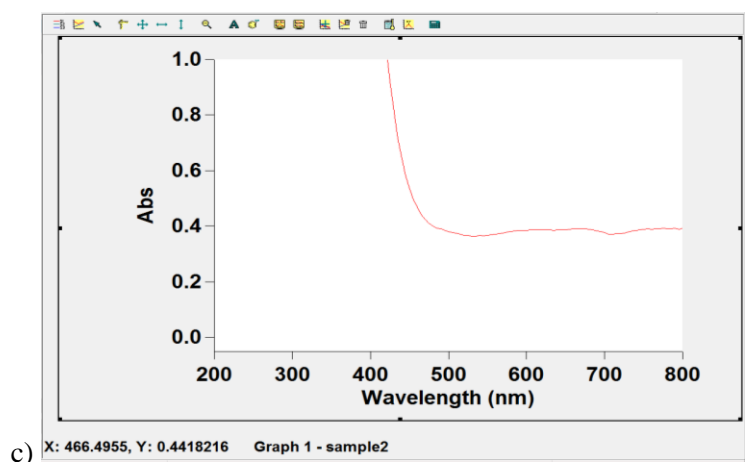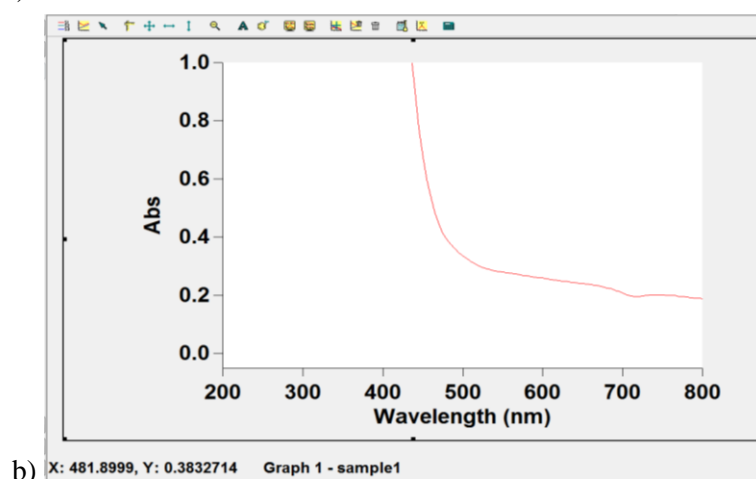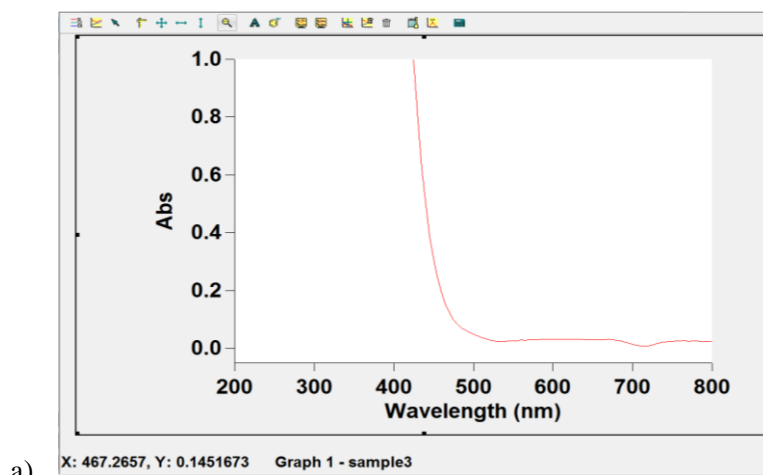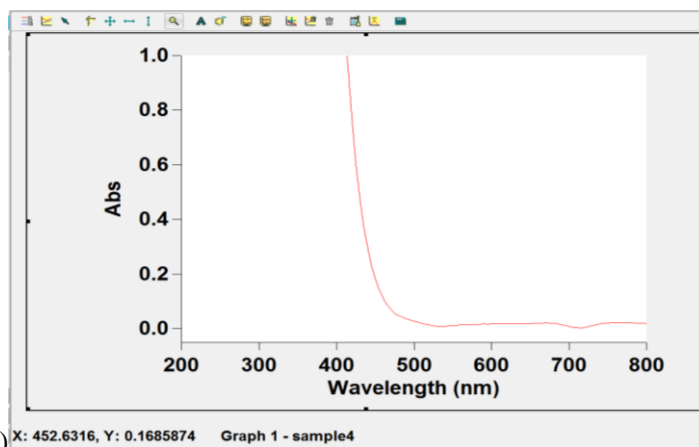
3.37-Rasm. a) L^1 b) $[Zn(L^1)_2(H_2O)_2]$ c) $[V_4O_{12}](L^1+H^+)_4$ d) $[Zn_2V_4O_{12}(L^1)_4]\cdot 2H_2O$ ning 1 mg/ml eritmasining konsentratsiyaga bog'liqlik ko'rsatgichi (nm)

Gomo- va geterometalli kompleks birikmalarning antioksidantlik faolligi o'zaro solishtirilganda, geterometalli kompleks birikmalarning faolligi yuqoriligi kuzatildi. Bu geterometalli kompleks birikmalar tarkibidagi eleltronodonor vazifasini bajarishi mumkin bo'lgan metall atomlarining ko'pligi orqali izohlandi.

3.23-Jadval

Ligand va kompleks birikmalarning antioksidantlik faolligi

Modda nomi	Modda miqdori	Eritmaning miqdori %	D_1	D_2	Tekshirilayotgan moddaning antioksidantlik faolligi (AF %)
L^1	100 mkg	10%	0,2125	0,1788	**15,85**
	250 mkg	25%	0,2424	0,1968	**18,81**
	500 mkg	50%	0,2539	0,2050	**19,26**
	750 mkg	75%	0,2468	0,1985	**19,05**
	1000 mkg=1mg	100%	0,3308	0,2499	**24,45**
L^2	100 mkg	10%	0,2014	0,1749	**13,15**
	250 mkg	25%	0,2294	0,1965	**14,42**
	500 mkg	50%	0,2684	0,2212	**15,38**
	750 mkg	75%	0,2750	0,2391	**16,36**

	1000 mkg=1mg	100%	0,4107	0,3268	**21,95**
L^3	100 mkg	10%	0,2571	0,2139	**16,8**
	250 mkg	25%	0,3097	0,2490	**19,6**
	500 mkg	50%	0,4074	0,3167	**22,26**
	750 mkg	75%	0,3781	0,2972	**21,4**
	1000 mkg=1mg	100%	0,7411	0,5193	**29,72**
[Co(L^1)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,9302	0,9087	**2,31**
	250 mkg	25%	1,059	1,024	**2,85**
	500 mkg	50%	1,152	1,102	**4,34**
	750 mkg	75%	1,342	1,248	**7**
	1000 mkg=1mg	100%	1,572	1,339	**14,89**
[Ni(L^1)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,9954	0,9486	**4,7**
	250 mkg	25%	0,9954	0,8418	**15,43**
	500 mkg	50%	0,9954	0,9757	**11,97**
	750 mkg	75%	0,9954	1,1187	**11,02**
	1000 mkg=1mg	100%	0,9954	1,2318	**19,05**
[Zn(L^1)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,629	0,538	**17,05**
	250 mkg	25%	1,072	0,8945	**19,89**
	500 mkg	50%	1,5443	1,285	**20,14**
	750 mkg	75%	1,373	1,113	**23,4**
	1000 mkg=1mg	100%	1,990	1,603	**24,2**
[Cu(L^1)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,611	0,5106	**16,44**
	250 mkg	25%	0,8424	0,6936	**17,85**
	500 mkg	50%	0,8207	0,6804	**17,07**
	750 mkg	75%	0,8804	0,7283	**17,93**

	1000 mkg=1mg	100%	1,5767	1,2230	**22,30**
[V$_4$O$_{12}$](L^1+H$^+$)$_4$	100 mkg	10%	0,9112	0,7343	**19,41**
	250 mkg	25%	1,3764	1,0391	**24,81**
	500 mkg	50%	1,7150	1,1594	**32,39**
	750 mkg	75%	1,6582	1,1471	**30,82**
	1000 mkg=1mg	100%	1,4193	1,0584	**25,42**
[Zn$_2$V$_4$O$_{12}$(L^1)$_4$]· 2H$_2$O	100 mkg	10%	0,2814	0,2228	**21,42**
	250 mkg	25%	0,4615	0,3427	**26,08**
	500 mkg	50%	0,6128	0,4447	**27,86**
	750 mkg	75%	0,7497	0,5214	**29,72**
	1000 mkg=1mg	100%	1,1642	0,7844	**32,75**
[Zn$_2$V$_4$O$_{12}$(L^2)$_4$]· 2H$_2$O	100 mkg	10%	0,616	0,531	**16,18**
	250 mkg	25%	0,786	0,65	**20,98**
	500 mkg	50%	0,979	0,771	**27,02**
	750 mkg	75%	1,015	0,7957	**27,66**
	1000 mkg=1mg	100%	0,966	0,7527	**28,4**
[Zn(L^3)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,987	0,7954	**24,18**
	250 mkg	25%	0,997	0,7954	**25,44**
	500 mkg	50%	1,030	0,7954	**29,56**
	750 mkg	75%	1,042	0,7954	**31,0**
	1000 mkg=1mg	100%	1,044	0,7954	**31,3**
[Cu(L^3)$_2$(H$_2$O)$_2$]	100 mkg	10%	0,563	0,49	**15,04**
	250 mkg	25%	0,962	0,8028	**19,88**
	500 mkg	50%	1,388	1,1287	**23,2**
	750 mkg	75%	1,129	0,91	**24,11**

	1000 mkg=1mg	100%	1,798	1,4434	**24,6**
$[V_4O_{12}](L^3+H^+)_4$	100 mkg	10%	1,138	0,9486	**20,01**
	250 mkg	25%	1,029	0,8418	**22,23**
	500 mkg	50%	1,235	0,9757	**26,58**
	750 mkg	75%	1,440	1,1187	**28,74**
	1000 mkg=1mg	100%	1,604	1,2318	**30,23**
$[Zn_2V_4O_{12}(L^3)_2]\cdot 2H_2O$	100 mkg	10%	0,9225	0,6995	**31,88**
	250 mkg	25%	0,965	0,7419	**30,19**
	500 mkg	50%	1,385	1,049	**32,05**
	750 mkg	75%	1,101	0,8077	**36,40**
	1000 mkg=1mg	100%	1,1387	0,8327	**36,75**

Ligandlarning sintez qilingan metallokomplekslar orasida, L^3 asosida sintez qilingan $[Cu(L^3)_2(H_2O)_2]$, $[Zn(L^3)_2(H_2O)_2]$ tarkibli komplekslarning antioksidantlik faolligi hamda eritmada barqarorligi boshqa ligandlarning metallokomplekslariga qaraganda yuqoriligi sababli, metallarni himoya qilish samaradorligini baholash metodologiyasi ishlab chiqilib, anaerob korroziyaning samarali ingibitori sifatida tajribaviy-sanoat sinovlaridan o'tkazildi (3.38-rasm).

a) "Muborak gazni qayta ishlash zavodi" MChJ

b)   c)   d)
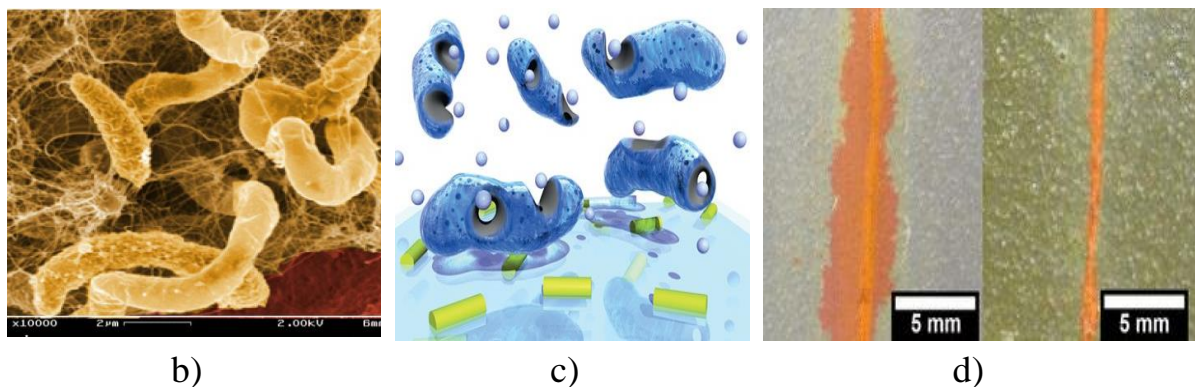
3.38-Rasm. a) "Muborak gazni qayta ishlash zavodi" MChJ b)litotrof bakteriyaning ko'rinishi; c)bakteriya qobig'ini yemirilishi; d)metal sirtidagi o'zgarish.

Bunda $[Cu(L^3)_2(H_2O)_2]$, $[Zn(L^3)_2(H_2O)_2]$ larning 10% li spirtdagi eritmasi, metallar korroziyasini keltirib chiqaruvchi litotrof bakteriyalarga qarshi yuqori ta'sirchanlikni namoyon qildi. Ishlab chiqilgan korroziya ingibitorining tajribaviy-sanoat sinovlari natijalari, mahalliy va xorijiy brendlarning mavjud ingibotorlari bilan taqqoslaganda ijobiy natijalarga erishildi – litotrof bakteriyalardan himoya ta'siri 76-80% ga teng. L^3 va uning metallokomplekslaridan $[Cu(L^3)_2(H_2O)_2]$, $[Zn(L^3)_2(H_2O)_2]$ "Muborak gazni qayta ishlash zavodi" MChJ ning "Texnik nazorat bo'limi" qoshidagi laboratoriyada sinovdan o'tkazildi va amaliyotga joriy qilindi, metall konstruksiya va qurilmalarida korroziya jarayoniga qarshi ingibitor sifatida qo'llash uchun tavsiya etildi.

III – bob bo'yicha xulosalar

Ushbu bobda ligandlarning tarkibi va tuzilishi element tahlil, rentgenofluoressent, differensial termik, mass-spektrometrik, rentgenfazaviy, rentgenstrukturaviy tahlil, IQ-, elektron diffuz qaytarilish spektroskopiyasi bilan o'rganildi. IQ spektroskopiyaga ko'ra, L^{1-2} qattiq holatda tiol holatda bo'lish aniqlandi hamda, ligand mono- va bidentantlikni namoyon qildi, gomometalli komplekslarni sintez qilishda $L^{1,2,3}$ ning etil spirtdagi eritmasiga bir nech tomchi ishqor qo'shish bilan reaksiya olib borilganda, $L^{1,2,3}$ lar bidentantlikni namoyon qilishi o'rganildi.

Ligandlar kvant-kimyoviy tahlil qilinganda, polifunksional ligandlarning koordinatsiyaga uchraydigan raqobatdosh donor markazlarni oldindan aytib berildi.

Bunda $L^{1,2}$ tiol holatda barqarorroq holatda bo'lishi aniqlandi. Kvant-kimyoviy hisoblash natijalariga ko'ra, oksadiazol halqasidagi o'rinbosarlarning umumiy elektron ta'siriga ko'ra quyidagi qatorda joylashtirish mumkin: $L^2 < L^1 < L^3$ (– Ph < – Py < –Ph, -(S)-CH_2-COOH). Kvant-kimyoviy tahlil natijalari olib borilgan zamonaviy fizik-kimyoviy tadqiqotlar asosida tasdiqlandi.

Sintez qilingan kompleks birikmalarning termik barqarorligi differensial termik tahlil orqali o'rganildi. Dastlabki ligandlar va sintez qilingan kompleks birikmalarning termogrammalarida endo- va ekzo- effektlarning hosil bo'lish sabablari yoritib berildi va parchalanish mahsulotlari aniqlandi.

Ilk marotaba rentgenstruktur tahlili bilan yangi polimer tuzilishli $[Zn(L^2)_2]_n$ kompleksning tuzilishi aniqlandi va uning tuzilishida molekulalararo va ichki molekulyar vodorod bog'larining roli isbotlandi. Rentgenstruktur tahlil natijalari CIF fayl ko'rinishida Kembridj kristallografik ma'lumotlar bazasiga (CCDC reference: 2184492, https://doi.org/10.1107/S2056989022006922) joylandi.

Kompleks hosil bo'lishning fotometrik tadqiqoti o'tkazildi hamda Babko usuli bo'yicha, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} va VO_2^+ larning komplekslarining eritmadagi barqarorlik konstantalari hisoblanib, Cu^{2+} va Zn^{2+} komplekslari uchun bu qiymatlar boshqa metall komplekslariga qaraganda yuqoriligi aniqlandi. Ushbu olingan natijalar Lambert Buger-Ber qonuniga muvofiqligi, eritmaning nur yutilish intensivligi konsentratsiyaga to'g'ri proporsional ravishda o'zgarishi kuzatildi. Gomo- va geterometalli kompleks birikmalarning barqarorligi taqqoslanganda gomometalli kompleks birikmalarning barqarorligi nisbatan yuqoriligi aniqlandi, buni geterometalli kompleks birikmalarning quyi gidratlanish energiyasiga ega bo'lishi hamda geterometalli kompleksning markaziy qismida zaryadlangan $[V_4O_{12}]^{4-}$ ning mavjudligi Gibbs energiyasining kamayishiga olib keladi, bu esa erituvchida kompleksning gidratlanishini oshishi hisobiga bo'lishi ko'rsatildi.

Fitokimyoviy tadqiqotlar natijasida sintez qilingan komplekslarning antioksidantlik faolligi aniqlandi va o'rganilgan komplekslar orasida ruxli (24,2%), vanadiyli (23,5%) va misli (23,1%) kompleks birikmaning antioksidantlik faolligi yuqoriligi aniqlandi. Ushbu komplekslar orasidan antioksidantlik faolligi hamda

eritmada barqarorligi yuqori bo'lgan [Cu(L^3)$_2$(H$_2$O)$_2$], [Zn(L^3)$_2$(H$_2$O)$_2$] lar anaerob korroziyaning samarali ingibitori sifatida tajribaviy-sanoat sinovidan o'tkazildi. Ushbu komplekslarning himoya ta'siri 76-80% samara bilan korroziya ingibitori sifatida qo'llashga tavsiya qilindi.

Olib borilgan fizik-kimyoviy tahlil natijalari shuni ko'rsatdiki, gomometalli kompleks birikmalarda L^1 va L^3 lar oktaedrik, L^2 tetraedrik tuzilishli kompleks birikmalar hosil qiladi. Geterometalli kompleks birikmalarda esa siqilgan tetraedr tuzilish namoyon bo'ldi. Olib borilgan fizik-kimyoviy tadqiqot usullari asosida kompleks birikmalarning tuzilishini quyidagicha taklif qilish mumkin:

Gomometalli kompleks birikmalar

I	II	III
L^1- (R)-Py	L^2- (R)-Ph	L^3- (R)-Ph

Oniyli kompleks birikmalar

IV	V
L^1- (R)-Py; L^2- (R)-Ph	L^3- (R)-Ph

Geterometalli kompleks birikmalar

VI	VII
L^2- (R)-Ph	L^3- (R)-Ph

Ushbu olib borilgan tadqiqot ishidan shularni xulosa qilishimiz mumkinki, birinchi marta Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} xloridli, nitratli hamda asetatli tuzlarini VO_2^+ hamda 1,3,4-oksadiazol hosilalari bilan gomo- va geterometalli yangi kompleks birikmalari sintez qilindi, fizik-kimyoviy tadqiqot usullari yordamida ularning tarkibi, tuzilishi aniqlanib bunda $L^{1,2}$ ligandlar tiol guruhining oltingugurt atomi va oksadiazol halqasining azot atomi orqali, L^3 esa karboksil guruhidagi kislorod atomlari orqali bidentat holatda birikishi aniqlandi. Ligandlar va sintez qilingan kompleks birikmalarning termogrammalaridagi endo- va ekzoeffektlarning hosil bo'lish sabablari aniqlanib, termik destruksiya mahsulotlari identifikasiyalandi. Gomometalli kompleks birikmaning termik barqarorligi geterometalli kompleks birikmanikidan yuqoriligi aniqlandi va bu holat geterometalli komplekslarda d-orbitallarning qoplanishi natijasidagi HOMO-LUMO=Δ ayirmasining farqi gomometalli komplekslardagiga nisbatan kichik bo'lishi bilan izohlandi. Babko usulida komplekslarning eritmadagi barqarorlik konstanta qiymatlarini Co(II)<Ni(II)<Zn(II)<Cu(II) ketma-ketligida ortishi Irving-Vilyams qatori qonuniyatlariga mos keldi. Geterometalli kompleks birikmalar tarkibida $[V_4O_{12}]^{4-}$ ionini saqlashi tufayli, ularning barqarorlik konstantasi va Gibbs energiyasining kamayishiga hamda gidratlanishining oshishiga olib kelishi ko'rsatildi. Ilk bor rentgen strukturaviy tahlil usuli yordamida $[Zn(L^2)_2]_n$ kompleksining tuzilishiga ichki va molekulalararo vodorod bog'larning ta'siri natijasida, polimer tuzilishli kompleksning [Zn-S-C-N-Zn-S-C-N] sakkiz a'zoli "kreslo" hosil qilishi va kompleksning geometriyasi siqilgan tetraedrik shaklga ega bo'lishi isbotlandi. L^1

asosida sintez qilingan [Cu$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O, [Zn$_2$V$_4$O$_{12}$(L^1)$_4$]·2H$_2$O, [V$_4$O$_{12}$](L^1+H$^+$)$_4$ komplekslar yuqori antioksidantlik faolligini namoyon qilishi aniqlandi. 2-Karboksimetiltio-5-fenil-1,3,4-oksadiazol va uning [Cu(L^3)$_2$(H$_2$O)$_2$], [Zn(L^3)$_2$(H$_2$O)$_2$] tarkibli metallokomplekslari metall konstruksiya va qurilmalarida anaerob sharoitda boradigan biokorroziya jarayoniga qarshi 76-80% samara bilan korroziya ingibitori sifatida "Muborak gazni qayta ishlash zavodi" ning amaliyotiga qo'llashga tavsiya etildi.

Shartli qisqartmalar

RFA – Rentgenfazaviy tahlil;

RSA – Rentgenstrukturaviy tahlil;

DQES – Diffuz qaytarilish elektron spektrlari;

EDA – Energiya dispersion tahlil;

SeM – Skanerlovchi elektron mikroskop;

T – Harorat, °C;

TG – Termogravimetriya;

DTG – Differensial termogravimetriya;

DTA – Differensial termik tahlil;

IQ–Infraqizil spektroskopiya;

UB –Ultrabinafsha spektroskopiya;

YuBMO (LUMO) – Yuqori egallangan molekulyar orbital;

QVMO (HOMO) – Quyi vakant molekulyar orbital;

DMFA-dimetilformamid;

DMSO-dimetilsulfomid;

MeOH– metanol;

EtOH– etanol;

s – soat;

$T_{suyuq.}$–suyuqlanish harorati;

Å- angsterm (10^{-10}m);

La - 2,5 bis(4-piridil)-1,3,4-oksadiazol

Lb - 2,5 bis(3-piridil)-1,3,4-oksadiazol

L^1 – 5-(4-piridin)-1,3,4-oksadiazol-2(3N)-tion;

L^2 – 5-fenil-1,3,4-oksadiazol-2(3H)-tion;

L^3 – 2-karboksimetiltio-5-fenil-1,3,4-oksadiazol;

Ph - fenil;

Py – piridil;

MEP – Manfiy effektiv potensial;

YuSSX – Mass-spektrometriya.

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