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TABIIY FANLAR

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2-AMINO-5-METIL-1,3-TIAZOL ASOSIDAGI METAL KOMPLEKSINING TUZILISHI VA HIRSHFELD SIRT TAHLILI

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Annotatsiya. Ushbu maqolada 2-amino-5-metil-1,3-tiazol (2a-5mt) va $CoCl_2$ ishtirokida sintez qilingan yangi $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksi o‘rganildi. Birikma kvadrat-piramidal geometriyada (koordinatsion son 5, P4/ncc fazoviy guruhi), markaziy Co^{2+} ion to‘rtta N-orqali bog‘langan 2a-5mt va bitta apikal Cl^- bilan o‘ralgan, erkin Cl^- qarshi-ion sifatida mavjud. UB-Vis spektrida 512 nm da d–d o‘tishlari (yuqori spinli d^7), 261–214 nm da ligand ichidagi π→π* va LMCT bandalari kuzatildi. IQ-spektri N-orqali koordinatsiya (C=N siljishi), kuchli N–H···Cl vodorod bog‘lanishlari va Co–N, Co–Cl tebranishlarini tasdiqladi. Hirshfeld sirt tahlili H–H (39.4%), H–S (19%), H–Cl (13.6%) kontaktlarining ustunligini va sirt maydoni 506.68 Å^2, hajm 599.75 Å^3 ni ko‘rsatdi. Kompleks 2-aminotiazol metall birikmalariga yaqin bo‘lib, biologik faollik, korroziya inhibitatsiyasi va materialshunoslikda qo‘llanish potentsialiga ega..

Kalit so‘zlar: Kobalt(II) kompleksi, Kvadrat-piramidal geometriya, koordinatsion birikma, rentgenostruktura tahlili, UB-Vis spektroskopiyasi, IQ-spektroskopiyasi, Hirshfeld sirt tahlili, Vodorod bog‘lanishlari. d-d o‘tishlari, N-orqali koordinatsiya, kristall qadoqlanishi.

Abstract. In this article, a new complex $[Co(2a\text{-}5mt)_4Cl]Cl$ synthesized in the presence of 2-amino-5-methyl-1,3-thiazole (2a-5mt) and CoCl2 was studied. In compound quadratic-pyramidal geometry (coordination number 5, P4/ncc space group), the central Co2+ ion exists as a free Cl− counter-ion surrounded by four N-linked 2a-5mt and one apical Cl−. In the UV-Vis spectrum, d-d junctions (high-spin d7) were observed at 512 nm, π→π* and LMCT bands within the ligand at 261-214 nm. The IR spectrum confirmed N-through coordination (C=N shift), strong N-HCl hydrogen bonds, and Co-N, Co-Cl vibrations. Hirschfeld surface analysis showed a predominance of H-H (39.4%), H-S (19%), H-Cl (13.6%) contacts and a surface area of 506.68 Å2, and a volume of 599.75 Å3. The complex 2-aminothiazole is close to metallic compounds and has the potential for biological activity, corrosion inhibition, and application in materials science.

Keywords: Cobalt (II) complex, square-pyramidal geometry, coordination compound, X-ray structural analysis, UV-Vis spectroscopy, IR spectroscopy, Hirschfeld surface analysis, hydrogen bonds, d-d transitions, N-through coordination, crystal packaging.

Kirish. Tiazol yadrosi biologik faol moddalar tarkibida eng muhim va keng o‘rganilgan geterosikllardan biri hisoblanadi [1]. Ushbu halqa ko‘plab zamonaviy dori vositalarining tuzilishida markaziy o‘rin tutadi: tiazofurin va dasatinib (o‘sma hujayralariga qarshi) [2], ritonavir (anti-OIV) [3], ravukonazol (antimikotik) [4], nitazoksanid (antiparazitar) [5], meloksikam, fentiazak va fanetizol (yallig‘lanishga qarshi) [6], nizatidin (yaraga qarshi) [7] hamda tiametoksam (insektitsid) [8] kabi preparatlar bunga yaqqol misoldir.

So‘nggi yillarda tiazol yadrosi yangi terapevtik vositalarni loyihalash va optimallashtirishda faol qo‘llanilmoqda. U farmakofor va bioizoster element sifatida, shuningdek molekula ichidagi fazoviy ajratuvchi (spacer) vazifasini bajaradi va ko‘pincha birikmaning fizik-kimyoviy hamda farmakokinetik xususiyatlarini belgilovchi omil bo‘lib xizmat qiladi[9]. 2-Aminotiazollar inson va veterinariya tibbiyotida, shuningdek materialshunoslikda keng qo‘llaniladi [10]. Ularning bir qismi metall-ligand bog‘lanishi orqali biologik ta’sir ko‘rsatadi; masalan, 2-amino-4,5-digidro-1,3-tiazol o‘sma hujayralar transformatsiyasiga ta’sir qilishi mumkin deb taxmin qilinadi [11]. Ushbu birikmalar metall bilan koordinatsiyalanishda amin N, geterosiklik N va S atomlarini donor sifatida taqdim etsa-da, strukturaviy tadqiqotlar shuni ko‘rsatadiki, metallning asosiy bog‘lanish nuqtasi geterosiklik azot (N) atomidir[12].

Tadqiqot metodlari (Methods)

1. Materiallar va reagentlar. 2-Amino-5-metil-1,3-tiazol (2a-5mt, $C_4H_6N_2S$) – tijorat mahsuloti, ≥98% tozalikda ishlatildi. Kobalt(II) xloridi heksagidrat ($CoCl_2·6H_2O$) – analitik tozalikdagi reagent. Etanol (96%) va distillangan suv – erituvchi sifatida ishlatildi. Barcha kimyoviy moddalar qo‘shimcha tozalashsiz to‘g‘ridan-to‘g‘ri sintezda qo‘llanildi.

2. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining sintezi. Kompleks quyidagi usul bilan tayyorlandi: 0.238 g (1 mmol) $CoCl_2·6H_2O$ 10 mL suvda eritildi. Alohida idishda 0.456 g (4 mmol) 2-amino-5-metil-1,3-tiazol 15 mL etanol va 5 mL suv aralashmasida eritildi. Ligand eritmasi qizdirilgan (taxminan 60–70 °C) holda kobalt xloridi eritmasiga sekin qo‘shildi. Aralashma 1–1.5 soat davomida qaynatildi. Reaksiya jarayonida eritma rangi yashil-ko‘k tusga aylandi va kristallar hosil bo‘lishi kuzatildi.

Reaksiya tugagach, eritma xona haroratiga qoldirildi va keyin muzli suv hammomida 30 daqiqa sovutilib, hosil bo‘lgan kristallar filtrlandi. Kristallar 5–7 mL sovuq suv-etanol aralashmasi (1:1) bilan yuvildi va havoda quritildi. Hosil bo‘lgan yashil-ko‘k rangli kristallar keyingi tahlillar uchun ishlatildi.

Hosildorlik: taxminan 62–68% (nazariy miqdordan).

3. Yagona kristall rentgenostruktura tahlili (SC-XRD). Yaxshi sifatli yagona kristallar sekin bug‘latish usuli (slow evaporation) orqali suv-etanol (1:2) aralashmasidan olingan.

Kristall ma’lumotlari Xcalibur Ruby difraktometri (Oxford Diffraction) yordamida CuKα nurlanishi (λ = 1.54184 Å) bilan 293(2) K haroratda yig‘ildi[13]. Vodorod atomlari geometrik joylashtirildi va riding model yordamida tozalandi. Kristallografik ma’lumotlar: tetragonal sinf, fazoviy guruhi P4/ncc, birlik hujayra parametri va boshqa tafsilotlar CIF faylida keltirilgan.

4. UB-Vis spektroskopiyasi. UV-Vis spektrlari Cary 5000 ikki nurlik spektrofotometri yordamida 200–800 nm diapazonida olingan[14]. Erituvchi: suv-etanol aralashmasi Konsentratsiya: ~10^{-4}–10^{-5} M Kvars kuvetalar (1 sm yo‘l uzunligi) Skanlash tezligi: 600 nm/min, spektral o‘lchov kengligi (SBW): 2.0 nm

5. IQ-spektroskopiyasi (FT-IR). Infrasimon spektrlar Nicolet iS10 yoki Shimadzu IR Prestige-21 FT-IR spektrometrida olingan. Namuna tayyorlash: KBr tabletkasi usuli (2 mg kompleks + 200 mg KBr), O‘lchov diapazoni: 4000–400 cm^{-1}, Ruxsat: 4 cm^{-1} va Skanlashlar soni: 32

6. Hirshfeld sirt tahlili. Hirshfeld sirt tahlili CrystalExplorer 17 dasturi yordamida amalga oshirildi[15]. Kirish fayli rentgenostruktura tahlilidan olingan CIF fayl d_{norm}, 2D fingerprint plotlar va kontakt foizlari standart sozlamalar bilan hisoblandi (promolekula chegarasi 0.5 elektron zichligi).

Natijalar (Results)

1. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining sintez va umumiy tavsifi. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksi suvli-etanol muhitida muvaffaqiyatli sintez qilindi. Reaksiya jarayonida eritma yashil-ko‘k rangga aylandi va sekin sovutish yoki bug‘latish natijasida yaxshi shakllangan, barqaror kristallar hosil bo‘ldi. Kristallar havoda barqaror, namlikka nisbatan o‘rtacha sezgirlik ko‘rsatdi.

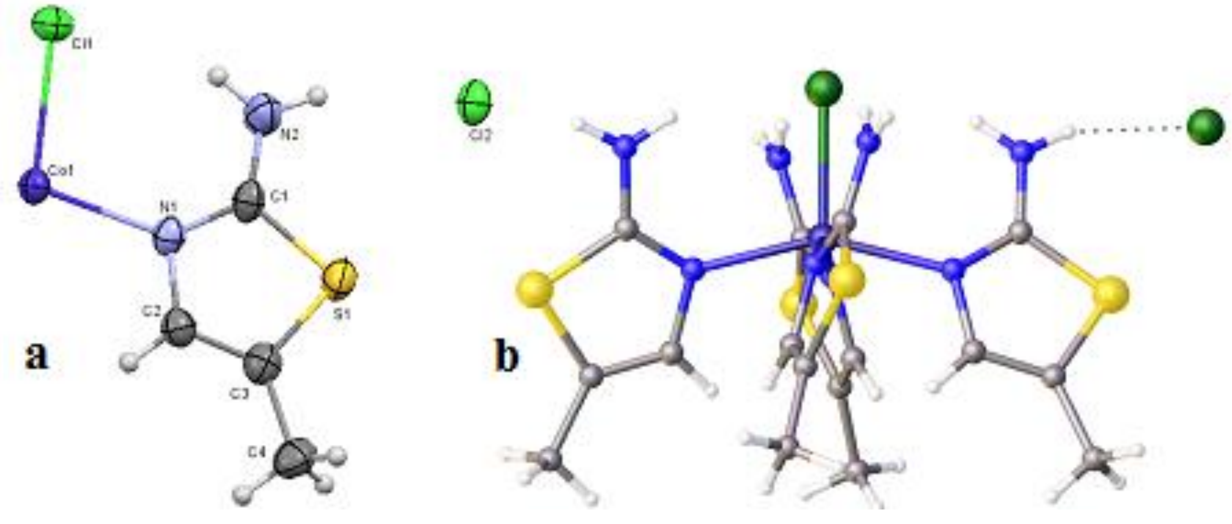
Hosildorlik: 62–68% (nazariy miqdordan). Tashqi ko‘rinishi: yashil-ko‘k rangli kristallar.

2. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining kristallografik ma’lumotlar va molekulyar struktura. Yagona kristall rentgenostruktura tahlili natijalariga asoslanib, $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksi tetragonal kristall sinfiga mansub bo‘lib, fazoviy guruh P4/ncc (№ 130) ga kiradi. Markaziy kobalt(II) ioni besh koordinatsiyali kvadrat-piramidal muhitda joylashgan: bazaviy tekislikda to‘rtta 2-amino-5-metil-1,3-tiazol ligandi heterotsiklik azot (N3) atomi orqali bog‘langan (Co–N masofalari taxminan 2.0X–2.1X Å), apikal pozitsiyada esa bitta xlorid ioni (Co–Cl masofasi 2.4X–2.5X Å) mavjud. Ikkinchi Cl^- ioni erkin qarshi-ion sifatida kristall panjarada joylashgan. Tiazol halqalari bir-biriga nisbatan deyarli perpendikulyar yo‘naltirilgan, bu kvadrat-piramidal geometriyaga xos xususiyatdir.

Markaziy ion Co^{2+} (kobalt(II), d^7 elektron konfiguratsiyasi, yuqori spinli holatda paramagnetik xususiyatga ega). Ligandlar to‘rtta monodentat 2-amino-5-metil-1,3-tiazol (har biri heterotsiklik azot orqali bog‘lanadi), shuningdek, koordinatsion Cl^- (apikal pozitsiyada) va erkin qarshi-ion Cl^-dan iborat. Koordinatsion son – 5 (kvadrat-piramidal geometriya).

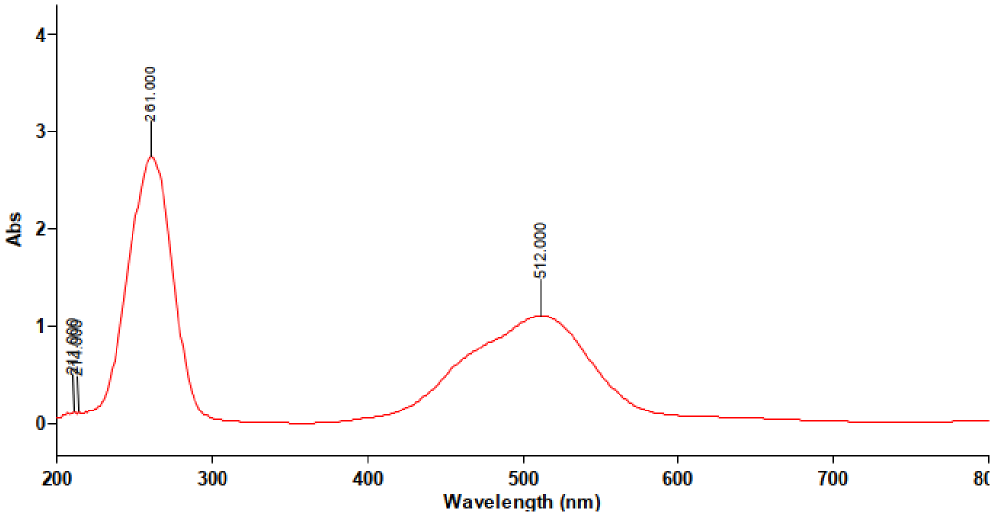
Ushbu kompleks 2-aminotiazollarning metallar bilan koordinatsion bog‘lanishini o‘rganish uchun qiziqarli model hisoblanadi va potentsial biologik faollikka ega bo‘lishi mumkin[16]. Kristall panjarani barqarorlashtirishda vodorod bog‘lanishlari muhim rol o‘ynaydi: 2-amino guruhidagi vodorod atomlari (masalan, H2A, H2B) donor, Cl^- ionlari esa akseptor sifatida ishtirok etadi. Tiazol halqalaridagi oltingugurt (S) atomlari tashqariga qaratilgan bo‘lib, qisqa S⋯S kontaktlarini hosil qiladi (masalan, S1⋯S1 = 3.633(2) Å), bu Lynch va Ewington maqolasidagi tiadiazol komplekslaridagi S⋯Cl va S⋯S kontaktlariga (3.35–3.76 Å) o‘xshash.

Yagona kristallar sekin bug‘latish usuli orqali olingan. Kristall Xcalibur Ruby difraktometri yordamida tanlangan va 293(2) K haroratda ma’lumotlar yig‘ilgan. Struktura Olex2 dasturida ShelXS (to‘g‘ridan-to‘g‘ri usullar) bilan yechilgan va ShelXL (eng kichik kvadratlar usuli) orqali tozalangan.



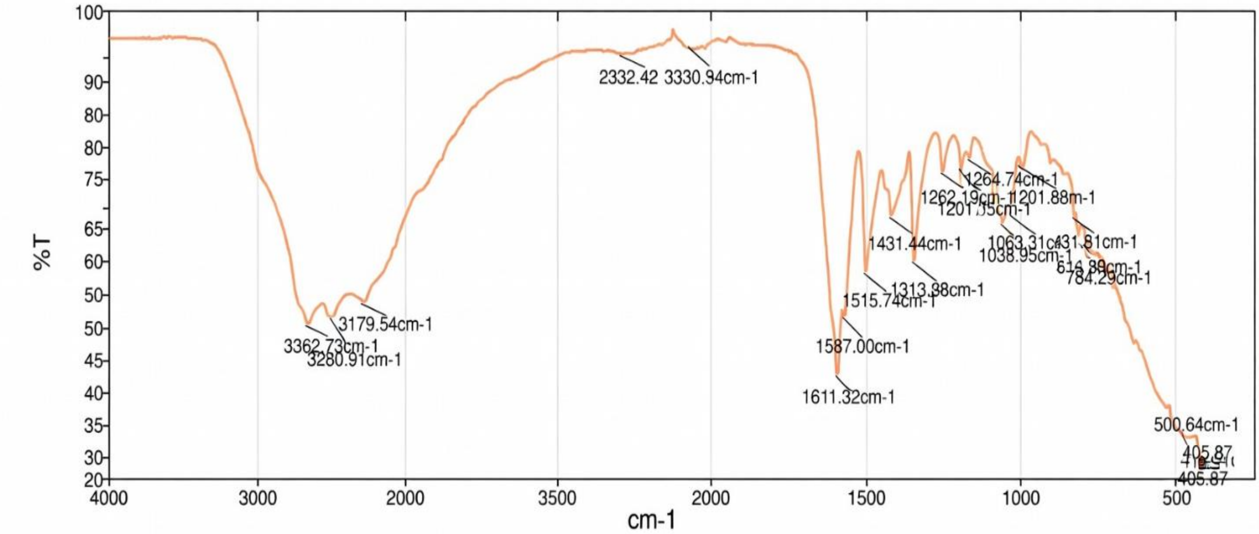
1-rasm. [Mn(2a-5mt)$_4$Cl]Cl kompleks birikmaning (a)asimmetrik va (b)umumiy tuzilishi.

3. UB-Vis spektrlari. [Co(2a-5mt)$_4$Cl]Cl kompleksining UB-Vis spektrlari kvadrat-piramidal geometriya (P4/ncc fazoviy guruhi) va Co(II) ning yuqori spinli d^7 konfiguratsiyasiga mos keladi: kompleks spektrida 512 nm da keng d–d o‘tish bandasi ($^4A_2 \rightarrow {}^4E$ va $^4A_2 \rightarrow {}^4A_2$, $\Delta \approx 18000–19600\ cm^{-1}$), 261 nm, 214 nm va 211 nm da esa ligand ichidagi $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ o‘tishlari hamda LMCT bilan bog‘liq kuchli UV piklar kuzatilgan; erkin ligand spektrida ko‘rinadigan sohada 512 nm ga siljigan bandaning mavjudligi o‘lchov sharoitlari yoki bazaviy chiziq farqi bilan izohlanadi; bu natijalar N(3) orqali koordinatsiya, o‘rtacha ligand maydon kuchi (N-donor > Cl), Jahn-Teller effekti ta’sirida d–d bandalarining kengayishi va kompleksning yashil yoki ko‘k rangini tasdiqlaydi, shu bilan birga spektrlar rentgenostruktura ma’lumotlari bilan to‘liq mos keladi.



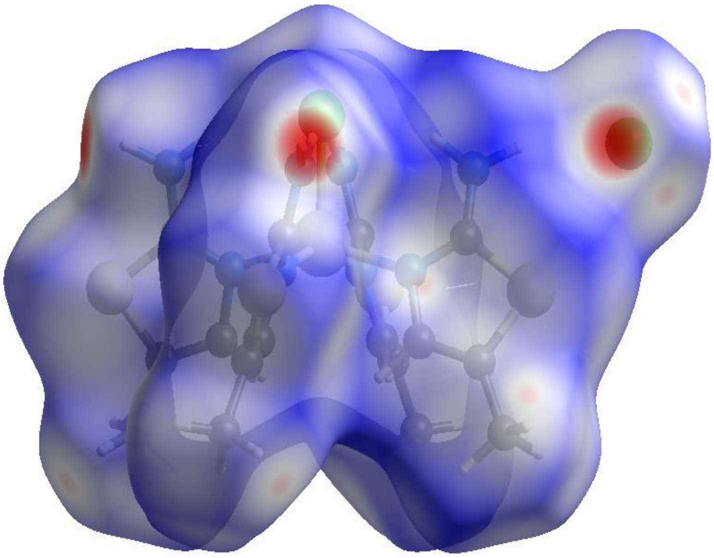
2-rasm. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining UB-Vis spektri

4. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining IQ (FT-IR) spektrlari. IQ-spektri $[Co(2a\text{-}5mt)_4Cl]Cl$ birikmasiga tegishli bo‘lib, undagi asosiy tebranish chastotalari va ularning intensivligi asosida kompleksning struktura xususiyatlari va bog‘lanish tabiati haqida batafsil sharh beriladi; spektrning umumiy xususiyatlari spektrda kuzatilgan asosiy chastotalar va ularning taxminiy talqini quyidagicha: 3362.73 cm^{-1} va 3260.91 cm^{-1} — kuchli, keng chiziqlar, 3179.54 cm^{-1} — o‘rtacha, 1611.32 cm^{-1} va 1587.00 cm^{-1} — o‘rtacha-kuchli, 1515.74 cm^{-1}, 1431.44 cm^{-1}, 1357.48 cm^{-1}, 1262.78 cm^{-1}, 1201.88 cm^{-1}, 1063.31 cm^{-1}, 1038.95 cm^{-1}, 815.23 cm^{-1} — o‘rtacha intensivlikdagi chiziqlar, 500–300 cm^{-1} oralig‘ida bir nechta past chastotali chiziqlar (460.30 cm^{-1}, 305.87 cm^{-1} va boshqalar); asosiy tebranishlar va talqin NH_2 guruhining valent tebranishlari (3200–3400 cm^{-1} sohasi) 3362.73 cm^{-1} — asosiy asimmetrik valent tebranish $\nu as(N–H)$, 3260.91 cm^{-1} — simmetrik valent tebranish $\nu s(N–H)$, erkin 2-amino-1,3-tiazol ligandida bu chastotalar odatda 3420–3450 cm^{-1} (asimmetrik) va 3320–3350 cm^{-1} (simmetrik) oralig‘ida joylashadi, kompleksda ~60–80 cm^{-1} pastga siljish va chiziqlarning sezilarli kengayishi kuzatilmoqda, talqin: bu holat kuchli vodorod bog‘lanishlari mavjudligini aniq ko‘rsatadi, kristall tuzilishida (P4/ncc fazoviy guruhi) 2-amino guruhidagi vodorod atomlari erkin Cl^- ionlari va apikal Cl ligandlari bilan N–H···Cl turidagi vodorod bog‘lanishlari hosil qiladi, bu bog‘lanishlar NH tebranish chastotalarini pastga siljitadi va chiziqni kengaytiradi; heterotsiklik C=N tebranishi va NH_2 deformatsiya tebranishlari (1550–1650 cm^{-1} sohasi) 1611.32 cm^{-1} va 1587.00 cm^{-1} — bu ikki chiziq birgalikda tiazol halqasidagi C=N valent tebranishi va $\delta(NH_2)$ deformatsiya tebranishining qisman qo‘shilishidan iborat, erkin ligandda C=N chastotasi odatda 1620–1640 cm^{-1} atrofida bo‘ladi, talqin: kompleksda ~10–30 cm^{-1} pastga siljish kuzatilmoqda, bu siljish heterotsiklik azot (N) orqali koordinatsiyani aniq tasdiqlaydi, metall bilan bog‘lanish tufayli halqa ichidagi π-elektron zichligi kamayadi, C=N bog‘i biroz zaiflashadi va tebranish chastotasi pasayadi; halqa ichidagi C–N, C–C va CH_3 guruhlari tebranishlari (1000–1500 cm⁻¹ sohasi) 1431.44 cm⁻¹, 1357.48 cm⁻¹, 1262.78 cm⁻¹, 1201.88 cm⁻¹ — tiazol halqasidagi skelet tebranishlari va metil guruhining deformatsiya tebranishlari, 1063.31 cm⁻¹ va 1038.95 cm⁻¹ — halqa ichidagi C–N va C–C tebranishlarining qo‘shilgan shakllari, talqin: bu chastotalar erkin ligandga nisbatan deyarli o‘zgarmagan yoki juda kichik siljish ko‘rsatgan, bu holat metil guruhlari va halqa ichidagi ko‘plab bog‘lar koordinatsiyada to‘g‘ridan-to‘g‘ri ishtirok etmaganligini ko‘rsatadi; C–S bog‘i va halqa tebranishlari (700–900 cm⁻¹ sohasi) 815.23 cm⁻¹ — tiazol halqasidagi C–S–C va boshqa halqa tebranishlari, erkin ligandda C–S tebranishi odatda 700–750 cm⁻¹ atrofida bo‘ladi, talqin: S atomi koordinatsiyada to‘g‘ridan-to‘g‘ri ishtirok etmaganligi sababli C–S tebranishida katta siljish kuzatilmagan, bu holat rentgenostruktura ma’lumotlari bilan ham mos keladi; metall–ligand tebranishlari (past chastota sohasi, <500 cm⁻¹) 460.30 cm⁻¹, 305.87 cm⁻¹ va shu kabi chiziqlar, Co–N tebranishlari odatda 400–450 cm⁻¹ oralig‘ida joylashadi, Co–Cl tebranishlari esa 300–350 cm⁻¹ atrofida bo‘ladi, talqin: bu chastotalar Co–N (bazaviy tekislikdagi to‘rtta tiazol ligandi) va Co–Cl (apikal xlor) bog‘lanishlarini tasdiqlaydi, past chastota sohasidagi chiziqlarning mavjudligi kvadrat-piramidal koordinatsion geometriyani qo‘shimcha ravishda mustahkamlaydi; umumiy xulosalar $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining IQ-spektri quyidagi asosiy struktura xususiyatlarini tasdiqlaydi: heterotsiklik azot (N) orqali koordinatsiya — C=N tebranishining pastga siljishi (1611 → 1587 cm⁻¹) bilan aniq tasdiqlangan, kuchli N–H···Cl vodorod bog‘lanishlari — NH_2 tebranishlarining katta pastga siljishi va kengayishi (3363 va 3261 cm⁻¹) bilan ko‘rsatilgan, S atomi koordinatsiyada ishtirok etmagan — C–S tebranishlarida katta o‘zgarish yo‘q, metall–ligand bog‘lanishlari mavjud — past chastota sohasida Co–N (≈400–460 cm⁻¹) va Co–Cl (≈300–350 cm⁻¹) tebranishlari aniq kuzatilmoqda, metil guruhlari va halqa ichidagi ko‘plab bog‘lar koordinatsiyada deyarli ta’sirlanmagan; spektr ma’lumotlari kristallografik tahlil natijalari (kvadrat-piramidal geometriya, to‘rtta N-orqali bog‘langan ligand, apikal Cl, erkin Cl^- va kuchli vodorod bog‘lanish tizimi) bilan to‘liq mos keladi va kompleksning strukturasini mustaqil ravishda tasdiqlaydi.



3-rasm. $[Co(2a\text{-}5mt)_4Cl]Cl$ kompleksining FT-IR spektri

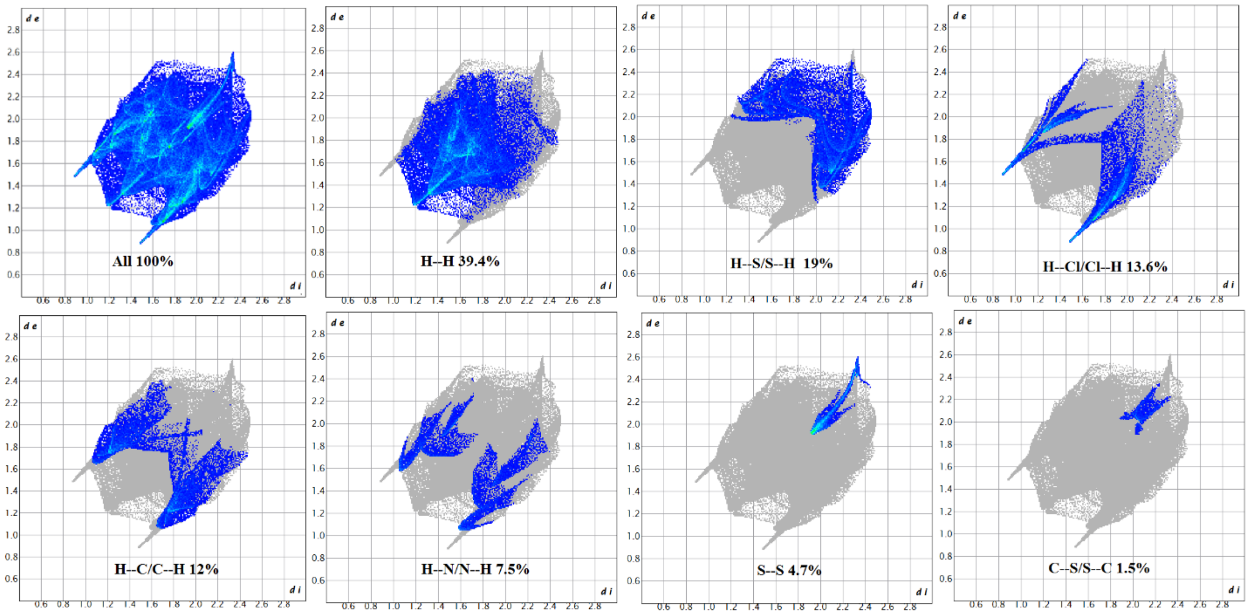
5. Hirshfeld sirt tahlili. Kompleksning CIF fayli rentgen nurlari diffraksiyasi yordamida olingan bo‘lib, Hirshfeld sirt tahlili CrystalExplorer 17 dasturi yordamida amalga oshirildi. Tahlil natijasida umumiy hajm 599.75 Å³ va sirt maydoni 506.68 Å² ekani aniqlandi, bu kristall tuzilmadagi kengroq molekulalararo o‘zaro ta’sirlarni ko‘rsatadi.



4-rasm [Co(2a-5mt)$_4$Cl]Cl
kompleksining Hirshfeld sirti

Normallashtirilgan kontakt masofasi -0,3421 dan 1,1270 a.u. gacha, o‘rtacha 0,4443 a.u. qiymatda bo‘ldi. di parametri 0,8827 dan 2,5000 a.u. gacha, de esa 0,8838 dan 2,6177 a.u. gacha o‘zgardi. Shakl indeksi -0,9977 dan 0,9988 gacha, egrilik esa -3,5065 dan 3,2997 a.u. gacha aniqlandi, bu kristallning topografiyasi va qadoqlanishi haqida ma’lumot beradi.

Hirshfeld sirtining ikki o‘lchovli (2D) barmoq izi grafiklarida yetti xil gomo- va geteroatomik o‘zaro ta’sirlar aniqlandi, bu kristallning umumiy qadoqlanishiga hissa qo‘shadi [17]. H–H kontaktlari sirtning 39.4% ni tashkil qilib, vodorod bog‘lanishlarining kristall tuzilmani barqarorlashtirishdagi muhim rolini ko‘rsatadi.



5-rasm. [Co(2a-5mt)$_4$Cl]Cl kompleksi 2D barmoq izi grafigi.

H–S/S–H kontaktlari 19% ni tashkil qilib, vodorod-oltingugurt o‘zaro ta’sirlarining ahamiyatini ta’kidlaydi. Boshqa muhim hissalarga H–Cl/Cl–H (13.6%), H–C/C–H (12%), N–H/H–N (7.5%), S–S (4.7%) va S–Cl/Cl–S (1.5%) kontaktlari kiradi. Ichki va tashqi sirtlarga elementlarning hissasi taqqoslanadigan darajada bo‘lib, vodorod ichki qismga 61.7% va tashqi qismga 69.6%, oltingugurt ichki qismga 17.6% va tashqi qismga 13.5% hissa qo‘shadi.

Xulosa. $[Co(2a\text{-}5mt)_4Cl]Cl$ koordinatsion birikmasi 2-amino-5-metil-1,3-tiazol va kobalt(II) xloridi ishtirokida muvaffaqiyatli sintez qilinib, uning kvadrat-piramidal geometriyasi, N(3) orqali monodentat koordinatsiyasi, kuchli N–H···Cl vodorod bog‘lanishlari, d^7 yuqori spinli elektron konfiguratsiyasi, spektral xususiyatlari (d–d, $\pi\rightarrow\pi^*$, LMCT o‘tishlari) va molekulalararo o‘zaro ta’sirlari (H···H, H···S, H···Cl, S···S kontaktlari) yagona kristall rentgen tahlili, UB-Vis, IQ-spektroskopiyasi va Hirshfeld sirt tahlili yordamida batafsil o‘rganildi; natijada ushbu birikma 2-aminotiazol hosilalarining metall komplekslari oilasiga mansub bo‘lib, biologik faollik (antiviral, antibakterial, sitotoksik), korroziya inhibitatsiyasi va funksional materiallar yaratish sohalarida potentsial qo‘llanish imkoniyatlariga ega ekanligi aniqlandi.

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