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Cu(II) NING 2,6-PIRIDINDIKARBON KISLOTA BILAN ARALASH LIGANDLI KOMPLEKS BIRIKMASI SINTEZI VA TADQIQI

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Annotatsiya: 2,6-piridindikarbon kislotasi mis(II)ioni bilan ta'sirlashishi va uning aralash ligandli metallokompleks birikmalarining xossalari tadqiq qilish maqsadida, mis(II) atsetat, 2,6-piridindikarbon kislotasi va 8-oksixinolin M:L:L 1:1:1 nisbatdagi aralash ligandli yangi kompleks birikmasi olinib, uning monokristali o'zgaririldi. Uning tarkibi va tuzilishi RTT yordamida aniqlandi. Kompleks birikmada 2,6-piridindikarbon kislotasi ligandi tridentant holatda koordinatsiyalangan. IQ spektri va kristallarning molekulararo ta'sirlashish energiyalari aniqlandi.

Kalit so'zlar: 2,6-piridindikarbon kislotasi (2,6-PDCA, dipic), mis(II) atsetat, xlorid kislotasi

СИНТЕЗ И ИССЛЕДОВАНИЕ КОМПЛЕКСА СМЕШАННЫХ ЛИГАНДОВ Cu(II) С 2,6-ПИРИДИНЕДИКАРБОНОВОЙ КИСЛОТОЙ

Аннотация: Для изучения взаимодействия 2,6-пиридиндикарбоновой кислоты с ионом меди(II) и свойств его металлокомплексных соединений со смешанными лигандами был получен новый комплексный продукт, состоящий из ацетата меди(II), 2,6-пиридиндикарбоновой кислоты и 8-оксихинолин, с соотношением смешанных лигандов 1:1:1, и выращен его монокристалл. Состав и структура комплекса были определены с помощью РСА. В комплексном соединении лиганд 2,6-пиридиндикарбоновой кислоты координирован в тридентатном состоянии. Были определены ИК-спектр и энергии межмолекулярного взаимодействия кристаллов.

Ключевые слова: 2,6-пиридиндикарбоновая кислота (2,6-ПДКА, дипик), ацетат меди(II), соляная кислота

SYNTHESIS AND STUDY OF A MIXED LIGAND COMPLEX OF Cu(II) WITH 2,6-PYRIDINEDICARBONIC ACID

Abstract: In order to study the interaction of 2,6-pyridinedicarboxylic acid with copper(II) ion and the properties of its mixed ligand metallocomplex compounds, a new complex compound of copper(II) acetate, 2,6-pyridinedicarboxylic acid and 8-oxyquinoline with a mixed ligand ratio of 1:1:1 was obtained and its single crystal was grown. Its composition and structure were determined using X-ray method. In the complex compound, the 2,6-pyridinedicarboxylic acid ligand is coordinated in a tridentate state. The IR spectrum and intermolecular interaction energies of the crystals were determined.

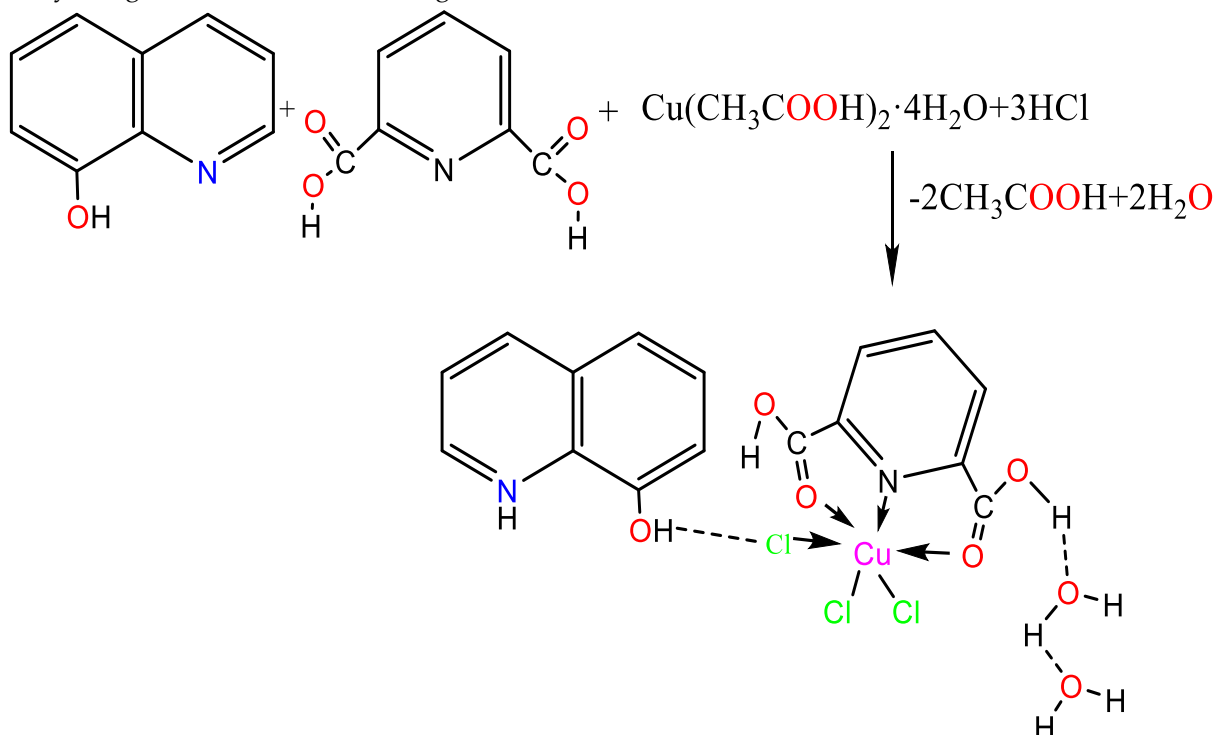
Keywords: 2,6-pyridinedicarboxylic acid (2,6-PDCA, dipic), copper(II) acetate, hydrochloric acid

Kirish. 2,6-piridindikarbon kislotasi (2,6-PDCA, dipic) komplekslar hosil qiluvchi ko'p qirrali N, O-xelatlovchi, bidentat va tridentat xelatlovchi liganddir [1-4]. Ushbu ligand H₂pda va markaziy piridin halqasi va ikkita karboksilat guruhi o'rtasida qattiq 120 ° burchakka ega va shuning uchun hosil bo'lish uchun turli xil bog'lanish usullarini ta'minlay oladi [5].

Hozirgi vaqtda kimyogarlar metall ionlariga birlashtirilgan donor atomlarining soniga qarab di, tri, tetra yoki ko'p ligandli komplekslar bo'lishi mumkin bo'lgan qiziqarli fizik-kimyoviy xossalari tufayli aralash ligand komplekslari bo'yicha keng qamrovli tadqiqotlar olib bormoqda [6-8]. Bis(piridin-2,6-dikarboksilato-N,O,OO) mis(II) monogidrat, [Cu(C₇H₄NO₄)₂]·H₂O va bis(piridin-2,6-dikarboksilato-N,O,OO) sink(II) trigidrat [Zn(C₇H₄NO₄)₂]·3H₂O komplekslari ham sintez qilingan va o'rganilgan. Ikkala metall ionlari ham to'rtta kislorod atomlariga bog'langan va ikkita piridin-N atomlari har biriga deyarli perpendikulyar holatda bog'langan. Mis(II) kompleksi ikki tomonlama kristallografik xususiyatga ega simmetriya va ikkita turli ligand molekularini o'z ichiga oladi, ulardan biri neytral va ikki marta ionlangan. Aksincha, Zn(II) kompleksida ikkita bir xil ionlangan molekular mavjud. Ikkala kompleksda ham suv molekulari bilan O...H...O bog'lari orqali barqarorlashgan [9-10]. Biz ushbu ishimizda aralashligandli kompleks birikmasi sintezi, kristall tuzulishi va tahlilini o'tkazdik.

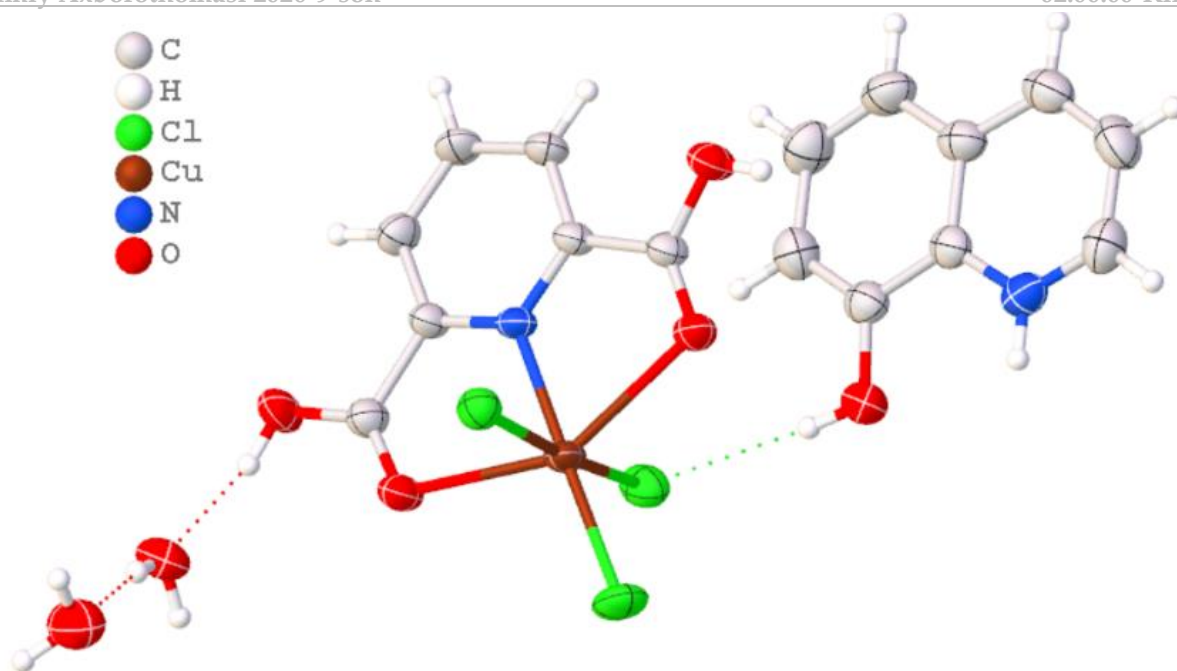
Tajribaviy qism. Yuqori sifatli kristallarni olish muhimligini hisobga olib, barcha ishlatiladigan kimyoviy moddalar va reagentlar tijorat manbalaridan (Sigma-Aldrich) olingan. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (98%) va 2,6-PDCA (99%), 8-HQ(98%) va qo' shimcha tozalashsiz ishlatilgan. Ushbu sintezda xlorid kislota va distillangan suv ham ishlatilgan.

[Cu(2,6-PDCA)(Cl)₃] C₉H₈NO(H₂O)₂ kompleksi sintezi. Aralash ligandli kompleks birikma olish maqsadida, Cu(II)atsetati kristallogidratidan ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) 0.254 gr (1 mmol), 0.167 gr (1mmol) 2,6-piridindikarbon kislota (C₇H₅NO₄) (2,6-PDCA) va 0.145 gr (1mmol) 8-oksixinolin (8-HQ) larni berilgan tartibda, tegishli suv, suv va etil spirtida eritib, 1;1;1 mol nisbatdagi eritmaları tayyorlandi. Eritma qizdirilgan holatda aralashtirildi. Cho' kma filtirdan ajratilib olinib, xlorid kislota eritmasi yordamida eritildi. Eritma kuchsiz kislotali ya'ni pH=6 ga teng bo' ldi. Kuzatishlar natijasida och ko' k rangli kompleks birikma monokristali o' sganligi kuzatildi. RTT analizi uchun yaroqli kristallar ajratilib, tekshirilganda [Cu(2,6-PDCA)(Cl)₃]C₉H₈NO(H₂O)₂ tarkibli ekanligi aniqlandi. Unumi 76% CuC₁₆H₁₇N₂O₇Cl₃ (Mr =519.64g/mol) C H N element tahlili hisoblandi: C 36.94, H 3.29, N 5.38% hisoblab chiqildi, aniqlandi C 36.86, H 3.21, N 5.31%. Reaksiya tenglamasi 1-sxemada keltirilgan.



1-sxema. [Cu(2,6-PDCA)(Cl)₃] C₉H₈NO(H₂O)₂ kompleksi sintezi reaksiyasi

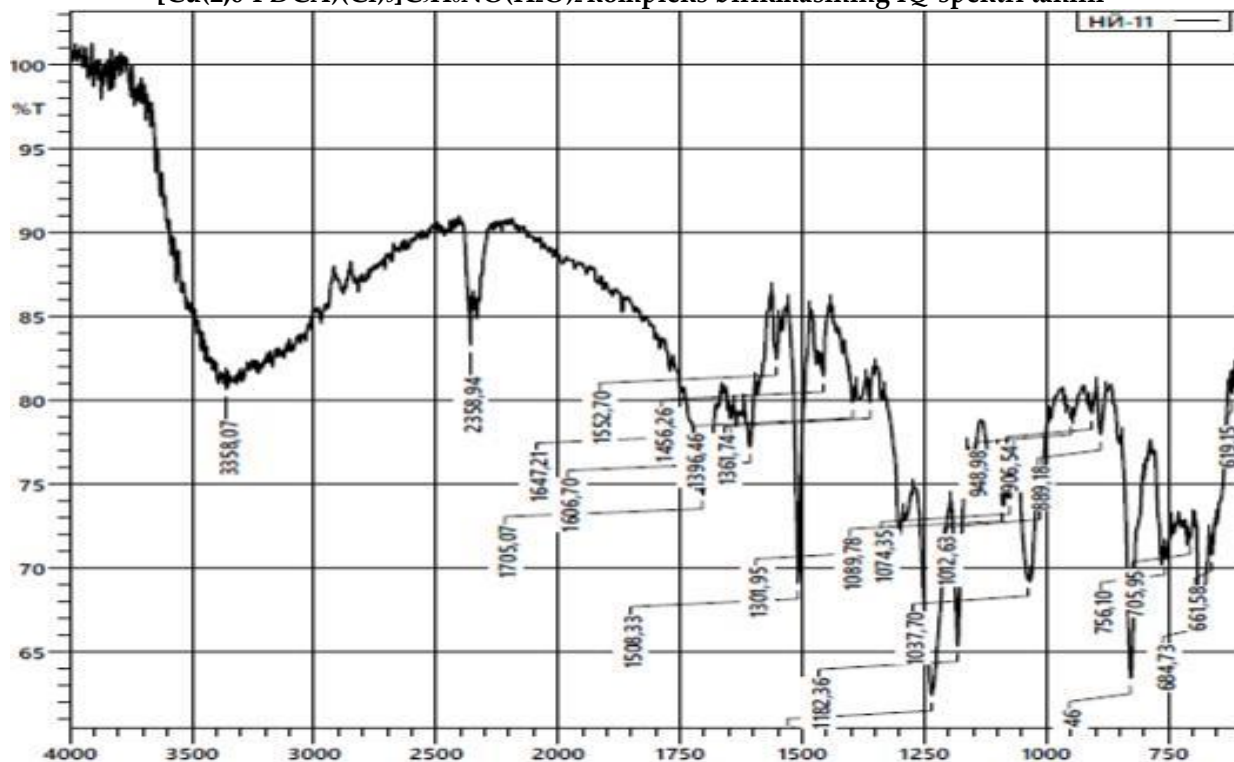
Tahlil natijalari. [Cu(2,6-PDCA)(Cl)₃]C₉H₈NO(H₂O)₂ kompleksining singoniyasi triklinik bo' lib, markaziy atom Cu ning koordinatsion soni 6 ga teng.



1-rasm. $[\text{Cu}(2,6\text{-PDCA})(\text{Cl})_3]\text{C}_9\text{H}_8\text{NO}(\text{H}_2\text{O})_2$ kompleks birikmasining molekulyar tuzilishi

Ushbu kompleks birikma $[\text{Cu}(2,6\text{-PDCA})\text{Cl}_3]^-$ anioni, 8HQ^+ kationi va ikkita suv molekulasidan iborat (1-rasm). Cu(II) ioni 2,6-PDCA ning ikki O atomi va bir N atomi orqali tridentat holatda, uchta xlorid atomi bilan muvofiqlashtirilgan CuO_2NCl_3 oktaedr geometriyasi buzilgan, Cu—N bog' lanish uzunligi 2.010 (2) Å, Cu—O bog' lanish uzunligi 2.365 (2) Å va 2.423 (2) Å va Cu—Cl bog' lanish uzunligi 2.2065 (9) Å va 2.4192 (10) Å, Kompleks tetragonal siqilgan oktaedrik tuzilishlidir. Simmetriyaning buzilishi tufayli Yan Teller effekti kuzatilgan. Tashqi sferada 8-oksinolininiy kationi va 2 ta suv molekullari mavjud bo'lib, ichki sferaga vodorod bog' lanish orqali bog' langan hamda kompleksning barqarorlashuviga olib kelgan.

$[\text{Cu}(2,6\text{-PDCA})(\text{Cl})_3]\text{C}_9\text{H}_8\text{NO}(\text{H}_2\text{O})_2$ kompleks birikmasining IQ-spektri tahlili

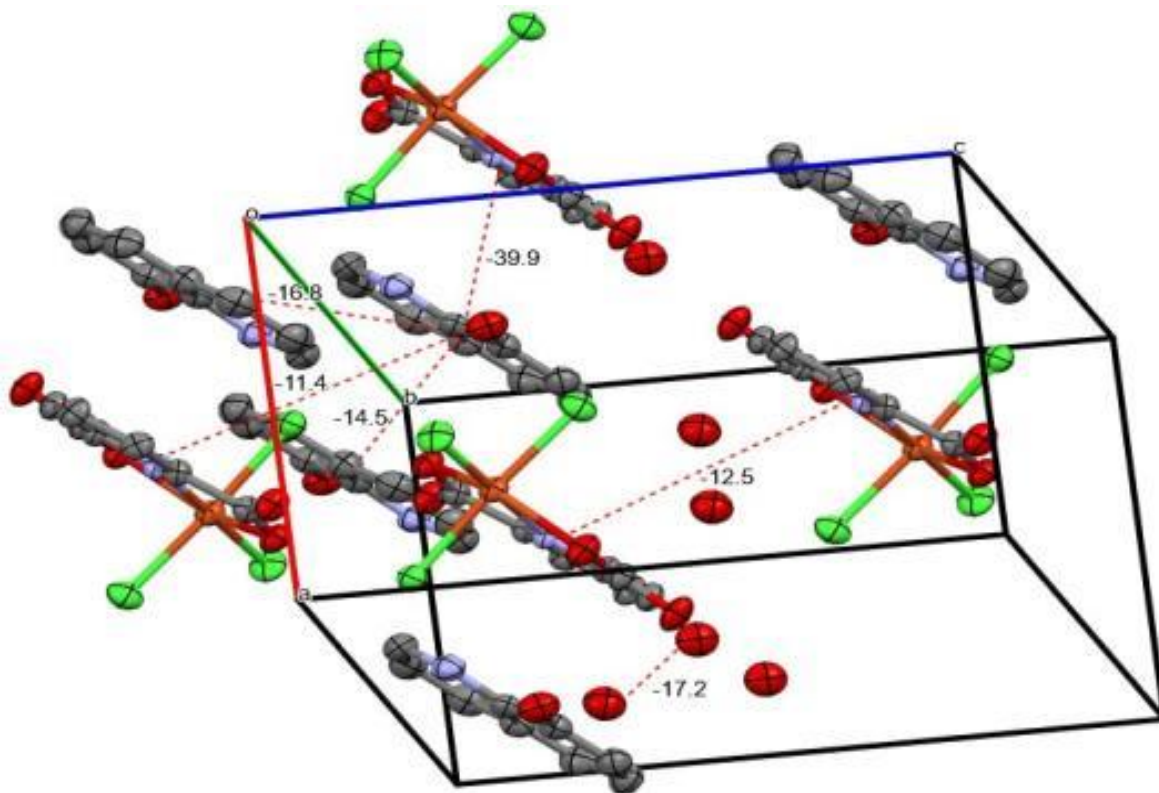


2-rasm. $[\text{Cu}(2,6\text{-PDCA})(\text{Cl})_3]\text{C}_9\text{H}_8\text{NO}(\text{H}_2\text{O})_2$ kompleksining IQ-spektri

Olingan tahlil natijasiga ko'ra, 3358.07 cm^{-1} sohasida OH- guruhiga xos intensivligi juda yuqori bo'lgan valent tebranish, 1552.70 cm^{-1} sohasida xolin halqasining halqa tebranishi, valent tebranish, 1647.21 cm^{-1} sohasida -C-N bog'ining valent tebranish chastotalari kuzatildi, 1089.78 cm^{-1} sohasida C-O guruhiga tegishli valent tebranishlar, 684.73 cm^{-1} sohasida Me-Cl bog'iga xos, 661.58 cm^{-1} sohasida Me-O bog'iga xos, 619.15 cm^{-1} sohasida Me-N bog'iga xos valent tebranish chastotalari kuzatildi (2-rasm). Kompleks birikmada 2,6-PDCA ligandi markaziy atom bilan tridentant holatda,

2 ta xlorid ionlari ham birikkan bo' lib, xelat kompleks hosil bo' lishiga sababchi bo' lgan. 2,6-PDCA dagi karboksil guruhining kislorod atomlari markaziy atom bilan bog' langan.

[Cu(C₇H₅NO₄)(Cl)₃](C₉H₈NO(H₂O)₂) kompleks kristalidagi molekulararo ta'sirlashish energiyasi Mercury dasturi yordamida hisoblandi.



3-rasm. [Cu(2,6-PDCA)(Cl)₃](C₉H₈NO(H₂O)₂) kompleks birikma kristalidagi molekulararo ta'sirlashish energiyasi, kJ/mol

Kompleks kristalidagi 4.01 Å, 2.73 Å, 6.30 Å, 5.96 Å, 6.37 Å, 6.73 Å masofalarda joylashgan molekulararo ta'sirlashish energiyalari mos ravishda -39.9 kJ/mol, -17.2 kJ/mol, -16.8 kJ/mol, -14.5 kJ/mol, -12.5 kJ/mol, -11.4 kJ/molni va umumiy ta'sirlashish energiyasi esa -183.8 kJ/molni taskil etdi (3-rasm).

Xulosa: Sintez qilingan kompleksning tarkibi va tuzilishi RTT yordamida aniqlandi. Kompleks birikmaning kristallografik ma'lumotlari Kembridj kristallografik ma'lumotlar bazasiga (Cambridge Crystallographic Data Center) ga kiritildi (CCDC2307012). <https://www.ccdc.cam.ac.uk/structures/Search?Ccdc=2307012 &Author=nazarov&Access=referee>. Kompleks tetragonal siqilgan oktaedrik tuzilishli bo' lib, Yan Teller effekti kuzatildi. IQ-spektri tahliliga ko' ra 3358.07 cm⁻¹ sohasida OH- guruhiga xos intensivligi juda yuqori bo' lgan valent tebranish, 1552.70 cm⁻¹ sohasida xinolin halqasining halqa tebranishi kuzatilgan. Kompleks birikmaning umumiy ta'sirlashish energiyasi esa -183.8 kJ/molni taskil etdi.

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