

Ni (II) NING 2,6-PIRIDINDIKARBON KISLOTASI VA MEA BILAN KOMPLEKS BIRIKMASI SINTEZI VA HIRSHFELD SIRTI TAHLILI

¹ Nazarov Y. E., ²Turayev X.X., ³Rahmonberdiyeva S. B.

¹Termiz davlat universiteti k.f.f.d.

²Termiz davlat universiteti k.f.f.d., prof.

³Termiz davlat universiteti talabasi

E-mail; nazarovy714@gmail.com

Annotatsiya. 2,6-piridindikarbon kislotasining metall ionlari bilan ta'sirlashishi va uning metallokompleks birikmalarining xossalarini tadqiq qilish maqsadida, Nikel(II) atsetat va MEA bilan M:L:L 1:2:2 nisbatdagi kompleks birikmasi sintez qilindi. Sintez qilingan kompleksning tarkibi va tuzilishi RTT yordamida aniqlandi. Molekulalararo o'zaro ta'sirlar xarakterini tavsiflash uchun Hirshfeld sirtini Crystal Explorer17.5 dasturi yordamida tahlil qilindi. Kompleksning UB spektroskopiyasi tahlili o'tkazildi.

Kalit so'zlar. 2,6-piridindikarbon kislotasi (2,6-PDCA, dipic), nikel(II) atsetat, MEA.

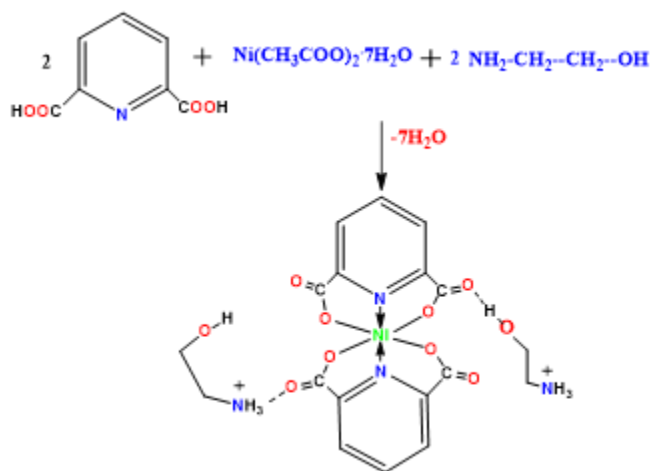
Kirish. 2,6-piridindikarbon kislotasi (2,6-PDCA, dipic) bir yoki bir nechta karboksilat kislorod atomlari orqali barqaror komplekslar hosil qiluvchi ko'p qirrali N, O-xelatlovchi, bidentat va tridentat xelatlovchi liganddir [1-4]. Qiziqishning sababi shundaki, ligand H₂pda va markaziy piridin halqasi 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].

So'nggi paytlarda monoetanolaminlar va oddiy bir o'rnini bosuvchi benzoy kislotalar asosidagi aralash ligandlardan tayyorlangan oltita muvofiqlashtirilgan mono- va ikki yadroli mis komplekslari, xususan, monoetanolamin (MEA) va p-nitroben kislotasi (p-nitrobenzo) va yuqori darajadagi mualliflar tomonidan nashr etilgan [Cu²⁺(MEA)₂] va [2Cu²⁺(MEA)₂(H₂O)₂]. Yann-Teller effekti tufayli buzilgan oktaedrik tuzilishli komplekslar . Bitta [Ni(dipic)₂](mea)₂ tarkibli yangi kompleks birikmaning monokristali piridin-2,6-dikarboksilik kislota (PDC yoki dipic) bilan (MEA) aralashgan holatda o'stirildi [6,7].

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[8-10].

Ushbu tadqiqot ishida biz bitta yangi kompleks haqida xabar berdik, $[\text{Ni}(\text{dipic})_2](\text{mea})_2$ (1-rasm) Piridin-2,6-dikarrik kislotasi (mono) (MEA) yordamchi ligandlar sifatida ishlatilgan.

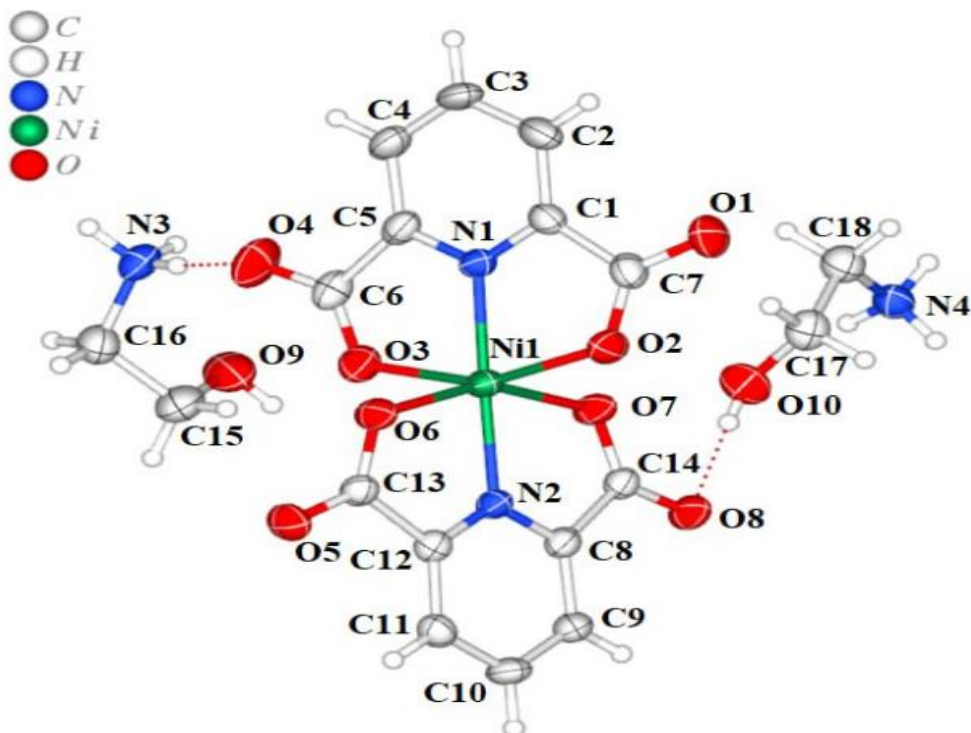
$[\text{Ni}(\text{dipic})_2](\text{mea})_2$ kompleksi sintezi. Nikel(II)atsetat kristallogidra tidan $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 7\text{H}_2\text{O}$ 0.1525 gr (0.5 mmol), 0.167 gr (1 mmol) 2,6 -PDCA ni tegishlicha suvda eritib, 1;2 mol nisbatdagi eritmaları tayyorlandi. Eritmalar aralashirildi. Aralash ligandli kompleks birikma olish maqsadida monoetanolamin (MEA) ning eritmasidan tomizildi. So'ngra magnitli aralashirgich yordamida 60°C da 30 minut davomida intensiv aralashirildi. Eritma xona haroratida qoldirildi. Natijada 10 kundan so'ng idish tubida och yashil rangli kompleks birikma monokristali o'sganligi kuzatildi. RTT analizi uchun yaroqli kristallar ajratilib, tekshirilganda $[\text{Ni}(\text{dipic})_2](\text{mea})_2$ tarkibli ekanligi aniqlandi. Unumi 86 % $[\text{Ni}(\text{dipic})_2](\text{mea})_2$ ($M_r=434.208\text{g/mol}$) $\text{C}_{16}\text{H}_{26}\text{N}_4\text{O}_{10}$ tahlili nazariy jihatdan: C 44.21, H 6.03, N 12.89, O 36.84 % ni ko'rsatdi: ma'lum bo'ldiki C 44.06, H 5.86, N 12.67, O 36.69 %. Reaksiya tenglamasi quyidagicha (1-sxema).



1-sxema. $[\text{Ni}(\text{dipic})_2](\text{mea})_2$ kompleks birikma sintezi.

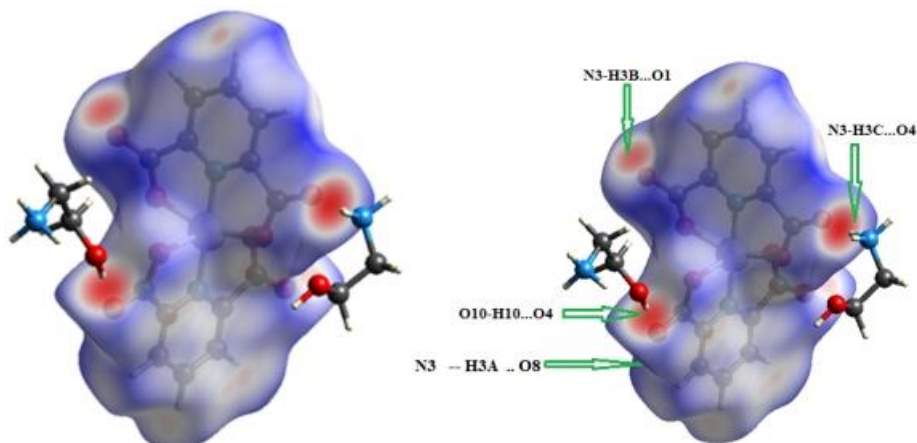
Tahlil natijalari.

Kompleksda ikkita azot va to'rtta kislorod atomi Ni atomlari bilan muvofiqlashtiriladi va hosil bo'lgan struktura bog'lanish uzunligi va bog'lanish burchagi qiymatlari asosida tasdiqlanadi. Ikki tridentat dipic ligandlarning har biri karboksilik guruhning ikkita kislorod atomi va dipic dianion ligandlarining piridin halqasining azot atomlari va monoetanolamin kationlari (MEA) orqali koordinatalanadigan qarama-qarshi ionlardir. Kompleksda ikkita azot va to'rtta kislorod atomi Ni atomlari bilan muvofiqlashtiriladi va hosil bo'lgan struktura bog'lanish uzunligi va bog'lanish burchagi qiymatlari asosida tasdiqlanadi.



1-rasm. [Ni(dipic)₂](mea)₂ kompleksining molekulyar tuzilishi

Ikki tridentat dipik ligandlarning har biri karboksilik guruhning ikkita kislorod atomi va dipik dianion ligandlarining piridil halqasining azot atomlari va monoetanolamin kationlari (MEA) orqali koordinatsiyalanadigan qarama-qarshi ionlardir. Oxir-oqibat, mualliflar tomonidan buzilgan oktaedral kompleks struktura taklif qilindi. [Ni(dipic)₂]²⁻ divalent anion 2[NH₃CH₂CH₂OH]⁺ ikki valentli kation bilan muvozanatlangan zaryaddir. Har bir dipiv ligandning karboksilik guruhining O atomi bilan vodorod aloqalari orqali bog'langan muvofiqlashtirilmagan ikkita monoetanolamin (MEA) molekulari. 1-rasmda ko'rsatilganidek, Ni(II) atrofidagi koordinatsiya geometriyasi buzilgan oktaedr bo'lib, har bir ikki valentli anion dipik ligand ekvatorial o'rinlarni ikkita kislorod atomi (Ni(1)– O(3) = 2,133(3) Å) va (Ni(1)– O(3) = 2,133(3) Å) va (Ni(1) (Ni(2) Å²) (Ni(2) = 1) egallaydi. Boshqa ekvatorial pozitsiyalarni boshqa dipic liganddan ikkita kislorod atomi (Ni(1)– O(7) = 2,136(3) Å va (Ni(1)–O(6) = 2,149(2) Å) egallaydi.



2-rasm. [Ni(dipic)₂](mea)₂ ning uch o‘lchamli Hirshfeld sirtining dnorm bo‘yicha xaritasi ko‘rinishi.

de va di funksiyalari yordamida olingan ikki o‘lchovli barmoq izining grafiklari ko‘rsatilgan bo‘lib, [Ni(dipic)₂](mea)₂ kompleksining Hirshfeld yuzalarida kristall o‘rash hosil bo‘lishiga individual o‘zaro ta’sirlarning hissasi ko‘rsatilgan. Shunday qilib, Hirshfeld yuzasini tahlil qilish natijasida quyidagi o‘zaro ta’sirlar aniqlandi: O... H/H... O (50,9%), H... H (18,7%), H... C/C... H (10,9%), C... C (9,1%), O... C/C... O (5,8%), H... N/N... H (2,6%), N... N/N... H (2,6%), N... C/C, N... C/C. O..Yo‘q/Yo‘q..O 0,4%. Chuqur qizil dog‘lar qo‘shni turlar bilan kuchli yaqin o‘zaro ta’sirni ko‘rsatadi. Kompleks birikmaning molekulasi uchun uchastkaning o‘rtasida qisqa va tor tikanlar bo‘lgan keng hudud umumiy Xirshfeld sirtlarining O-H/H-O o‘zaro ta’siri sifatida aks ettiriladi va bu kompleks-1 uchun hisoblangan eng yuqori foizdir va bu dipik lagandning metall kompleksi bilan solishtirish mumkin. Ni (II) kompleksining dnormasi uchun Hirshfeld yuzasi xaritasi (2-rasm) ko‘rinib turibdiki, o‘tkir qizil rang monoetanolamin (MEA) ning vodorod aloqasi va dipic ligandning karboksilik guruhining kislorodli aloqasi o‘rtasida molekulalararo vodorod bog‘lanish kuzatilganligini ko‘rsatadi.

Xulosa: Tadqiqotlar natijasida 2,6-piridindikarbon kislotasining Nikel(II) atsetat va MEA bilan M:L:L 1:2:2 nisbatdagi kompleks birikmasi sintez qilindi. 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 (CCDC 2256725).<https://www.ccdc.cam.ac.uk/structures/Search?Ccdc=2403742&Author=nazarov&Access=referee>. Kompleksning molekulalararo o‘zaro ta’sirlari xarakterini tavsiflash uchun Hirshfeld sirti tahlili o‘tkazildi. Ushbu tahlil natijasiga ko‘ra o‘zaro ta’sirlarning asosiy qismini O... H/H... O (50,9%), H... H (18,7%) tashkil qildi.

Foydalanilgan adabiyotlar ro‘yxati.

1. Mirzaei M. et al. On the importance of non-covalent interactions in the structure of coordination Cu (II) and Co (II) complexes of pyrazine-and pyridine-dicarboxylic acid derivatives: experimental and theoretical views //CrystEngComm. – 2014. – T. 16. – No. 27. – pp. 6149-6158.
2. Das B., Baruah J. B. Water clusters in mixed ionic complexes with metal dipicolinate anions //Journal of molecular structure. – 2013. – T. 1034. – C. 144-151.
3. Hadadzadeh H. et al. Pyridine-2, 6-dicarboxylic acid (Dipic): crystal structure from co-crystal to a mixed ligand nickel (II) complex //Journal of Chemical Crystallography. – 2010. – T. 40. – C. 48-57.
4. Ilkimen H. et al. Synthesis and characterization of a novel proton salt of 2-amino-6-nitrobenzothiazole with 2, 6-pyridinedicarboxylic acid and its metal complexes and their antimicrobial and antifungal activity studies // Journal of Molecular Structure. – 2016. – T. 1120. – P. 25-33.
5. Ghasemi K. et al. Potential antidiabetic drug involving a zinc anionic complex of dipic and metformin as counter ions: Synthesis, characterization, crystal structure and electrochemical studies //Journal of Molecular Structure. – 2014. – T. 1074. – C. 79-84.
6. Khayit Kh. Turaev, Yusufjon E. Nazarov, Abdukadir Kh. Tashkulov, Sherzod A. Kasimov, Bekmurod Kh. Alimnazarov, Jamshid M. Ashurov, Aziz B. Ibragimov, Takashiro Akitsu, Changkun Xia, Abul Monsur Showkot Hossain. Synthesis of mononuclear Ni (II) and binuclear Cu (II) complexes from pyridine-2, crystal structure and Hirshfeld surface analysis, 6-dicarboxylic acid with monotholenamine and hydrochloric acid solution //Structural Chemistry. – 2025. – C. 1-13 <https://link.springer.com/article/10.1007/s11224-025-02468-9>
7. Ghosh S. K., Ribas J., Bharadwaj P. K. Metal-organic framework structures of Cu (II) with pyridine-2, 6-dicarboxylate and different spacers: identification of a metal bound acyclic water tetramer //CrystEngComm. – 2004. – T. 6. – No. 45. – C. 250-256.
8. Ghosh S. K., Ribas J., Bharadwaj P. K. Characterization of 3-D Metal– Organic Frameworks Formed through Hydrogen Bonding Interactions of 2-D Networks with Rectangular Voids by CoII-and NiII-Pyridine-2, 6-dicarboxylate and 4, 4 ‘-Bipyridine or 1, 2-Di (pyridyl) ethylene //Crystal growth & design. – 2005. – T. 5. – No. 2. – C. 623-629.
9. Chihaoui N. et al. A new mononuclear complex: structure, vibrational (FT-IR and Raman), Hirshfeld surfaces analysis, electrical properties and equivalent circuit //J Phys Chem Biophys. – 2016. – T. 6. – No. 216. – C. 2161-0398.10002.

10. Nazarov Y.E., Turaev Kh.Kh., Suyunov J.R., Ibragimov B.T., Alimnazarov B.Kh., Ashurov J.M. 8-Hydroxyquinolinium trichlorido(pyridine-2,6-dicarboxylic acid- κ^3O,N,O')copper(II) dihydrate Acta Crystallographica Section E: Crystallographic Communications, 2024, 80(10), c 1049–1053
<https://doi.org/10.1107/S2056989024009186>