

Ni (II) IONI VA 1,10-FENONTROLIN BILAN ARALASH LIGANDLI KOMPLEKS SINTEZI VA TADQIQOTI

**¹Toshtemirov Abdurasul Erkin o'g'li, ²To'rayev Xayit
Xudaynazarovich, ³Umbarov Ibragim Amonovich, ⁴Ashurov Jamshid
Mengnorovich, ,
⁵DJalilov Abdulaxat Turapovich**

¹Termiz davlat universiteti doktoranti

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

³Termiz davlat universiteti t.f.d., prof.

⁴O'zRFA O.S. Sodiqov nomidagi Bioorganik kimyo instituti, k.f.d., prof.

⁵O'zRFA akademigi, Toshkent kimyo-texnologiya ilmiy tadqiqot instituti
k.f.d., prof.

E-mail: tosabdurasul20@gmail.com

Annotatsiya

Bu ishda birinchi marta kompleks birikma $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ (Triaqua-chlorido-(1,10-phenanthroline-k₂N,N')-nikel (II) chloride monohydrate) sintez qilindi. Hosil bo'lgan kompleks birikmaning tarkibi va kristall tuzilishi rentgen nurlari difraksion analizi (XRD) yordamida o'rganildi. Hirshfeld sirt tahlili hisoblandi va kristall taxlanishida H...H 40,5%, Cl...H/H...Cl 28,6%, H...C/C...H 10,5%, O...H/H...O 9,4%, C..C 9% tasirlar asosiy hissaga to'g'ri kelishi aniqlandi.

Kalit so'zlar: 1,10-fenontrolin, xlorid kislota, kristall struktura, kompleks, Hirshfeld yuzasi.

ИЗУЧЕНИЕ СИНТЕЗА КОМПЛЕКСА СО СМЕШАННЫМ ЛИГАНДОМ С ИОНОМ Ni(II) И 1,10-ФЕНАНТРОЛИНОМ И ЕГО ИССЛЕДОВАНИЕ

**¹Тоштемиров Абдурасул, ²Тураев Хайит Худайназарович, Умбаров
Ибрагим Амонович, ⁴Ашуров Жамшид Менгнорович, ⁵Джалилов
Абдулахат Турапович**

¹ Термезский государственный университет докторант

² Термезский государственный университет д.х.н., проф.

³ Термезский государственный университет д.т.н., проф.

⁴ УзРФА Институт биоорганической химии имени О.С.Содикув д.х.н., проф.

⁵ Академик АН РУз., директор Ташкентского научно-исследовательского института химической технологии д.х.н., проф.

E-mail: tosabdurasul20@gmail.com

Аннотация: В данной работе проведено исследование впервые синтезированного комплекса на основе $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ (Триаква-хлоридо-(1,10-фенантролин- $k_2\text{N},\text{N}'$)-никель (II) хлорид моногидрат). Состав и кристаллическую структуру полученного комплекса изучали методом рентгеноструктурного анализа (РСА). Проведен поверхностный анализ Хиршфельда и установлено, что основной вклад в кристалл: Н...Н 40,5%, Cl...H/H...Cl 28,6%, Н...C/C...H 10,5%, О...H/H... О 9,4%, С..С 9% контактов.

Ключевые слова: 1,10-фенантролин, соляная кислота, кристаллическая структура, комплекс, поверхность Хиршфельда.

STUDYING OF SYNTHESIS OF COMPLEX WITH MIXED LIGAND WITH Ni (II) ION AND 1,10-PHENANTHROLINE AND ITS RESEARCH

¹Toshtemirov Abdurasul ²Hayit Turaev ³Umbarov Ibragim ⁴Jamshid
Ashurov ⁵Abdulahat Jalilov

¹Termez State University doctoral student

²Termez State University Doctor of Chemical Sciences, professor

³Termez State University, Doctor of Technical Sciences, Professor

⁴Institute of Bioorganic Chemistry, Academy of Sciences of Uzbekistan
Doctor of Chemical Sciences, professor

⁵Tashkent Chemical Technology Research Institute, Doctor of chemical sciences, prof., academician of the Academy of Sciences of the Republic of Uzbekistan

Abstract: In this paper, the study of the first-time syntheses complex based on $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ (tri aqua-chloride-(1,10-phenanthroline-k2N, N')-nickel (II) chloride monohydrate). The composition and crystal structure of the resulting complex were studied using X-ray diffraction analysis (XRD). The Hirshfeld surface analysis was performed, and it was found that the main contribution to crystal: H...H 40.5%, Cl...H/H...Cl 28.6%, H...C/C...H 10.5%, O...H/H...O 9.4%, C...C 9% contacts.

Keywords: 1,10-phenanthroline, hydrochloric acid, crystal structure, complex, Hirshfeld surface.

Kirish. Aralash ligandli metall komplekslari o'ziga xos fizik-kimyoviy xossalari tufayli keng qo'llaniladi [1]. Nikelning 1,10-fenantrolin va uning hosilalari bilan kompleks birikmalari ko'plab sintez qilingan. Masalan: E. Freire, S. Baggio, R. Baggio, L.lar tomonidan triaqua(1,10-phenanthroline-N,N') (thiosulfato-S)nickel(H) monohydrate komplekslari sintez qilingan hamda fizik kimyoviy xossalari o'rganilgan [2]. 3 d metallar komplekslarining antibakterial va zamburug'larga biologik faolliklarini o'rganilgan. Xususan nikel va 1,10-fenantrolin kompleks birikmalarining biologik faolliklarini Viganor L. va boshqalar tomonidan organilgan [3].

1,10-fenantrolin (phen) - trisiklik, aromatik, N - geterosiklik organik birikma. Koordinatsion kimyoda phen mashhur klassik bidentatli ligand bo'lib, asosan $[\text{M}(\text{phen})_3]\text{X}_2$ tipidagi komplekslardan metall galogenidlar bilan ishlov berilganda hosil bo'ladi (bu yerda M-metall va X-galogen) [4]. Misol uchun tarkibida 1,10-fenantrolin (phen) bo'lgan komplekslar analitik kimyo, magnitkimyo katalizda, muhim rol o'ynaydi [5]. 1,10-fenantrolin (phen) va uning o'rnini bosuvchi hosilalari oraliq metall ionlari bilan barqaror komplekslar hosil qiluvchi eng keng tarqalgan va ko'p ishlatiladigan metall ionlarini bog'laydigan bidentat ligandlar qatoriga kiradi. Shu sababli, koordinatsion kimyo va fenantrolin-metall ion komplekslarini qo'llash bo'yicha ko'plab tadqiqotlar olib borilgan [6]. Ma'lumki, 1,10-fenantrolin va uning hosilalari, va ularga mos keladigan metall

komplekslari zamburug' patogenlarining mitoxondrial funktsiyasini buzish, nafas olishni ajratish, o'ziga xos bo'lmagan DNK bo'linishini keltirib chiqarish, hujayra bo'linishini buzish va zamburug' hujayralari morfologiyasida qo'pol buzilishlarni keltirib chiqarish orqali ularning ko'payishini inhiye qiladi [7, 8]. 1969 yilda Dwyer va boshqalar. Dikatsion Mn(II) Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) va Ru (II) larning 1,10-fenantrolin va uning hosilalari asosidagi ligandlarni o'z ichiga olgan xelat komplekslarning *in vitro* va *in vivo* antibakterial faoliyatiga oid yuqori darajali, muhim maqolalarini nashr etdilar. [9, 10]. Natijalar shuni ko'rsatdiki, metall xelatlar "metalsiz" 1,10-fenantrolin ligandga qaraganda *M. tuberculosis*, *S. aureus*, *S. pneumonia*, *C. Perfringens*, *E. coli* va *P. Vulgaris*ga qarshi faolroq. Silga qarshi kamroq faollikka ega, antibakterial faollik ko'p jihatdan mavjud bo'lgan metall turiga bog'liq emas. G.S. Malik, S.P. Singx va J.P. Tandonlar phen va 2,2-bipiridin asosida biologik faollikka ega Zn (II), Ni (II), Cd (II) aralash ligandli komplekslarning sintez sharoitlari, barqarorliklarini o'rganishgan [11].

Tajribaviy qism.

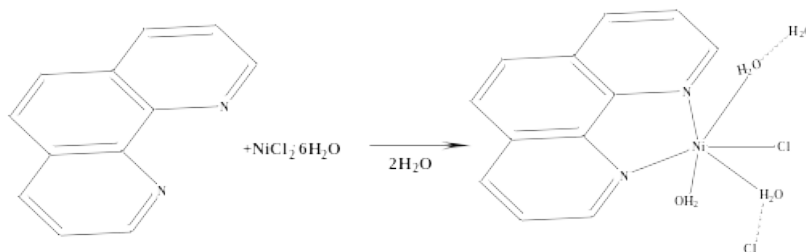
Ushbu tadqiqot ishini bajarishda ishlatiladigan moddalar va reagentlar tijorat manbalaridan («MEDXIMFARMSTROY») olingan.

Metod va materiallar. Kimyoviy moddalar, asboblari. Barcha reagentlar tijorat manbalaridan olingan va tozalashlarsiz ishlatilgan. Kristallning strukturasi aniqlash Oksford difraksion Xcalibur-R CCD difraktometrida (CuK α , - nurlanish, $\lambda=1,54184 \text{ \AA}$, ω - skanerlash rejimi, grafit monoxromatorida (293K da)) amalga oshirilgan [12].

Kompleksning vodorod bog'lanish geometriyasi, ayrim bog' uzunligi va burchaklari qiymati 1 va 2-jadvalda keltirilgan. Struktura SHELX-97 dasturiy paketi yordamida olindi [13]. Kristall tarkibidagi molekulalarning elementar yacheykada taxlanishida molekulalararo ta'sirlashuv CrystalExplorer 17.5 dasturi yordamida Hirshfeld yuzasi tahlili yordamida o'rganildi [14].

Kompleks birikma sintezi. Nikel (II) xlorid kristallogidratidan (NiCl $_2$ ·6H $_2$ O) 0.237 gr (1 mmol), va 0.18021 gr (1mmol) 1,10-fenantrolinni

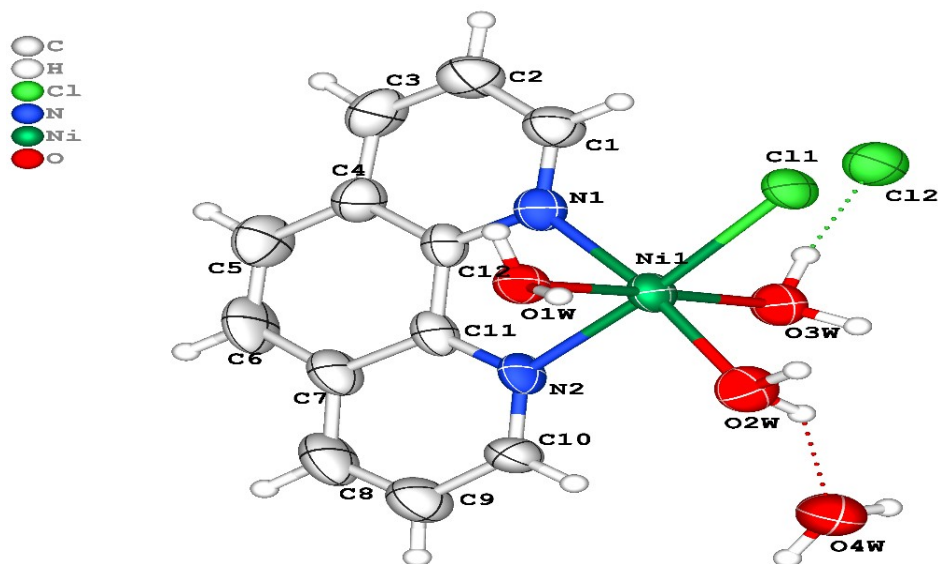
tegishli suv va etil spirtida eritib, 1:1 nisbatdagi eritmaları tayyorlandi va aralshtirildi. Hosil bo'lgan cho'kma suyultirilgan xlorid kislotaning 2 tomchisi yordamida eritildi. So'ngra magnitli aralashtirgich yordamida 60 °C da 30 minut davomida intensiv aralashtirildi. Eritma xona haroratida qoldirildi. Natijada bir necha kundan so'ng idish tubida moviy rangli kompleks birikma kristali o'sganligi kuzatildi. RTT analizi uchun yaroqli kristallar ajratilib, tekshirilganda $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ tarkibli Triaqua-chlorido-(1,10-phenanthroline-k2N,N')-nikel(II) chloride monohydrate kompleksi ekanligi aniqlandi. Reaksiya unumi 75 %. $\text{C}_{12}\text{H}_{14}\text{ClN}_2\text{NiO}_3\cdot\text{Cl}\cdot\text{H}_2\text{O}$ ($M_r=381.88$ g/mol). Elemental Analizi: C, 37.74; H, 4.22; Cl, 18.57; N, 7.34; Ni, 15.37; O, 16.76. Reaksiya tenglamasi quyidagicha.



1-rasm. $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ kompleksi sintezi reaksiyasi.

Kompleks birikma tuzilishi. Turli xil anionlarga ega bo'lgan ba'zi tetraaqua (1,10-fenantrolin) metall ionli komplekslar ko'plab olimlar tomonidan o'rganilgan. Bularga misol qilib Liu va boshq., 2006; Zhang va boshq., 1999; lar ishlarini keltirishimiz mumkin. Biz bu sohadagi tadqiqotimizda nikel komplekslarini o'rganishni davom ettirish uchun ligand sifatida 1,10-fenantrolinni tanladik. Bu yerda biz rentgen kristallografiyasi diffraktsiyasi bilan tavsiflangan yangi kompleks birikmaning tuzilishi haqida ma'lumotlar keltiramiz. Kompleks birikmada (2-rasm) Ni (II) ioni va 1,10-fenontrolin ligandining ikkita azot atomi bilan koordinatsion bog' orqali bog'langan ($\text{Ni}-\text{N}_1$ 2,064 Å va $\text{Ni}-\text{N}_2$ 2,097 Å) va yana modentatli ligand xlorid ioni ($\text{Ni}-\text{Cl}_1$ 2,43 Å) hamda uchta suv molekulalari bilan monodentat holatda bog'langan. Kompleks oktedrik tuzilishli sp^3d^2 gibridlangan. Molekulalararo O—H...Cl va O—H...O vodorod bog'lari (1-jadval) kristall o'ramini birlashtiruvchi keng uch o'lchamli vodorod bog'lanish tarmog'ini hosil qiladi.

Kompleks birikma singoniyasi monoklinik bo'lib, kristall yacheyka parametrlari; fazoviy guruhi P 21/n, $a=7.5904(4)\text{\AA}$, $b=12.3624(8)\text{\AA}$, $c=16.8716(14)\text{\AA}$, $\alpha=90$, $\beta=102.005(6)$, $\gamma=90$ V= $1548.53(19)\text{\AA}^3$, Z=4, T=293 K.



2-rasm. $[\text{NiC}_{12}\text{H}_8\text{N}_2\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ kompleksining molekulyar tuzulishi.

Punktr chiziqlar vodorod bog'lanishni ifodalaydi.

Vodorod bog'lanish

1-jadval

D-H... Å	D-H, Å	H...A, Å	D...A, Å	D-H...A, ($^\circ$)
O1W--H1WA .. Cl2	0.9000	2.2400	3.120(7)	169.00
O1W--H1WB .. Cl1	0.9000	2.2700	3.145(6)	164.00
O3W--H3WA .. Cl1	0.9100	2.2500	3.144(6)	165.00
O3W--H3WB .. Cl2	0.9200	2.2600	3.132(7)	159.00
O2W--H2WA .. Cl2	0.8700	2.5100	3.272(7)	146.00
O2W--H2WB .. O4W	0.8700	1.9400	2.686(11)	143.00
O4W--H4WA .. Cl2	0.8500	2.3300	3.179(9)	175.00
O4W--H4WB .. Cl1	0.8500	2.7400	3.309(9)	125.00
C1--H1 .. Cl1	0.9300	2.8000	3.399(9)	123.00

Simmetriya kodlari.(I) $1+x,y,z$ (II) $2-x,-y,1-z$ (III) $1-x,-y,1-z$ (IV)

$1/2+x,1/2-y,1/2+z$ (V) $1-x,-y,1-z$.

[NiC₁₂H₈N₂Cl(H₂O)₃]Cl•H₂O kompleksining ayrim bog‘ uzunligi va burchaklari.

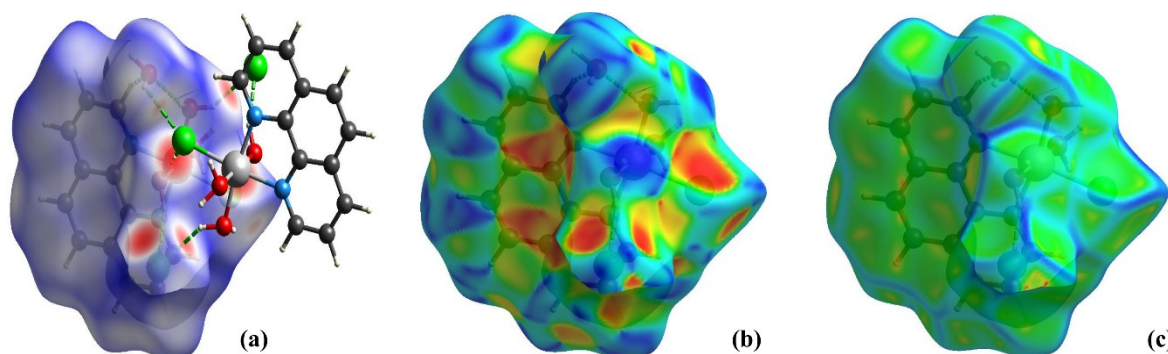
2-jadval.

Bog‘ burchagi	(°)	Bog‘ uzunligi	(Å)
Cl1 -Ni1-O1W	90.09(17)	Ni1 -Cl1	2.432(2)
Cl1-Ni1-O2W	92.73(18)	Ni1 -O1W	2.065(6)
Cl1 -Ni1-O3W	91.64(19)	Ni1 -O2W	2.085(7)
Cl1 -Ni1 -N1	95.20(19)	Ni1 -O3W	2.058(6)
Cl1 -Ni1 -N2	175.1(2)	Ni1 -N1	2.064(7)
O1W-Ni1-O2W	89.7(2)	Ni1 -N2	2.097(6)
O1W-Ni1-O3W	178.2(3)	N1 -C1	1.344(11)
O1W-Ni1-N1	89.9(2)	N1 -C12	1.359(10)
O1W -Ni1 -N2	88.9(2)	O1W -H1WB	0.9000
O2W -Ni1 -O3W	89.7(3)	O1W -H1WA	0.9000
O2W -Ni1 -N1	172.1(3)	N2 -C10	1.323(11)
O2W -Ni1 -N2	92.1(3)	N2 -C11	1.346(10)
O3W -Ni1 -N1	90.6(3)	O2W -H2WA	0.8700
O3W -Ni1 -N2	89.4(2)	O2W -H2WB	0.8700

[NiC₁₂H₈N₂Cl(H₂O)₃]Cl•H₂O ning kristall tuzilishi va Hirshfeld yuzasi tahlili

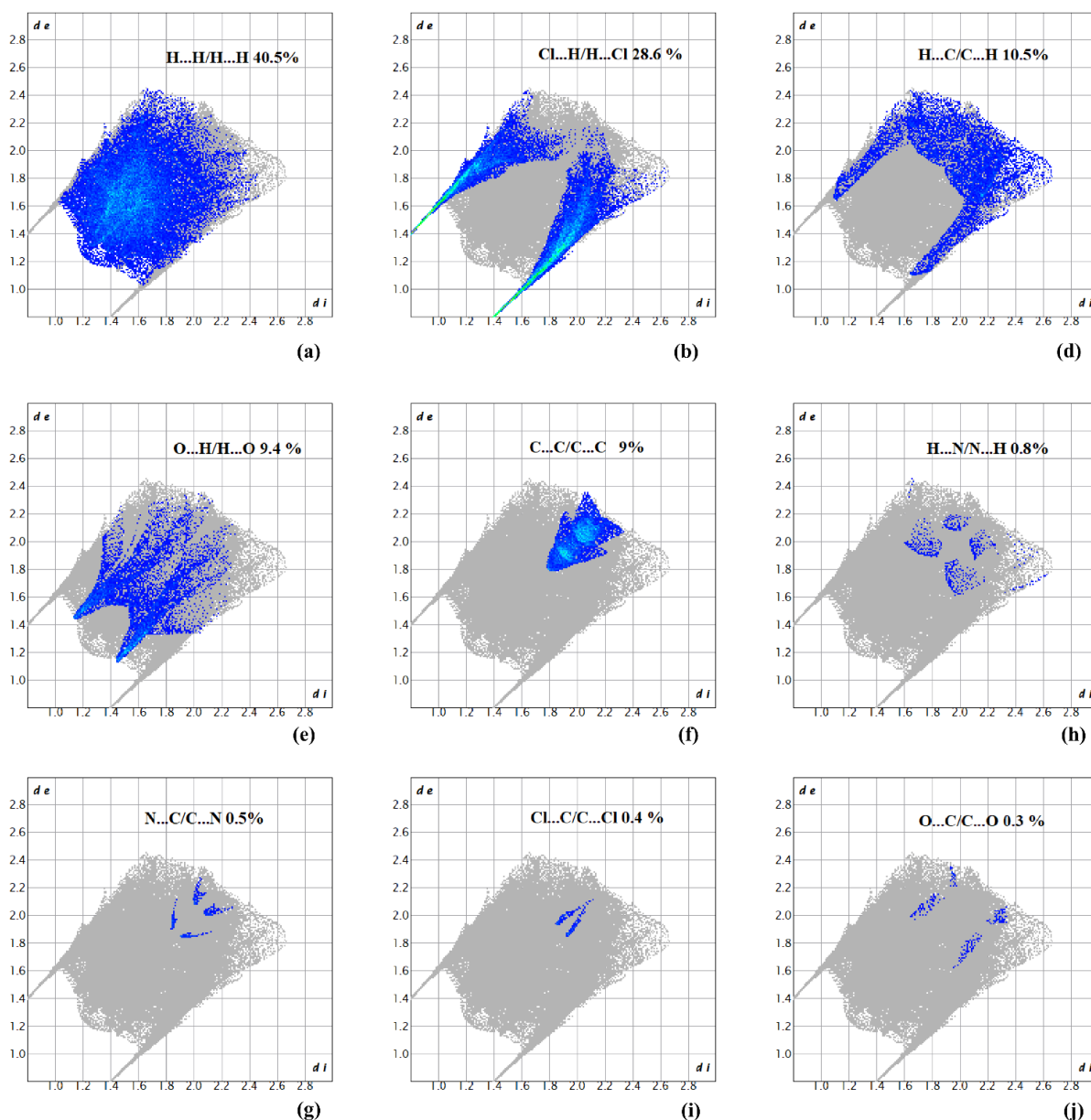
Kristall tarkibidagi molekularning elementar yacheykada taxlanishida molekulararo ta’sirlashuv CrystalExplorer 17.5 dasturi yordamida Hirshfeld yuzasi tahlili yordamida o’rganildi. Bunda alohida ta’sirlashuv turlari ikki o’lchamli barmoq izlari yordamida tahlil qilindi yoki ularning umumiy ta’sirlashuvga qo’shgan hissalarini aniqlandi. d_{norm} maydoni tashqi d_e va ichki d_i masofalarni eng yaqin yadrogacha hisoblash yo’li bilan aniqlandi, hajmi 380,09 Å³ da va yuzasi 332,18 Å² hamda o’lchamlari -0,5016 (qizil) 1,0776 gacha (ko’k) maydonda ko’rildi (3.a-rasm). Shakl-indeks va egri chiziqlar jadvallari mos

ravishda -1,0000 dan 1,0000 a.b. va -4,0000 dan 0,4000 a.b. gacha hosil qilindi (3.b-c-rasm).



3-rasm. (a) Hirshfeld yuzasi d_{norm} ustida qisqa tutashgan joylarni yashil chiziqli chiziqlar sifatida ko'rsatgan, (b) shakl ko'rsatkichlari maydoni va (c) o'zaro ta'sir hududlarini ko'rsatadigan egri chiziq maydoni

Hirshfeld yuzasidagi o'rta to'q va yon tomoni och qizil rangdagi dog'lar (3(a)-rasm). Barcha bog'lar uchun ikki o'lchovli barmoq izlari maydoni 4.a-rasmدا tasvirlangan. H...H (40,5%) ta'sirlari Hirshfeld yuzasiga eng katta hissa qo'shganligini kuzatish mumkin. Ushbu ta'sirlar, shuningdek, atomlar orasidagi masofa sifatida kristallning taxlanishiga katta hissa qo'shadi.



4-rasm. Kompleks kristallida o‘zaro ta’sirlashuvlarni ifodalovchi ikki o‘lchovli barmoq izlari maydoni

Ularning ta’sir masofalari esa Van der Vaals radiusidan bir oz kamroq. Cl...H/H...Cl o‘zaro ta’sirining atomlararo ta’sirlari Hirshfeld sirtining 28,6% ini hosil qiladi (4.b-rasm). H...C/C...H o‘zaro ta’siri atomlararo umumiy ta’sirning 10,5% ni tashkil qiladi (4.d-rasm). 4.e-rasmdagi ichki ikkita qanot O...H/H...O ta’sirlariga tegishli bo‘lib, ular umumiy sirtning 9,4% ini tashkil qiladi. C...C ta’sirlarining nisbati Hirshfeld sirtining 9% va H...N/N...H aloqalarining ta’sir nisbati ham 0,8% ni tashkil etadi (4.f,g-rasm). Hirshfeld yuzasiga N...C/C...N ta’sirlar ham o‘zining 0,5% kichik hissasini qo’shadi. Boshqa ta’sirlarning

hissalari, jumladan, Cl...C/C...Cl 0,4%, O...C/C...O 0,3% bo'lib, ular Hirshfeld yuzasining juda oz ulushini tashkil qiladi.

Xulosa

Ilk bor $[C_{12}H_8N_2Cl(H_2O)_3Ni]Cl \cdot H_2O$ tarkibli kompleks birikma sintez qilindi va uning molekulyar va kristall tuzilishi rentgen nurlari difraksiyasi usuli bilan kristall yacheyka parametrlari; fazoviy guruhi $P\ 21/n$, $a=7.5904(4)\text{\AA}$, $b=12.3624(8)\text{\AA}$, $c=16.8716(14)\text{\AA}$, $\alpha=90$, $\beta=102.005(6)$, $\gamma=90$ $V=1548.53(19)\text{\AA}^3$, $Z=4$, $T=293\text{ K}$ aniqlanadi.

Kompleksning Hirshfeld sirt tahlilida o'zaro ta'sirlarning asosiy qismini $H...H$ 40,5%, $Cl...H/H...Cl$ 28,6%, $H...C/C...H$ 10,5%, $O...H/H...O$ 9,4%, tashkil qilishi hamda hajmi $380,09\text{\AA}^3$ da va yuzasi $332,18\text{\AA}^2$ ekanligi aniqlandi.

Foydalanilgan adabiyotlar

1. Zhou S. B. et al. A series of new mixed-ligand complexes based on 3, 6-bis (imidazol-1-yl) pyridazine: syntheses, structures, and catalytic activities //CrystEngComm. – 2017. – T. 19. – №. 23. – C. 3124-3137. <https://doi.org/10.1039/C7CE00394C>

2. Freire E. et al. Triaqua (2, 2'-bipyridyl-N, N')(thiosulfato-S) nickel (II) dihydrate and triaqua (1, 10-phenanthroline-N, N')(thiosulfato-S) nickel (II) monohydrate //Acta Crystallographica Section C: Crystal Structure Communications. – 1999. – T. 55. – №. 11. – C. 1780-1784.

3. Viganor L. et al. The antibacterial activity of metal complexes containing 1, 10-phenanthroline: potential as alternative therapeutics in the era of antibiotic resistance //Current topics in medicinal chemistry. – 2017. – T. 17. – №. 11. – C. 1280-1302

4. Alramadhan S. A. et al. Structures, characterization and DFT studies of four novel nickel phenanthroline complexes //Crystals. – 2023. – T. 13. – №. 5. – C. 738. <https://www.mdpi.com/2073-4352/13/5/738>

5. Golovnev N. N. et al. Two novel mixed-ligand Ni (II) and Co (II) complexes with 1, 10-phenanthroline: Synthesis, structural characterization, and

thermal stability //Chemical Physics Letters. – 2018. – T. 708. – C. 11-16.
<https://doi.org/10.1016/j.cplett.2018.07.058>

6. Bencini A., Lippolis V. 1, 10-Phenanthroline: A versatile building block for the construction of ligands for various purposes //Coordination Chemistry Reviews. – 2010. – T. 254. – №. 17-18. – C. 2096-2180.
<https://doi.org/10.1016/j.ccr.2010.04.008>

7. McCann, M.; Geraghty, M.; Devereux, M.; O'Shea, D.; Mason, J.; O'Sullivan, L. Insights into the mode of action of the anti-Candida activity of 1,10-phenanthroline and its metal chelates. *Met. Based Drugs.*, 2000, 7, 185-193.

8. Coyle, B.; Kavanagh, K.; McCann, M.; Devereux, M.; Geraghty, M. Mode of anti-fungal activity of 1,10-phenanthroline and its Cu(II), Mn(II) and Ag(I) complexes. *Biometals.*, 2003, 16, 321-329.

9. Dwyer, F.P.; Reid, I.K.; Shulman, A.; Laycock, G.M.; Dixon, S. The biological actions of 1,10-phenanthroline and 2,2'-bipyridine hydrochlorides, quaternary salts and metal chelates and related compounds. 1. Bacteriostatic action on selected gram-positive, gram-negative and acid-fast bacteria. *Aust. J. Exp. Biol. Med. Sci.*, 1969, 47, 203-218.

10. Kilah, N.H; Meggers, E. Sixty Years Young: the diverse biological activities of metal 1240 polypyridyl complexes pioneered by Francis P. Dwyer. *Aust. J. Chem.*, 2012, 65, 1325-1332..

11. Malik G. S., Singh S. P., Tandon J. P. Studies on the Mixed Ligand Complexes Involving Ligands of Biological Importance (Ni (II)/Zn (II)/Cd (II)-1, 10-phenanthroline-2, 2'-bipyridyl-phenylalanine) //Zeitschrift für Naturforschung B. – 1977. – T. 32. – №. 4. – C. 426-429. <https://doi.org/10.1515/znb-1977-0415>

12. Xcalibur. Oxford Diffraction Ltd. CrysAlisPro. Version.1.171.33.44, 2009.

13. G. M. Sheldrick, "SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement,"University of Gottingen, Gottingen, 1997.

14. 68. J.J. McKinnon, D. Jayatilaka, M.A. Spackman. Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces//Chemical Communications. – 2007. – №. 37. – P. 3814-3816.