

Mn(II) IONINING 2,6-PIRIDINDIKARBON KISLOTASI

BILAN ARALASH LIGANDLI KOMPLEKS
BIRIKMASI SINTEZI VA TADQIQI

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Annotatsiya.

Ushbu maqolada 2,6-piridindikarbon kislotasi (2,6-PDCA)ning metall ionlari bilan ta'sirlashishi va uning metallokompleks birikmalarining xossalari tadqiq qilish maqsadida, marganes(II) atsetat va xlorid kislotasi bilan M:L:L 1:1:1 nisbatdagi koordinatsion soni yettiga teng bo'lgan, polimer tuzilishli aralash ligandli yangi kompleks birikmasi olinib, uning monokristali o'stirildi. Uning tarkibi va tuzilishi RTT yordamida aniqlandi. Kompleks birikmada 2,6-piridindikarbon kislotasi ligandi tridentant holatda koordinatsiyalangan. Hirshfeld sirtini Crystal Explorer17.5 dasturi yordamida tahlil qilindi.

Kalit so'zlar.

RTT, 2,6-piridindikarbon kislotasi (2,6-PDCA, dipic), marganes(II) atsetat, xlorid kislotasi,

Abstract.

To study the interaction of 2,6-pyridinedicarboxylic acid (2,6-PDCA) with metal ions and the properties of its metal complex compounds, a new complex compound with a mixed ligand of polymeric structure with a coordination number of seven in the ratio M:L:L = 1:1:1 with manganese(II) acetate and hydrochloric acid was obtained, and its single crystal was grown. The composition and structure were determined by X-ray. In the complex compound, the ligand of 2,6-pyridinedicarboxylic acid is coordinated in the tridentate state. The Hirshfeld surface was analyzed using Crystal Explorer17.5 software.

Key words:

X-ray, 2,6-pyridinedicarboxylic acid (2,6-PDCA, dipic), manganese(II) acetate, hydrochloric acid

Аннотация.

Для изучения взаимодействия 2,6-пиридиндикарбоновой кислоты (2,6-PDCA) с ионами металлов и свойств её металлокомплексных соединений получено новое комплексное соединение со смешанным лигандом полимерного строения с координационным числом семь в соотношении M:L:L = 1:1:1 с ацетатом марганца(II) и соляной кислотой, а также выращен его монокристалл. Состав и структура определены методом РСА. В комплексном соединении лиганд 2,6-пиридиндикарбоновой кислоты координирован в тридентатном состоянии. Поверхность Хиришфельда анализировалась с помощью программного обеспечения Crystal Explorer17.5.

Ключевые слова:

РСА, 2,6-пиридиндикарбоновая кислота (2,6-PDCA, дипик), ацетат марганца(II), соляная кислота

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-xelatlovchi¹, bidentat² va tridentat xelatlovchi liganddir^{3,4}. 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^{4,5-6}.

So'nggi paytlarda monoetanolinlar va oddiy bir o'rni bosuvchi benzoy kislotalar asosidagi aralash ligandlardan tayyorlangan oltita muvofiqlashtirilgan mono- va ikki yadroli mis komplekslari⁷, xususan, monoetanolin (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 kislotasi (PDC yoki dipic) bilan (MEA) aralashgan holatda o'stirildi⁶⁸.

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.

Tajribaviy qism.

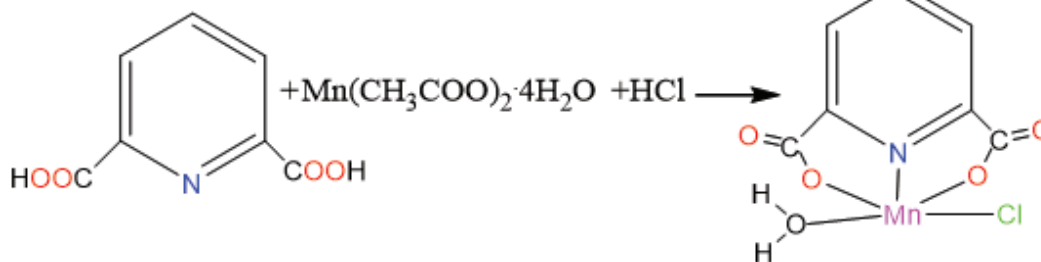
Yuqori sifatli kristallarni olish muhimligini hisobga

olib, barcha ishlatiladigan kimyoviy moddalar va reagentlar tijorat manbalaridan (Sigma-

Aldrich) olingan. Mn(CH₃COO)₂·4H₂O (98%) va 2,6 -PDCA (99%) qo'shimcha tozalashsiz ishlatilgan. Ushbu sintezda xlorid kislotasi va distillangan suv ham ishlatilgan. Marganes(II)atsetat kristallogidratidan Mn(CH₃COO)₂·4H₂O 0.245 gr (1 mmol), 0.167 gr (1 mmol) 2,6 -PDCA ni tegishli suvda hamda xlorid kislotaning suyultirilgan eritmasini 1;1;1 mol nisbatdagi eritmalar tayyorlandi. Eritmalar aralashirildi. Hosil bo'lgan cho'kmani xlorid kislotaning suyultirilgan eritmasidan tomizildi. So'ngra magnitli aralashtirgich yordamida 60 °C da 30 minut davomida intensiv aralashirildi. Eritma xona haroratida qoldirildi. Natijada 10 kundan so'ng idish tubida sariq rangli kompleks birikma kristali o'sganligi kuzatildi. RTT analizi uchun yaroqli kristallar ajratilib, tekshirilganda [Mn(2,6-PDCA)(Cl)(H₂O)]_n tarkibli ekanligi aniqlandi. Unumi 86 % {Mn(2,6-PDCA)(Cl)(H₂O)}_n (Mr=220.5 g/mol) C₇H₇NO₅Cl tahlili nazariy jihatdan: C 38.09, H 3.17, N 6.35, O 36.28 Cl 16.1 % ni ko'rsatdi: ma'lum bo'ldiki C 37.86, H 3.08, N 6.16, O 36.16, Cl 15.90 %. Reaksiya tenglamasi quyidagicha(1-sxema).

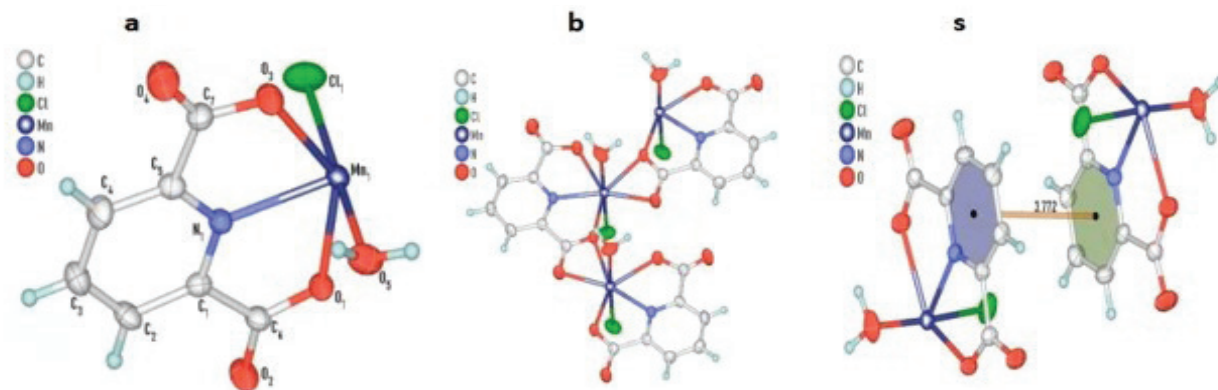
Tahlil natijalari.

Ushbu kompleks birikma {Mn(2,6-PDCA)(Cl)(H₂O)}_n ((C₇H₅ClMnNO₅)_n) tarkibli, monoclinic singoniyaga ega bo'lib, P21/c fazoviy guruhiga mansubdir.



1-sxema. {Mn(2,6-PDCA)(Cl)(H₂O)}_n kompleksi sintezi

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1-rasm. $\{Mn(2,6-PDCA)(Cl)(H_2O)_n\}_n$ kompleksining (a) molekulyar tuzilishi, (b) polimer zanjir hosil qilishi

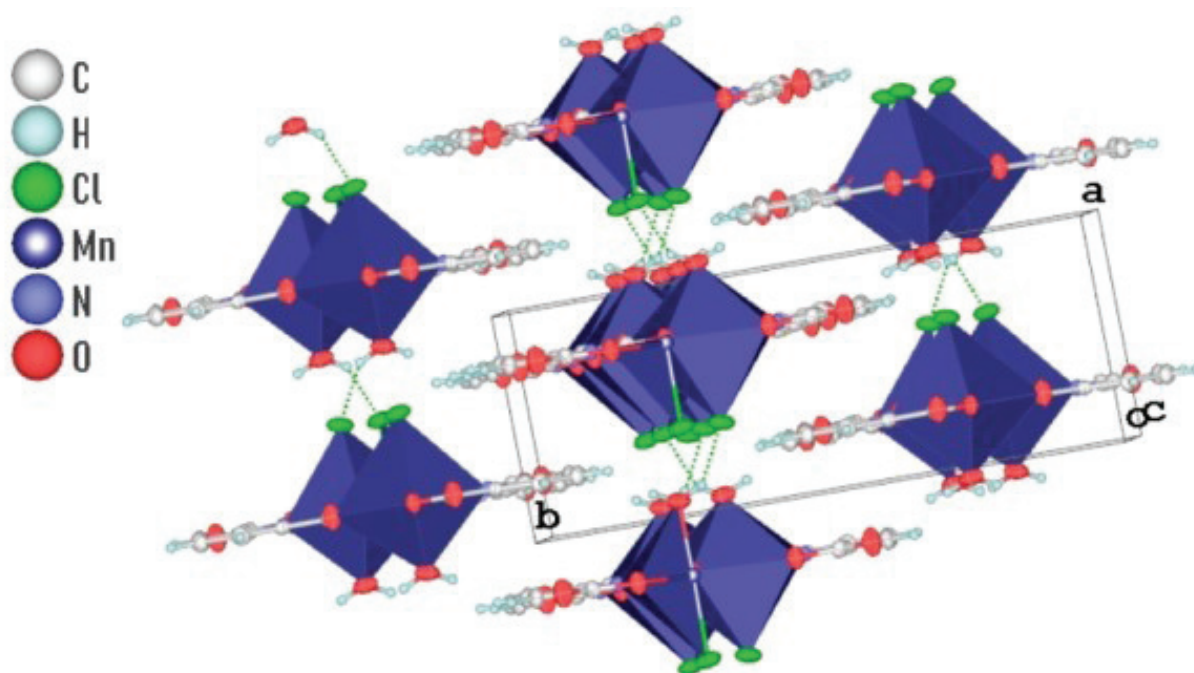
Strukturada 2,6-PDCA ligandining karboksil guruhining ikkita O atomi va 2,6-PDCA dagi piridinning N atomi orqali marganesga ion va donor akseptor bog‘lanish orqali bog‘lanib, ligandning tridentant holatda birikishini ta‘minlagan. Shu bilan birgalikda xlorid ioni birikkan bo‘lib, bir molekula suv donor-akseptor bog‘lanish orqali bog‘langan. Mn(II) ioni qo‘shni 2,6-PDCA ning karboksil ioni orqali bog‘lanishi marganesning koordinatsion yetti bo‘lishini ta‘minlagan, shuning hisobiga kompleks polimer tuzilishli bo‘lgan. $\pi - \pi$ stacing orasidagi mosafa 3.772 Å ekanligi pluton dasturi yordamida aniqlangan.

1-jadval.

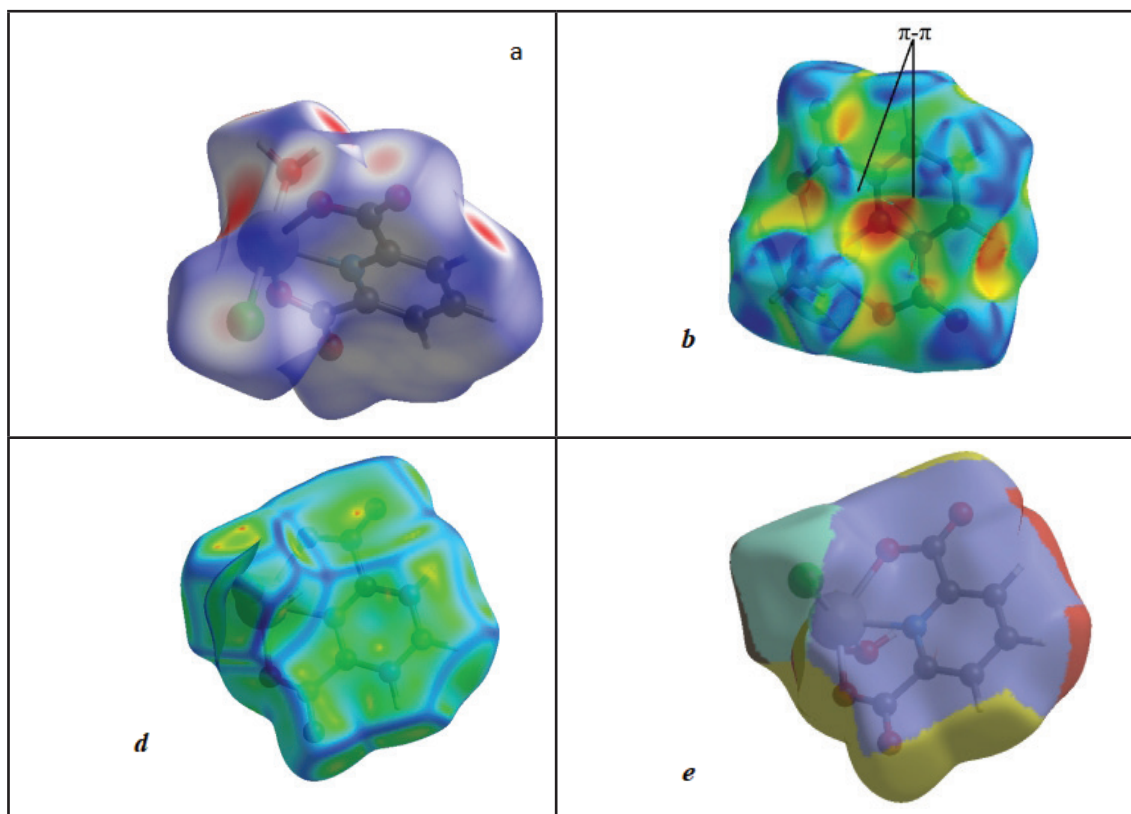
$\{Mn(2,6-PDCA)(Cl)(H_2O)_n\}_n$ kompleksdagi vodorod bog‘lar geometriyasi (Å)(°)

D-H-A	D-H, Å	H...A, Å	D...A, Å	D-H...A, (°)
O5 - H5B .. Cl1	0.9100	2.2700	3.069(3)	147.00
C2 -- H2 .. O4	0.9300	2.5000	3.420(4)	173.00

Simmetriya kodlari: (i) $1+x, 3/2-y, 1/2+z$, (ii) $x, y, -1+z$



2-rasm. Kompleksning kristall tahlanishi. Punktir chiziqlar vodorod bog‘lanishni ifodalaydi.



3-rasm. Hirshfeld surface (a), shape index(b), curvedness (c) and fragment patches(d).

Bog'lanish uzunligi Mn1 -Cl1= 2.4404(10), Mn1 -O1= 2.250(2), Mn1 -N1= 2.266(2) va Mn1 -O3 = 2.423(2), Mn1 -O5=2.156(3) Å. Bog' burchaklarining ham turli xil ekanligi kuzatiladi. Cl1 -Mn1 -O1 94.53(6), Mn1-N1 -C5 123.47(18), Cl1 -Mn1 -O3 90.67(7), Cl1 -Mn1 -O5 176.56 (7). Ligand geometriyasi tomonidan qo'yilgan cheklovlar tufayli sezilarli darajada egilgan aksel pozitsiyalarni kislorod atomlari egallaydi.

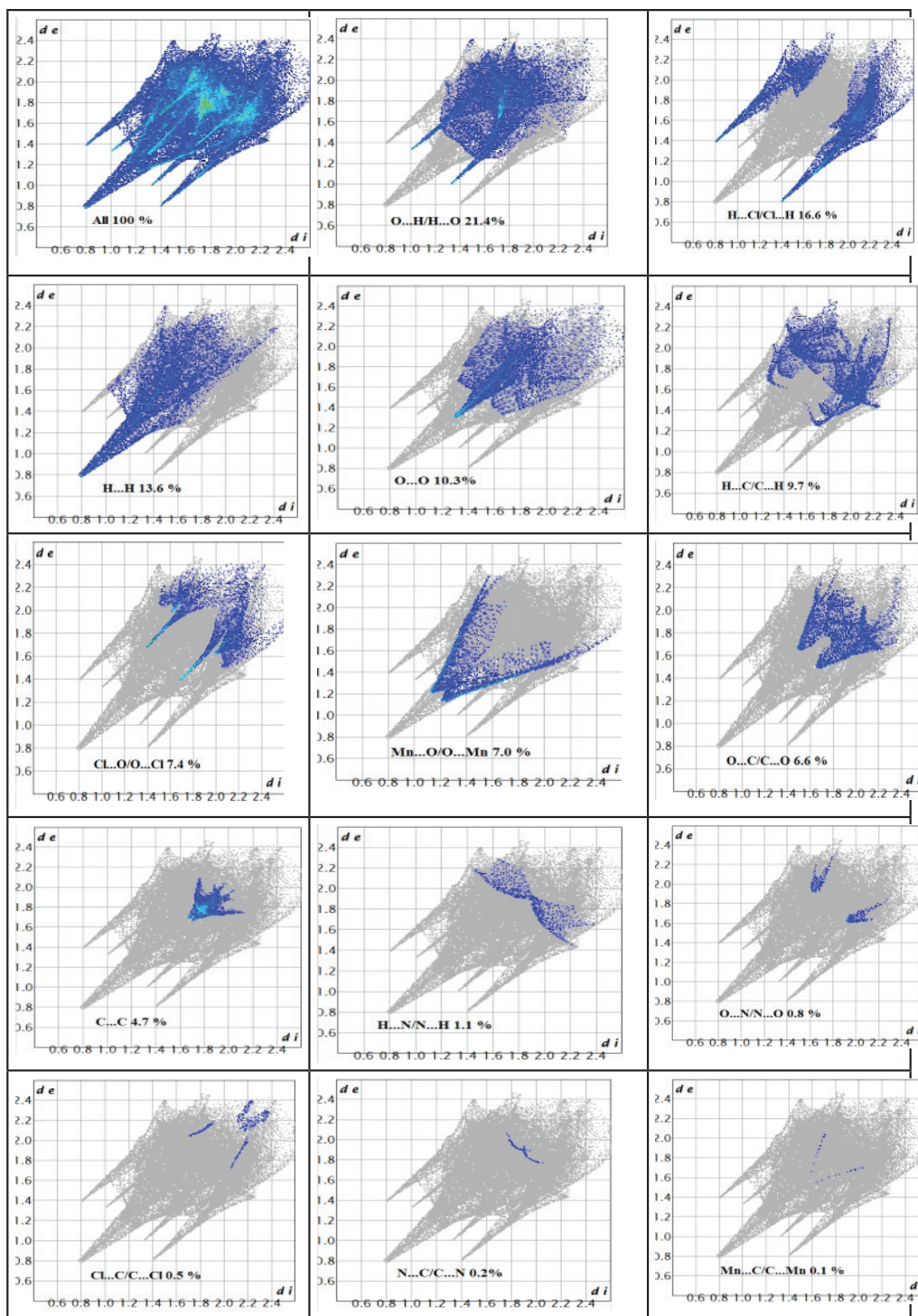
Hirshfeld sirtini Crystal Explorer17.5 dasturi yordamida tahlil qilindi ⁷⁹⁻¹⁰. Qizil va ko'k dog'larning d_{norm} bo'yicha standart o'lchamlari mos ravishda -0,6476 va 1,1469 ga teng.

Tahlilga ko'ra, qizil rang van der Waals radiuslari yig'indisiga yaqinroq ta'sirlashishni ko'rsatadi. Ko'k dog'lar esa van der Waals radiuslari yig'indisidan uzoqroq aloqalarni ko'rsatadi. Ushbu kompleks birikmaning d_{norm} bo'yicha molekulaning Hirshfeld sirtida qizil dog'larning asosiy qismini vodorod bog'lar tashkil qiladi (3-rasm). Hirshfeld sirt yuzasi $S= 222,94 \text{ \AA}^2$ va hajmi $V= 227,52 \text{ \AA}^3$ ga teng. Kristall tarkibida ichki zarrachalarning o'zaro ta'siri *di* va kristall sirtidagi o'zaro ta'sirlarni *de* ikki o'lchamli funksiyalari yordamida aniqlandi.

Molekula tarkibidagi atomlarning asosiy o'zaro ta'sirlashuvlarni O...H/H...O (21.4%), H...Cl/Cl...H (16.6%), H...H (13.6%), O...O 10.3%, H...C/C...H 9.7%, Cl...O/O...Cl 7.7%, Mn...O/O...Mn 7.0 %, O...C/C...O 6.6 %, C...C 4.7%,H...N/N...H 1.1 %, O...N/N...O 0.8%, Cl...C/C... Cl 0.5%, N...C/C...N 0.2%, Mn...C/C...Mn 0.1% bog'lari hissasiga to'g'ri keladi (4-rasm).

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4-rasm. $\{Mn(2,6-PDCA)(Cl)(H_2O)\}_n$ kompleks birikmaning juft atomlarining hissasini tavsiflovchi ikki o'lovchi barmoqlari (%).

Xulosa:

Tadqiqotlar natijasida 2,6-piridindikarbon kislotasining marganes(II) atsetat va xlorid kislotaning M:L:L 1:1:1 nisbatdagi polimer tuzilishli 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 (CCDC2403742). <https://www.ccdc.cam.ac.uk/structures/Search?Ccdc=2403742&Author=nazarov&Access=referee>. Hirshfeld sirti tahliliga ko'ra molekula tarkibidagi atomlarning asosiy o'zaro ta'sirlashuvlarni O...H/H...O (21.4%), H...Cl/Cl...H (16.6%), H...H (13.6%).