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Cu(II) NING 6-AMINOPIRIDIN-2-KARBON KISLOTASI BILAN KOMPLEKS BIRIKMASI SINTEZI VA KRISTALL TUZILISHI

Annotatsiya

6-aminopiridin-2-karbon kislotaning metall ionlari bilan ta’sirlashishi va uning metallokompleks birikmalarining xossalarini tadqiq qilish maqsadida, Cu(II)xlorid kristallogidrati bilan M:L 1:2 nisbatdagi koordinatsion soni oltiga teng bo‘lgan, yangi kompleks birikmasi olinib, uning monokristali o‘stirildi. Uning tarkibi va tuzilishi RTT yordamida aniqlandi. Markaziy atom Cu(II) ning koordinatsion soni 6, sp^3d^2 holatda gibridlanishga ega. Ushbu kompleks birikmada ikkala APY anioni Cu(II) ioniga karboksil ionidagi kislorod atomi va piridin halqasidagi azot atomi orqali bidentant holatda koordinatsiyalangan.

Kalit so‘zlar. 6-aminopiridin-2-karbon kislota (APY), sirka kislota, mis(II)xlorid, monokristall.

СИНТЕЗ И КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА КОМПЛЕКСНОГО СОЕДИНЕНИЯ Cu(II) С 6-АМИНОПИРИДИН-2-КАРБОНОВОЙ КИСЛОТОЙ.

Аннотация

Для изучения взаимодействия 6-аминопиридин-2-карбоновой кислоты с ионами металлов и свойств ее металлокомплексных соединений был получен новый комплексный продукт с кристаллическим гидратом хлорида Cu(II) и координационным числом шесть в соотношении M:L 1:2, и выращен его монокристалл. Его состав и структура были определены с помощью Рентгеноструктурный анализ. Центральный атом Cu(II) имеет координационное число 6 и гибридизован в sp^3d^2-состоянии. В этом комплексном соединении оба аниона APY координированы с ионом Cu(II) в бидентатном состоянии через атом кислорода карбоксильной группы и атом азота пиридинового кольца.

Ключевые слова: 6-аминопиридин-2-карбоновая кислота (APY), уксусная кислота, хлорид меди(II), монокристалл.

SYNTHESIS AND CRYSTAL STRUCTURE OF THE COMPLEX COMPOUND OF Cu(II) WITH 6-AMINOPYRIDINE-2-CARBOXYLIC ACID

Annotation

To study the interaction of 6-aminopyridine-2-carboxylic acid with metal ions and the properties of its metal complexes, a new complex product with crystalline Cu(II) chloride hydrate and a coordination number of six was prepared in a 1:2 M:L ratio, and its single crystal was grown. Its composition and structure were determined using X-ray method. The central Cu(II) atom has a coordination number of 6 and is hybridized in the sp^3d^2 state. In this complex, both APY anions are coordinated to the Cu(II) ion in a bidentate state via the oxygen atom of the carboxyl group and the nitrogen atom of the pyridine ring.

Keywords: 6-aminopyridine-2-carboxylic acid (APY), acetic acid, copper(II) chloride, single crystal.

Kirish. Jahonda 2,6-almashingan piridin hosilalari hamda ularning d-metall tuzlari bilan hosil qilgan aralash ligandli kompleks birikmalarining tadqiqoti, ularning tarkibi, tuzilishi, xossalari bo‘yicha ko‘plab izlanishlar olib borilmoqda. Bu borada, yuqori konformasion harakatchan karbon kislotalar asosidagi ligandlarning oraliq metallar bilan yangi tuzilish va funksiyalarni o‘zida namoyon etuvchi kompleks birikmalari sintezi, hosil bo‘lgan kompleks birikmalar tuzilishining turli omillarga, jumladan, metall tabiatiga, ligand o‘rinbosarining mavjudligiga bog‘liqligini, shuningdek, markaziy ionga ligandning koordinasiyalanishi, bog‘ tabiati hamda fizik-kimyoviy va biologik xossalarini aniqlash katta ahamiyat kasb etadi

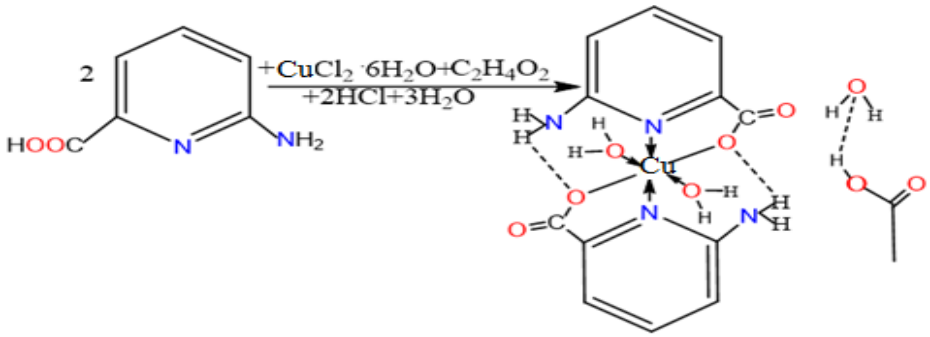
Adabiyotlarning tahlili. 6-aminopiridin-2-karbon kislotaning kompleks hosl qiluvchi xususiyatidan foydalanib, uning turli xil tarkibli kompleks birikmalari olingan. Tarkibida Cu(II) markazi buzilgan kvadrat tekislikda joylashgan geometriya ikkita karboksilat kislorod atomi va ikkitasi bilan yakunlangan L-anionlardan piridil azot atomlarining masofalari Cu—O bog‘lari 1.9268(18) Å va Cu—N bog‘lanish masofasi mos ravishda 2.011(2) Å ga teng. Cu(II) ga nisbatan bog‘lanish burchaklari markazlari 83.06(8)° dan 180° gacha [1]. Bundan farqli o‘laroq ko‘p tishli ligandning kutilishi, L- ligandlar koordinatasi diskret $Cu(L)_2$ strukturasini hosil qilish uchun N,O xelatsiya rejimi bilan. $Cu(L)_2$ molekulasi umuman tekislikka yaqin. Bundan tashqari, aniq yuzma-yuz –π-π stacking shovqinlari mavjud hosil bo‘lishiga hissa qo‘shadigan L-anionlar o‘rtasida uch o‘lchovli arxitektura [2].

Piridin hosilalarining luminesans, biologik faollik, kataliz va magnit hususiyatlari komplekslari o‘rganilgan [3]. Shu sababli, almashtirilgan piridin asosidagi metall komplekslarini o‘rganishga ko‘proq e’tibor berilmoqda. Bu sohada tadqiqotlar olib borilgan [4,5]. Mn(II) ionini o‘z ichiga oluvchi ikkita 2-amino -6-piridinkarboksilat ligandlari va ikkita koordinatali etanol molekulalari. Mn(II)ioni koordinatsiyalangan to‘rtta O atomi (O2, O2A, O3 va O3A) va ikitasi bilan N atomlari (N2 va N2A) ikki

xil 2-amino-6-piridinkarboksilat ligandlari va ikki xil koordinatali etanol molekulalari, buzilgan oktaedrik koordinatsiyani tashkil etgan.

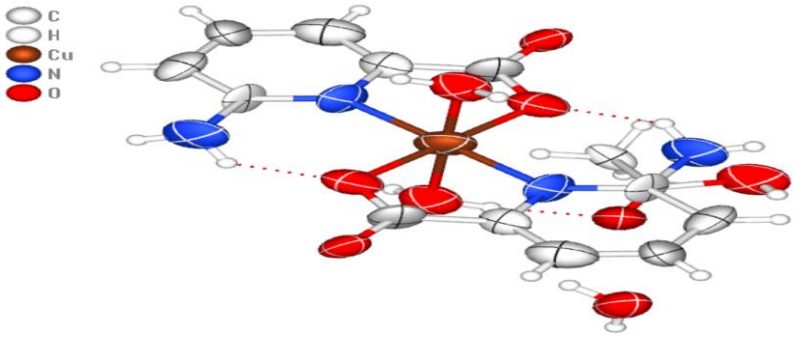
Hozirgi vaqtda kimyogarlar metall ionlariga biriktirilgan donor atomlarining soniga qarab di, tri, tetra yoki ko‘p ligandli komplekslar bo‘lishi mumkin bo‘lgan qiziqarli fizik-kimyoviy xossalari tufayli aralash ligand komplekslari bo‘yicha keng qamrovli tadqiqotlar olib borilmoqda [6-10].

Tajribaviy qism. Mis(II)xlorid kristallogidratidan $CuCl_2 \cdot 6H_2O$ 0.1185 gr (0.5 mmol), 0.138 gr (1 mmol) APY ni tegishlicha suv va sirka kislotada eritib, 1;2 mol nisbatdagi eritmalari tayyorlandi. Eritmalar aralashtirildi. So‘ngra magnitli aralashtirgich yordamida 60 ^{0}C da 30 minut davomida intensiv aralashtirildi. Eritma xona haroratida qoldirildi. Natijada 10 kundan so‘ng idish tubida ko ‘k rangli kompleks birikma kristali o‘sganligi kuzatildi. RTT uchun yaroqli kristallar ajratilib, tekshirilganda $[Cu(APY)_2(H_2O)_2](AcOH)(H_2O)$ tarkibli ekanligi aniqlandi. Unumi 86 % $[Cu(APY)_2(H_2O)_2](AcOH)(H_2O)$ (Mr=450.16 g/ mol) $CuC_{14}H_{20}O_9N_4$ tahlili nazariy jihatdan: C 37.65, H 4.51, N 12.55, O 32.27 % ni ko‘rsatdi: ma’lum bo‘ldiki C 37.24, H 4.16, N 12. 28.O 32.18 %. Reaksiya tenglamasi quyidagicha (1-sxema).



1-sxema. [Cu (APY)$_2$ (H$_2$O)$_2$] (AcOH) (H$_2$O) kompleksining olinish reaksiyasi

Tahlil va natijalar.



1-rasm. [Cu (APY)$_2$ (H$_2$O)$_2$] (AcOH) (H$_2$O) kompleksining molekulyar tuzilishi

$[Cu(APY)_2 (H_2O)_2](AsOH)(H_2O)$ kompleksining singoniyasi triclinic bo‘lib, a, b° mos ravishda 111.45(3), 98.576(13). Markaziy atom Cu(II) ning koordinatsion soni 6 va sp^3d^2 holatda gibridlanishga ega. Ushbu kompleks birikmada ikkala APY anioni Cu(II) ioniga karboksil ionidagi kislorod atomi va piridin halqasidagi azot atomi orqali bidentant holatda koordinatsiyalangan. Bundan tashqari ikki suv molekulasi ham markaziy atomga donor-akseptor bog‘lanish orqali bog‘langan, natijada oktaedrik shakl yuzaga kelgan. Cu1-O1 bog‘lanish uzunligi 2.035(6) Å, Cu1-O3 bog‘lanish uzunligi 2.129(4)Å, Cu1-N1 2.127(3) Å, Cu1-O3_a 2.129(4)hamda Cu1-N1_a 2.128 (5) Å. Bog‘ uzunligi va burchagi haqidagi ma’lumotlar 2, 3-jadvallarda keltirilgan.

1-jadval.

$[Cu(APY)_2(H_2O)_2](AsOH)(H_2O)$ kompleksining asosiy kristallografik ma’lumotlari

Parametr	Qiymatlar	Parametr	Qiymatlar
Brutto formulasi	$CuC_{14}H_{20}N_4O_9$	Z	2
Molekulyar massa	.	Dcalc (Mg m^{-3})	1.578
Singoniya	triclinic	F(000)	274
Fazoviy guruhi	P^{-1}	Kristall o‘lchami (mm)	0.28,0.24,0.20
a, Å	7.476(8)	Diffraktometr	diffractometer Bruker APEXII
b, Å	9.735(12)	Radiation [Angstrom]CuKa	1.54184
a, b °	111.45(3), 98.576(13)	Theta Min-Max [Deg]	5.0, 76.1
V /Å^3	542.4(2)	Nref, Npar	2215, 158
Min. and Max. Resd. Dens. [e/Ang^3]	-1.55, 1.11	Dataset	-8: 8 ; -9: 10 ; -12: 11

2-jadval.

$[Cu(APY)_2 (H_2O)_2](AsOH)(H_2O)$ kompleksining bog‘ uzunligi

Bog‘ uzunligi	(Å)	Bog‘ uzunligi	(Å)
Cu1 -O1	2.035(6)	N2 -H2B	0.8600
Cu1 -O3	2.129(4)	C3 -C4	1.382(10)
Cu1 -N1	2.127(3)	C4 -C5	1.377(10)
Cu1 -O1_a	2.035(6)	O4 -C8	1.217(8)

Cu1 -O3_a	2.129(4)	C5 -C6	1.499(9)
Cu1 -N1_a	2.128(5)	O5 -C8	1.295(9)
O1 -C6	1.286(8)	C2 -H2	0.9300
O2 -C6	1.243(7)	C3 -H3	0.9300
N1 -C1	1.328(8)	C4 -H4	0.9300
N1 -C5	1.360(8)	O5 -H5	0.8200
N2 -C1	1.358(9)	C7 -C8	1.488(12)
O3 -H3B	0.8500	O6 -H6A	0.8500
O3 -H3A	0.8500	O6 -H6B	0.8500
C1 -C2	1.406(10)	C7 -H7C	0.9600
C2 -C3	1.365(10)	C7 -H7A	0.9600
N2 -H2A	0.8600	C7 -H7B	0.9600

3-jadval.

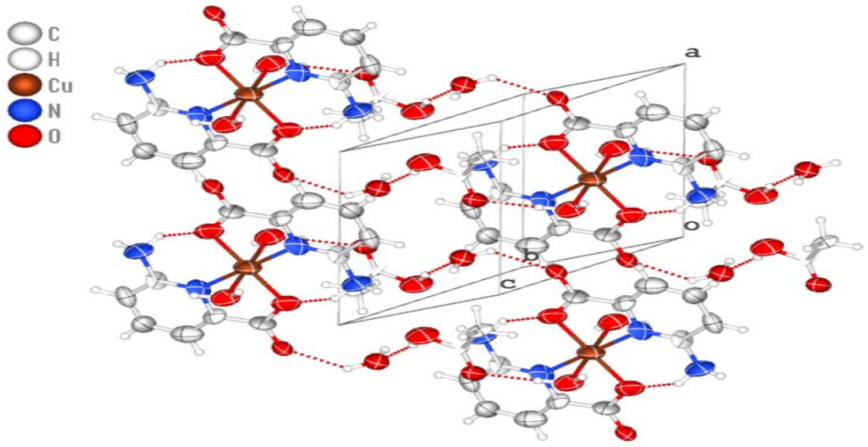
[Cu(APY)$_2$ (H$_2$O)$_2$](AsOH)(H$_2$O) kompleksining bog‘ burchagi

Bog‘ burchagi	(°)	Bog‘ burchagi	(°)
O1 -Cu1 -O3	89.55(18)	C1 -N2 -H2A	109.00
O1 - Cu 1 -N1	80.23(19)	C1 -N2 -H2B	109.00
O1 - Cu 1 -O1_a	180.00	C2 -C3 -C4	119.8(7)
O1 - Cu 1 -O3_a	90.46(18)	C3 -C4 -C5	118.3(6)
O1 - Cu 1 -N1_a	99.77(19)	N1 -C5 -C6	115.7(5)
O3 - Cu 1 -N1	90.55(19)	N1 -C5 -C4	122.6(6)
O1_a - Cu 1 -O3	90.46(18)	C4 -C5 -C6	121.6(6)
O3 - Cu 1 -O3_a	180.00	O2 -C6 -C5	120.9(6)
O3 - Cu 1 -N1_a	89.45(19)	O1 -C6 -O2	122.9(6)
O1_a - Cu 1 -N1	99.77(19)	O1 -C6 -C5	116.2(5)
O3_a - Cu 1 -N1	89.45(19)	C1 -C2 -H2	120.00
N1 - Cu 1 -N1_a	180.00	C3 -C2 -H2	120.00

4-jadval.

[Cu(APY)$_2$(H$_2$O)$_2$](AsOH)(H$_2$O) kompleksidagi vadorod bog‘lanish uzunligi (Å) va burchaklari (°)

D-H-A	D-H, Å	H···A, Å	D···A,Å	D-H···A, (°)
N2 -- H2B .. O1	0.8600	2.0900	2.825(8)	142.00
O3 -- H3A .. O2	0.8500	1.9200	2.755(6)	164.00
O3 -- H3B .. O4	0.8500	1.9600	2.816(6)	173.00
O5 -- H5 .. O6	0.8200	2.1000	2.616(8)	121.00
O6 -- H6A .. O5	0.8500	2.2100	2.616(8)	109.00
O6 -- H6A .. N2	0.8500	2.6200	3.378(6)	149.00
Simmetriya kodlari;(i) -x,1-y,1-z,(ii) 1-x,1-y,1-z,(iii) -1+x,-1+y,-1+z,(iiii) 1+x,1+y,1+z				



2-rasm. [Cu(APY)$_2$ (H$_2$O)$_2$](AsOH)(H$_2$O) kompleksining kristall taxlanishi (Punktir chiziqlar vodorod boglanishni bildiradi).

Tashqi sferada bir molekula sirka kislotasi va suv molekulasi o‘zaro vodorod bog‘lanish orqali bog‘langan. Kompleksning ichki sferada N2--H2B..O1 vodorod bog‘lanishi mavjud.

Xulosa. Mis(II)xlorid kristallogidrati va 6-aminopiridin-2-karbon kislota (APY) ni tegishlicha suv va sirka kislotada eritib, 1;2 mol nisbatdagi eritmalarini mehanik arlashtirish orqali [Cu(APY)$_2$ (H$_2$O)$_2$](AsOH)(H$_2$O) tarkibli kompleks birikma olinib, monokristallari o‘stirildi. RTT yordamida uning tuzilishi aniqlandi. Cu va tegishli O va N atomlarining bog‘ uzunligida farqlar tufayli Yann-Teller effikti kuzatildi.

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