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Synthesis, Structure, and Properties of the Complex [Cu(L)Cl] · $2H_2O$

A. M. Magerramov[a], G. V. Tsintsadze[b], R. A. Alieva[a], F. O. Mamedova[c], F. S. Alieva[a], F. N. Bakhmanova[a, *], A. V. Kurbanov[a], and F. M. Chyragov[a]

[a] *Baku State University, Baku, Azerbaijan*
[b] *Georgian Technical University, Tbilisi, Georgia*
[c] *Ganja State University, Ganja, Azerbaijan*
**e-mail: fidan_chem@rambler.ru*

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Abstract—The crystal structure of copper(II) complex with the HL ligand obtained from 3-[4-carboxyphenylazo]penta-2,4-dione and ethylenediamine (En) was determined by X-ray diffraction. The crystals are orthorhombic: a = 7.329(3), b = 15.393(5), c = 18.474(7) Å, V = 2084.1(12) $Å^3$, space group $P2_12_12_1$, Z = 4, $\rho_{(calcd.)}$ = 1.486 g/cm^3, R = 0.0441. The copper atom is coordinated by four nitrogen atoms of two En ligands and by the chlorine atom in an axial position according to the extended square pyramid geometry (4 + 1) (CIF file CCDC no. 1436882).

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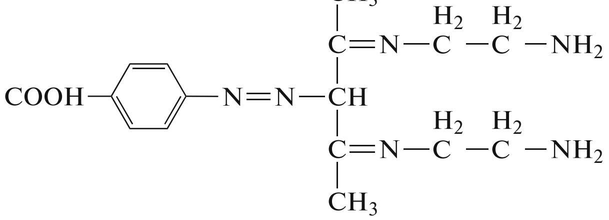
INTRODUCTION.

This paper continues our research into the methods of synthesis, structure, and reactivity of metal compounds containing β-diketone moieties [1–5]. Copper(II) complexes show a broad range of synthetic and structural options, the conditions of synthesis being crucial for the formation of these compounds. Earlier investigations of carboxyl-containing complexes are represented by few publications [6], which demonstrated the possibility of crystal formation involving amine nitrogen atoms.

This study is devoted to the synthesis and structure of the complex [Cu(L)Cl] · H_2O, where HL = $C_{16}H_{24}N_6O_2$.

EXPERIMENTAL

3-[4-Carboxyphenylazo]penta-2,4-dione (CPP) was synthesized by a reported procedure [7]. Using template synthesis, it was converted to 4-(2,4-bis((2-aminoethyl)imino)pentan-3-yl)diazenyl (HL):



(HL)

Synthesis of HL. CPP (0.1 mol) was dissolved in ethanol (50 mL) and the solution was transferred into a one-necked flask equipped with a mechanical stirrer and a reflux condenser. Then two drops of HCl and ethylenediamine (En) (0.2 mol) in ethanol (5 mL) were added and the mixture was heated for 2 h at 60°C. After 2 h, the reaction mixture was transferred into a beaker. After a week, reddish needle single crystals of HL appeared on the beaker bottom.

For $C_{16}H_{24}N_6O_2$

anal. calcd., %:	C, 57.83;	H, 7.23;	N, 25.30.
Found, %:	C, 57.02;	H, 6.93;	N, 24.94.

NMR: 18.1 (CH_3), 43.6(CH_2), 164.2 (C), 169.3 (C), 127.2 (C), 130.8 (C), 122.5 (C), 156.1 (C), 122.5 (C).

NMR: 1.94 (CH_3), 1.77 (CH_2), 2.7 (CH_2), 1.5 (CH), 1.5 (NH_2), 12.71 (HO), 8.18 (C), 7.45 (C).

Synthesis of [Cu(L)Cl] · $2H_2O$ (I). HL (0.2 mol) was dissolved in a 1 : 3 water–ethanol mixture (50 mL) and the solution was transferred into a one-necked flask equipped with a mechanical stirrer and a reflux condenser. Then $CuCl_2 \cdot 3H_2O$ (0.1 mol) in water (5 mL) was added and the mixture was heated for 2 h at 60°C. The reaction mixture was transferred into a beaker. After a week, greenish needle single crystals of **I** appeared on the beaker bottom.

For $C_{16}H_{27}N_6O_4ClCu$

anal. calcd., %:	C, 41.16;	H, 5.78;	N, 18.01;	Cl, 7.61;	Cu, 13.72.
Found, %:	C, 40.05;	H, 5.44;	N, 17.85;	Cl, 7.16;	Cu, 13.18.

X-ray diffraction. The crystal structure of **I** was determined on a Bruker SMART APEX II CCD automated diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, φ–ω scan mode). The calculations were carried out using the SHELXTL program package [8] with 5036 independent reflections. The X-ray experiment details and some crystallographic characteristics are summarized in Table 1. The structure was solved by the direct method and refined in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom positions were calculated geometrically and refined in the riding model. Selected interatomic distances and bond angles are summarized in Table 2 and the geometric parameters of hydrogen bonds are in Table 3.

The atom coordinates and other structure parameters of the complex are deposited with the Cambridge Crystallographic Data Centre (no. 1436882); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data and structure refinement parameters for **I**

Parameter	Value
M	466.43
Temperature, K	296(2)
System	Orthorhombic
Space group	$P2_12_12_1$
a, Å	7.329(3)
b, Å	15.393(5)
c, Å	18.474(7)
V, Å^3	2084.1(12)
Z	4
$\rho_{(calcd.)}$, g/cm^3	1.486
Crystal size, mm	0.30 × 0.25 × 0.20
μ_{Mo}, mm^{-1}	1.210
F(000)	972
Range of θ, deg	2.20–28.00
Ranges of h, k, l	$-9 \leqslant h \leqslant 9, -20 \leqslant k \leqslant 20, -24 \leqslant l \leqslant 24$
Number of collected reflections	23753
Number of unique reflections	5036
R_{int}	0.0441
Number of refined parameters	259
GOOF for F^2	1.003
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0441, wR_2 = 0.0845$
R-factor (all data)	$R_1 = 0.0785, wR_2 = 0.0950$

Table 2. Selected interatomic distances and bond angles in **II**

Bond	d, Å	Bond	d, Å	Bond	d, Å
Cu(1)–N(3)	1.984(3)	O(2)–C(14)	1.253(4)	N(4)–C(7)	1.280(4)
Cu(1)–N(2)	1.992(3)	N(1)–C(1)	1.472(5)	N(4)–C(4)	1.474(4)
Cu(1)–N(4)	1.992(3)	N(2)–C(2)	1.463(5)	N(5)–C(6)	1.305(4)
Cu(1)–N(1)	2.004(3)	N(3)–C(5)	1.273(4)	N(5)–N(6)	1.324(4)
Cu(1)–Cl(1)	2.4816(13)	N(3)–C(3)	1.468(4)	N(6)–C(8)	1.403(4)
O(1)–C(14)	1.240(4)				
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
N(3)Cu(1)N(2)	167.45(13)	C(2)N(2)Cu(1)	106.7(2)	N(3)C(3)C(1)	108.3(3)
N(3)Cu(1)N(4)	90.94(12)	C(5)N(3)C(3)	119.9(3)	N(4)C(4)C(2)	108.1(3)
N(2)Cu(1)N(4)	84.02(12)	C(5)N(3)Cu(1)	126.4(3)	N(3)C(5)C(6)	120.1(3)
N(3)Cu(1)N(1)	83.34(12)	C(3)N(3)Cu(1)	112.9(2)	N(3)C(5)C(15)	121.8(3)
N(2)Cu(1)N(1)	95.45(13)	C(7)N(4)C(4)	120.0(3)	N(5)C(6)C(7)	112.5(3)
N(4)Cu(1)N(1)	150.70(14)	C(7)N(4)Cu(1)	126.5(3)	N(5)C(6)C(5)	124.3(3)
N(3)Cu(1)Cl(1)	92.49(9)	C(4)N(4)Cu(1)	112.3(2)	N(4)C(7)C(6)	119.7(3)
N(2)Cu(1)Cl(1)	99.85(10)	C(6)N(5)N(6)	120.4(3)	N(4)C(7)C(16)	122.4(3)
N(4)Cu(1)Cl(1)	103.46(9)	N(5)N(6)C(8)	118.3(3)	C(9)C(8)N(6)	121.3(3)
N(1)Cu(1)Cl(1)	105.47(11)	N(1)C(1)C(3)	107.8(3)	O(1)C(14)O(2)	124.9(3)
C(1)N(1)Cu(1)	107.3(2)	N(2)C(2)C(4)	109.2(3)	O(1)C(14)C(11)	117.6(3)

Table 3. Geometric parameters of hydrogen bonds in **II***

D–H···A	Distance, Å			DHA angle, deg
	D–H	H···A	D···A	
N(1)–H(1*C*)···O(1)$^{\#1}$	0.90	2.09	2.907(4)	150
N(1)–H(1*D*)···O(4)$^{\#2}$	0.90	2.14	2.983(5)	155
N(2)–H(2*D*)···O(2)$^{\#3}$	0.90	2.29	3.110(5)	151
N(2)–H(2*C*)···O(2)$^{\#1}$	0.90	2.04	2.924(4)	166
O(3)–H(3*C*)···O(1)$^{\#4}$	0.92	1.89	2.793(7)	167
O(3)–H(3*D*)···O(4)$^{\#4}$	0.92	1.99	2.903(7)	174
O(3')–H(3*F*)···O(1)$^{\#4}$	0.92	1.91	2.678(9)	140
O(4)–H(4*C*)···O(2)$^{\#5}$	0.92	1.94	2.822(4)	160
O(4)–H(4*D*)···Cl(1)$^{\#6}$	0.92	2.33	3.104(4)	141

* Symmetry codes: $^{\#1}$ $x, y-1, z$; $^{\#2}$ $x+1, y-1, z$; $^{\#3}$ $x-1/2, -y+1/2, -z$; $^{\#4}$ $-x+1, y-1/2, -z+1/2$; $^{\#5}$ $x-1/2, -y+3/2, -z$; $^{\#6}$ $x, y+1, z$.

RESULTS AND DISCUSSION

The study demonstrated that HL reacts with copper(II) in the presence of ethylenediamine with evolution of two water molecules to give the molecular complex [Cu(L)Cl] · $2H_2O$.

The structural units of **I** are the complex molecules [Cu(L)Cl] · $2H_2O$ (Fig. 1) and water molecules of crystallization.

The copper atom is coordinated by four nitrogen atoms of two En residues of the L^- ligand in the equatorial plane by the chlorine atom in the axial position of an extended (4 + 1) square pyramid.

The copper atom is displaced from the equatorial plane of the N(1), N(2), N(3), and N(4) atoms towards Cl by 0.122 Å. The angle between the normal to the mean plane and the Cu(1)–Cl(1) bond is 3°.

The oxygen atoms of the L^- ligands and the hydrogen atoms of water molecules are connected by O–H···O hydrogen bonds (Fig. 2).

The bond lengths in compound **I** are as follows: Cu–N, 1.984(3)–2.004(3) Å (Table 2). In compound Cu–N=N–$C_6H_4SO_3H$ · HCl · $3H_2O$ (**II**), the average Cu–N distance is 1.947(3) Å [6]. The Cu–Cl distances in the two compounds are substantially different: 2.481(1) Å for (**II**) and 2.685(1) Å for **II**.

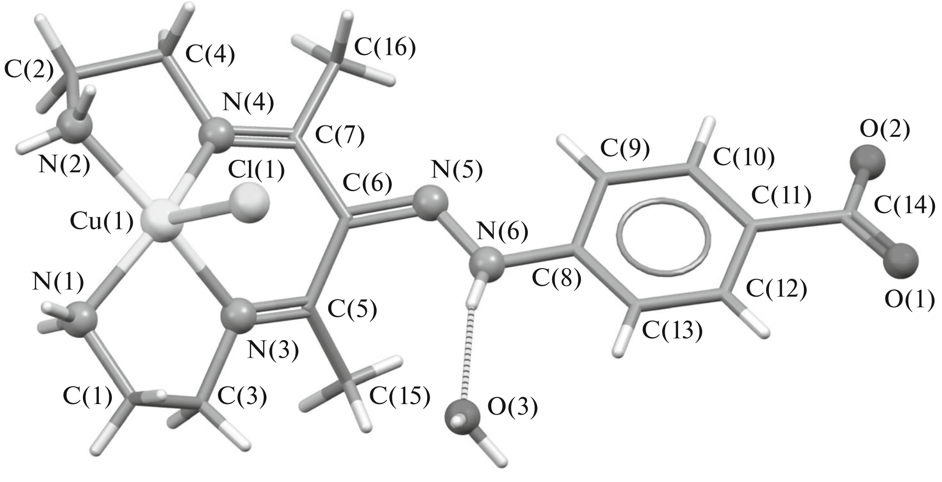


Fig. 1. Structure of the reagent molecule.

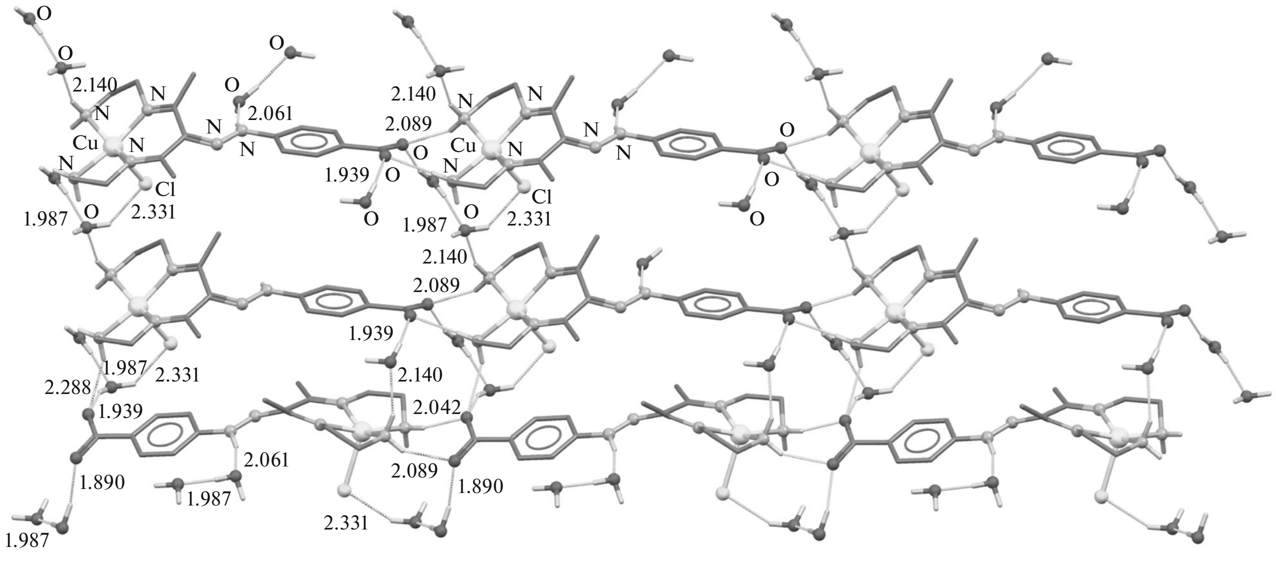


Fig. 2. Hydrogen bonds between the complex and water molecules.

Thus, it was found by X-ray diffraction that the template synthesis of 3-[4-carboxyphenylazo]penta-2,4-dione with ethylenediamine gave a ligand producing a stable copper chelate.

REFERENCES

1. Magerramov, A.M., Alieva, R.A., Bakhmanova, F.N., et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 1, p. 45.
2. Magerramov, A.M., Alieva, R.A., Kurbanov, A.V., et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 6, p. 428.
3. Solhnejad, R.H., Bahmanova, F.N., Maharramov, A.M., et al., *Inorg. Chem. Commun.*, 2013, vol. 35, p. 13.
4. Maharramov, A.M., Mardanova, V.I., Chyraqov, F.M., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2012, vol. 68, p. m128.
5. Alieva, R.A., Mardanova, V.I., Chyraqov, F.M., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2012, p. 68, p. m127.
6. Murman, R.K., Chipley, J., and Droege, P., *J. Chem. Crystallogr.*, 1998, vol. 28, no. 6, pp. 465–473.
7. Busev, A.I., *Sintez novykh organicheskikh reagentov dlya neorganicheskogo analiza* (Synthesis of New Organic Reagents for Inorganic Analysis), Moscow: MGU, 1972.
8. Sheldrick, G.M., *SHELXTL. Version. 6.12. Structure Determination Software Suite*, Madison: Bruker AXS, 2001.

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