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Crystal Structure of the $CuCl_2$ Complex with Two Molecules of *N*',*N*'-Dimethyl-*para*-*tert*-Butylbenzohydrazide $[Cu(p\text{-}(t\text{-}Bu)C_6H_4CONHN(Me)_2)_2]Cl_2 \cdot 1.34\ H_2O$

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Abstract—Complex $[Cu(HL^1)_2]Cl_2 \cdot 1.34\ H_2O$ ($HL^1 = p\text{-}(t\text{-}Bu)C_6H_4CONHN(Me)_2$) is studied by X-ray diffraction analysis. The coordination polyhedron of the copper atom is a distorted tetragonal pyramid, whose base is formed by the amine N and O atoms of two ligands HL^1, and one of the chlorine atoms occupies the vertex. The second chlorine atom does not enter into the coordination sphere of copper but is linked through an intramolecular hydrogen bond with the NH group. Reagent HL^1 forms a five-membered metallocycle with the central atom. The metallocycle exists in an envelope conformation with the copper atom in the flap. CIF file CCDC no. 1453151.

Keywords: *N*',*N*'-dimethyl-*para*-*tert*-butylbenzohydrazide, copper(II) chloride, cationic complex, X-ray diffraction analysis

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INTRODUCTION

Hydrazides with metal ions can form coordination compounds of two types: cationic compounds in which hydrazides are present in the neutral form and intracomplex compounds with hydrazides in the deprotonated form [1]. Hydrazides of unsubstituted carboxylic acids (HR) efficiently extract Cu(II) in the form of cationic complexes of the general formula $[Cu(HR)_3]^{2+}$, whereas their *N*',*N*'-dialkyl derivatives (HL) form intracomplex compounds CuL_2 under the same conditions [2]. This difference in compositions and structures of the extracted complexes cannot be explained by the difference in the acid–base properties of the ligands, since the latter are rather similar. It is most likely that the reason should be searched for in the structures of the complexes formed.

The structures of several copper(II) complexes with HL are described in the literature. The intracomplex compound with *N*',*N*'-dimethyl-*N*-(2,4-dichlorophenoxy)acetylhydrazine was studied by X-ray diffraction analysis [3] and found to be planar. The coordination polyhedron of the copper(II) atom is a slightly distorted square. The methyl groups are arranged symmetrically at both sides of the planes of the metallocycles. The structures of two $CuCl_2$ complexes with benzoic acid *N*',*N*'-diethylhydrazide (HL^2) are described [4]: the cationic complex with one ligand molecule of the general formula $[Cu(HL^2)]Cl_2$ and intracomplex compound $Cu(L^2)_2$. The coordination polyhedron of the copper atom in the former complex is a distorted tetrahedron with the donor atoms of ligand HL^2 and chlorine atoms in the vertices. The latter complex is planar, the coordination polyhedron of the central atom is a parallelogram, and the ethyl groups are arranged symmetrically at both sides of the plane of the metallocycles. The structure of the copper(II) intracomplex compound with *para*-*tert*-butylbenzoic acid *N*',*N*'-dimethylhydrazide (HL^1) was shown [5] to be similar to the structure of this compound with HL^2.

As can be seen, there are sufficient data on the structures of the Cu(II) intracomplex compounds with HL, whereas the cationic complexes with these ligands remain almost unstudied using X-ray diffraction analysis. Therefore, it is impossible to elucidate why they are not extracted. To answer this question, it was necessary to study the structures of the copper(II) cationic complexes with two HL molecules. For this purpose, we synthesized complex $[Cu(HL^1)_2]Cl_2 \cdot 1.34H_2O$ (**I**), where $HL^1 = p\text{-}(t\text{-}Bu)C_6H_4CONHN(Me)_2$, and studied it by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis of complex I. A solution of HL^1 (5 mmol) in an EtOH–acetone (1 : 1) mixture (6 mL) was added

Table 1. Crystallographic data and characteristics of the diffraction experiment for complex **I**

Parameter	Value
FW	598.50
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, Å	23.519(3)
b, Å	10.4300(11)
c, Å	13.1430(15)
β, deg	104.428(12)
V, Å^3	3122.3(6)
ρ_{calcd}, g/cm^3	1.270
μ, mm^{-1}	0.90
F(000)	1260
θ range, deg	1.79–29.45
Number of measured reflections	17186
Number of independent reflections (R_{int})	7461 (0.038)
Reflections with $I > 2\sigma(I)$)	5901
$\sin(\theta/\lambda)_{max}$, Å^{-1}	0.692
h, k, l range	$-31 \le h \le 29$, $-14 \le k \le 8$, $-17 \le l \le 16$
R ($F^2 > 2\sigma(F^2)$)	0.044
wR (F^2), S	0.128
GOOF	0.956
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.49/–0.39

with stirring to a solution of $CuCl_2 \cdot 2H_2O$ (2 mmol) in 2 mL of the same mixture of solvents. Blue crystals precipitated from the solution on storage. The crystals were filtered off, washed with cooled acetone, and dried in air. The yield was 0.77 g (64%).

For $C_{26}H_{42}N_4O_{3.34}Cl_2Cu$

	C	H	N	Cu
anal. calcd., %:	C, 52.13;	H, 7.02;	N, 9.36;	Cu, 10.61.
Found, %:	C, 51.84;	H, 6.86;	N, 9.28;	Cu, 10.20.

IR, ν, cm^{-1}: 3150 ν(NH), 1598 ν(C=O).

Elemental analysis was carried out on a CHNS-932 analyzer (LECO Corporation, USA). The copper(II) content was determined complexonometrically [6]. The IR spectrum of compound **I** was recorded on a VERTEX 80V FT-IR spectrometer (Bruker, Germany). The single crystals were obtained from the mother liquor kept at room temperature.

The X-ray diffraction analysis of a crystal 0.42 × 0.30 × 0.30 mm in size was carried out on an Xcalibur R single-crystal diffractometer with a CCD detector using a standard procedure (MoK_α radiation, graphite monochromator, 295(2) K, ω scan mode, scan increment 1°) [7]. An absorption correction was applied empirically using the SCALE3 ABSPACK algorithm [8]. The structure was determined by a direct method using the SHELXS-97 program and refined by full-matrix least squares on F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [8]. The hydrogen atom of the NH group was localized from the electron density difference syntheses and refined in the isotropic approximation with $U_{iso}(H) = 1.2U_{eq}(N)$. The N–H interatomic distance was fixed with the mild DFIX restraint. Other hydrogen atoms were included into the refinement in the riding model in the isotropic approximation with dependent thermal parameters. Restraints of the DFIX, SADI, SIMU, and DELU types were imposed on a series of thermal and geometric parameters of atomic disordering components. The characteristics of the diffraction experiment and the crystallographic data for compound **I** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The CIF file containing the full information about the studied structure of compound **I** was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1453151; www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of complex **I**, dichloro[di(*N'*,*N'*-dimethyl-*para*-*tert*-butylbenzohydrazide)copper(II)], is shown in Fig. 1. The copper atom is coordinated by two molecules of ligand HL^1 existing in the *trans* position to each other. The coordination polyhedron of copper is a tetragonal pyramid. Its base is formed by the N(4), O(1), N(3), and O(2) donor atoms of two ligands HL^1, and the vertex is occupied by the Cl(1) atom. The atoms of the base do not lie in one plane: the N(3) atom is arranged 0.330 Å lower than the plane passing through other atoms. The Cu atom is located 0.289 Å higher than the plane. The *N'*,*N'*-methyl groups are arranged at different sides from the plane of the base. The distance between the groups with the C(13) and C(14) atoms is insufficient for the Cl(1) atom to be placed freely. To occupy the site at the vertex of the tetragonal pyramid, the Cl(1) atom moves apart these groups, resulting in the elongation of the distance between them and, correspondingly, in a decrease in the distance between the methyl groups arranged at the opposite side of the base (C(13)···C(14) 5.801(4) Å, C(12)···C(15) 4.707(4) Å). This induces the deformation of the base: the plane of one metallocycle is inclined (angle N(1)CuN(2) 156.08(6)°) and turns toward another metallocycle

Table 2. Bond lengths (d, Å) and bond angles (ω, deg) in complex **I**

Bond	d, Å	Bond	d, Å
Cu–Cl(1)	2.4098(7)	Cu–N(3)	2.0521(19)
C(1)–O(2)	1.254(3)	Cu–N(4)	2.0542(18)
C(1)–N(2)	1.323(3)	N(1)–N(4)	1.428(2)
C(16)–O(1)	1.255(2)	N(1)–H(1)	0.836(17)
C(16)–N(1)	1.318(3)	N(2)–N(3)	1.417(3)
Cu–O(2)	1.9500(15)	N(2)–H(2)	0.823(16)
Cu–O(1)	1.9510(15)		
Angle	ω, deg	Angle	ω, deg
O(2)C(1)N(2)	120.75(19)	N(4)CuCl(1)	101.19(6)
O(1)C(16)N(1)	120.66(19)	C(16)N(1)N(4)	117.61(17)
O(2)CuO(1)	162.94(8)	C(1)N(2)N(3)	117.95(18)
O(2)CuN(3)	82.31(7)	N(2)N(3)Cu	105.35(13)
O(1)CuN(3)	92.55(7)	C(13)N(3)Cu	112.25(16)
O(2)CuN(4)	95.66(7)	C(12)N(3)Cu	111.69(15)
O(1)CuN(4)	81.93(7)	N(1)N(4)Cu	105.22(12)
N(3)CuN(4)	154.35(8)	C(14)N(4)Cu	113.67(16)
O(2)CuCl(1)	99.77(5)	C(15)N(4)Cu	110.76(14)
O(1)CuCl(1)	97.26(6)	C(16)O(1)Cu	113.76(14)
N(3)CuCl(1)	104.36(6)	C(1)O(2)Cu	113.37(13)

Table 3. Geometric parameters of hydrogen bonds in the structure of complex **I***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(1w)–H(2w)···Cl(1)$^{\text{i}}$	0.82(2)	2.31(2)	3.125(3)	171(4)
O(1w)–H(1w)···Cl(2)	0.82(2)	2.39(2)	3.200(2)	173(4)
N(1)–H(1)···Cl(2)	0.84(2)	2.27(2)	3.088(2)	167(2)
N(2)–H(2)···O(1w)$^{\text{ii}}$	0.82(2)	1.97(2)	2.779(2)	168(2)

* Symmetry codes: $^{\text{i}}\,x, -y + 3/2, z + 1/2$; $^{\text{ii}}\,x, y, z - 1$.

(the dihedral angle between the planes passing through the CuN(2)C(1) and CuN(4)O(1) atoms is 27.64°). These changes induce internal strains decreasing the stability of the complex. The distance between the C(12) and C(15) atoms is insufficient for the Cl(2) atom to enter into the coordination sphere of copper (and to form an octahedron). Therefore, this atom is located in the external sphere and forms a hydrogen bond with the N(1)H group (Table 3).

Ligands HL^1 form five-membered metallocycles CuOCNN with the central atom. The metallocycles look like envelopes with the Cu atom in the flap. The torsion angles are as follows: C(1)N(2)N(3)Cu 1.2(2)°, C(16)N(1)N(4)Cu 8.1(2)°, N(1)C(16)O(1)Cu –4.3(3)°, and N(2)C(1)O(2)Cu–5.7(3)°. The lengths of the Cu–O and Cu–N donor–acceptor bonds and the bond angles involving these bonds almost coincide with their values in complex $[Cu(HL^2)]Cl_2$ [4]. The N(3) and N(4) atoms have the tetrahedral configuration with the accuracy to 109° ± 4°. The planes of the benzene rings are turned toward the planes of the metallocycles (torsion angles N(2)C(1)C(2)C(7) 24.8(3)°, N(1)C(16)C(17)C(18) –9.1(4)°). The large angle of turn of one of the rings is related, most likely, to the influence of the adjacent molecule in the crystalline lattice.

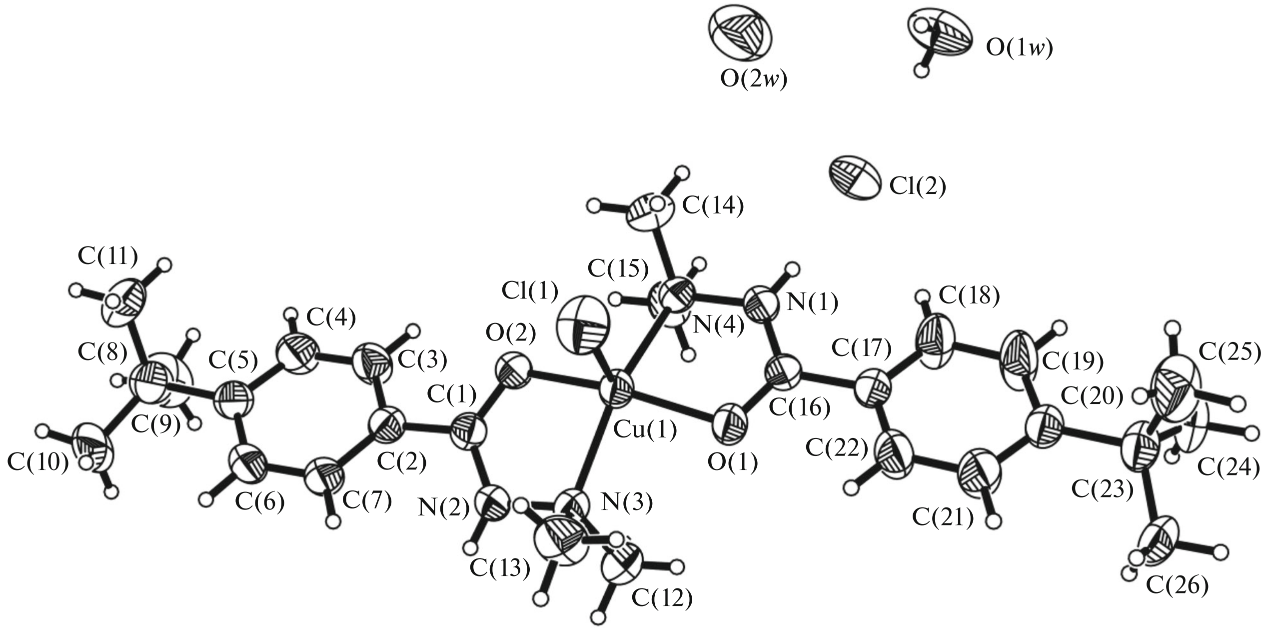

Fig. 1. General view and the numeration of atoms in complex **I**.

The crystal packing of the molecules of compound **I** represents intersecting layers (Fig. 2) formed by chains of the molecules arranged as on a chessboard. The vertices of the coordination polyhedron of the molecules in the nearest chains are directed oppositely (Fig. 3). Along with the intermolecular interaction, the chains are linked to each other by intermolecular hydrogen bonds involving molecules of crystallization H_2O that form two intermolecular hydrogen bonds with the adjacent molecules through the NH group and Cl(2) atom. Water of crystallization forms the third intermolecular hydrogen bond with the Cl(1) atom of the complex existing in another layer (Fig. 4). The geometric data on the intermolecular hydrogen bonds are presented in Table 3. The second water molecule (O(2*w*)) is probably disordered. An appropriate refinement result can be obtained if this water molecule is considered to fall onto three molecules of the complex. The hydrogen atoms for this molecule are not localized.

A comparison of the structures of complex **I** and the intracomplex compound with the same ligand [5] shows that the latter is planar and have no strains that deforms its structure and, hence, this compound is more stable.

To conclude, assuming that the structure of complex **I** in solution is similar to its structure in the crystalline state, we can conclude that steric hindrances

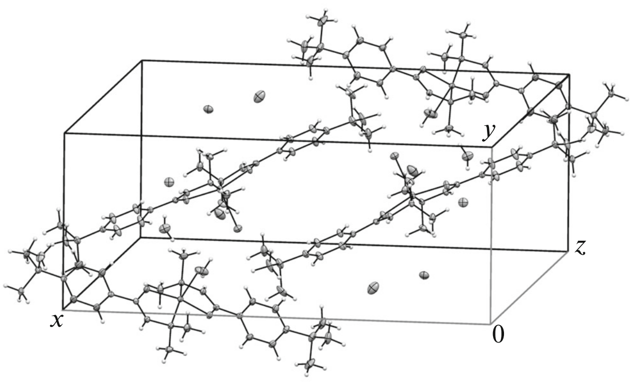

Fig. 2. Molecular packing in crystal of complex **I**.

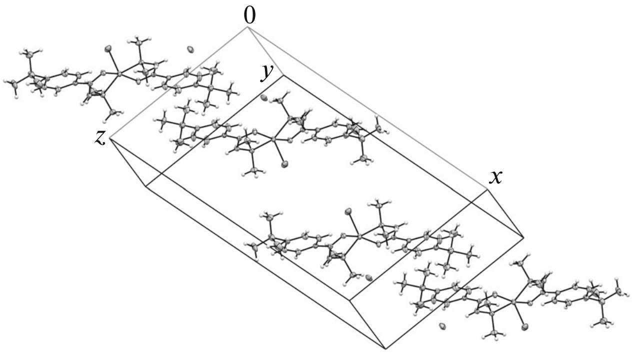

Fig. 3. Fragment of the packing. Orientation of the molecules in the adjacent rows of one layer.

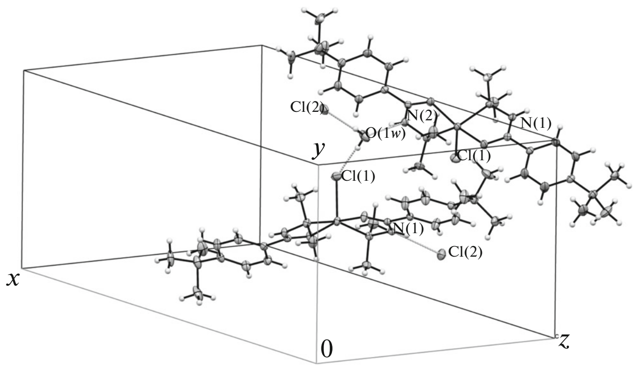

Fig. 4. Hydrogen bonds formed by water of crystallization and in the structure of complex **I**.

created by the *N*',*N*'-alkyl groups deform the structure of this cationic complex and thus decrease its stability. The strongly polar medium (water) facilitates the elimination of the acid molecules, inducing the transition of the complex (at the moment of formation in the aqueous phase) into a more stable intracomplex compound (Eq. (1)), which is extracted to the organic phase

$$Cu^{2+} + 2HL^1 \rightarrow [Cu(HL^1)_2]^{2+} \rightarrow Cu(L^1)_2 + 2H^+. \quad (1)$$

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