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COORDINATION COMPOUNDS

Crystal Structures of Two Copper(II) Complexes with *N*,*N*-Diethylbenzhydrazide

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Abstract—The copper(II) complexes with *N*,*N*-diethylbenzhydrazide, $[Cu(C_6H_5CONHN(C_2H_5)_2)]Cl_2$ (**I**) and $Cu(C_6H_5CONN(C_2H_5)_2)_2$ (**II**), have been studied by X-ray diffraction analysis. In the both compounds, the reactant acts as a bidentate (O, N(2)) ligand, forming five-membered chelate rings with copper. In cationic complex **I**, the O⟶Cu and N⟶Cu bond lengths are 1.954(2) and 2.070(3) Å, respectively, and the O(1)CuN(2) chelate angle is 81.89(10)°. The Cl^- ions are in the coordination sphere of copper (Cu–Cl, 2.1974(11) and 2.2178(10) Å). The chelate ring has an envelope conformation with the copper atom in the flap position. The coordination polyhedron of the copper atom is a strongly distorted tetrahedron. Neutral complex **II** is an inner complex salt. The reactant forms with copper two planar chelate rings. The Cu–O and N⟶Cu bond lengths are 1.8901(9) and 2.0175(11) Å, respectively, and the O(1)CuN(2) chelate cycle is 83.70(4)°. Complex **II** is planar, and the coordination polygon of the copper atom is a parallelogram. The thermal stability of complexes **I** and **II** has been studied.

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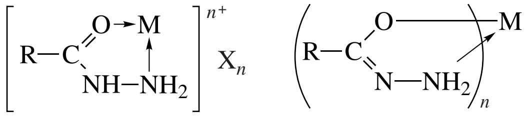
Hydrazides of carboxylic acids, being bidentate ligands, coordinate metal atoms through the oxygen atoms and terminal nitrogen atoms to form five-membered chelate rings. This coordination mode is indicated by a low-frequency shift of C=O and NH_2 stretching vibration bands observed in the IR spectra [1] and by X-ray diffraction data [2]. Hydrazides with metal ions can form complexes of two types: (a) cationic complexes containing hydrazide in the neutral form and (b) uncharged complexes, classified as inner complex salts containing hydrazide in the deprotonated form [3].



(a) (b)

Scheme 1.

N,N-Substituted hydrazides have been poorly studied as ligands. The syntheses of complexes of selected nonferrous metals with *N*,*N*-dimethylhydrazides of aryloxycarboxylic and 4-nitrobenzoic acids have been described [4, 5]. Based on the IR spectra of the synthesized complexes, which show the low-frequency shift of the C=O stretching vibration band, it is believed [4, 5] that these ligands are coordinated with metal atoms similarly to unsubstituted hydrazides. However, their IR spectra exhibit no absorption band of the NH_2 group, because its hydrogen atoms are substituted by methyl radicals. Therefore, IR spectra cannot provide an unambiguous conclusion about the participation of the terminal nitrogen atom in chelation.

The substitution of alkyl groups for the hydrogen atoms at the terminal nitrogen atom creates steric hindrance, which can impede the involvement of the nitrogen atom in coordination with metal ions. In this case, other coordination modes can take place. For example, *N*,*N*-dialkylhydrazides can act as monodentate (O) ligands or form four-membered rings of the amide type. We found no studies devoted to investigation of metal complexes with *N*,*N*-dialkylhydrazides by X-ray crystallography. Therefore, it was of interest to perform X-ray diffraction analysis of compounds of the above type for the direct determination of the coordination mode of ligand molecules and the structures of the complexes. In the present work, we report the synthesis and crystal structures of copper(II) complexes with *N*,*N*-diethylbenzhydrazide ($C_6H_5CONHN(C_2H_5)_2$) of both types.

EXPERIMENTAL

Synthesis of $[Cu(C_6H_5CONHN(C_2H_5)_2)]Cl_2$ (I). A solution of *N*,*N*-diethylbenzhydrazide (1 g, 5 mmol) in ethanol (6 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.88 g, 5 mmol) in ethanol (5 mL). The mixture was stirred with heating for 15 min, one-half of the ethanol volume was distilled off, and the remaining mixture was placed in a refrigerator. Blue crystals that formed were washed with cooled ethanol. The yield was 0.77 g.

A blue single crystal was obtained by crystallization from acetone.

Synthesis of $Cu(C_6H_5CONN(C_2H_5)_2)_2$ (II). A 10 M solution of NH_3 (~3 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.7 g, 4 mmol) in water (2 mL) until a blue solution of a copper ammine complex was formed. Then a solution of the reactant (1.8 g, 8 mmol) in ethanol (18 mL) was added. The mixture was stirred with heating for 30–40 min. The brown precipitate that formed was washed with water and cooled ethanol. The yield was 1.7 g. A red single crystal was obtained by crystallization from ethanol.

X-ray diffraction analysis. Experimental sets of reflections for the determination of structures **I** and **II** were obtained on an Xcalibur 3 X-ray diffractometer with a Sapphire CCDT detector (MoK_α radiation, graphite monochromator, detection temperature 295(2) K, ω and φ scan modes, scan increment 0.5°). The diffraction experiment details and crystallographic data are given in Table 1. Absorption correction was applied analytically according to the polyhedral crystal model. Structures **I** and **II** were solved by direct methods and refined by the full-matrix least-squares method (on F^2) in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined in the isotropic approximation by the riding model. All calculations on the determination and refinement of the structures of complexes **I** and **II** were performed using the SHELXS97 program package [6].

Differential thermal analysis. Thermal stability of complexes **I** and **II** was studied on a Q-1500 D Paulik–Paulik– Erdey derivatograph in air in the temperature range 23–880°C. The heating rate was 5 K/min.

RESULTS AND DISCUSSION

The crystal of complex **I** contains two crystallographically independent molecules with close values of bond lengths and bond angles. The atomic coordinates and temperature parameters and bond lengths and bond angles are given in Tables 2 and 3, respectively (for the second molecule, all non-hydrogen atoms are designated by index A). The molecular structure of complex **I** is shown in Fig. 1 (no figure of the second molecule is presented, because its geometry is similar). *N*,*N*-Diethylbenzhydrazide coordinates the copper atom in the bidentate mode through the oxygen atom and the terminal nitrogen atom, closing the five-membered chelate ring. In addition to the donor oxygen and nitrogen atoms, the coordination sphere of the copper atom contains two chlorine anions. The copper atom is out of the ring plane: the CuO(1)C(1)N(1) and CuN(2)N(1)C(1) torsion angles are 2.95° and –5.29°, respectively. The difference in angles is due to the fact that the ligand molecule is not planar but slightly bent (the O(1)C(1)N(1)N(2) torsion angle is 2.04°). Thus, the chelate ring has an envelope conformation with the copper atom in the flap position. The copper atom forms the donor–acceptor bond with the oxygen atom ($Cu \leftarrow O(1)$ 1.954 Å), which is 0.064 Å longer than the sum of the covalent radii of the Cu and O atoms for $CN_{Cu} = 4$ (1.27 + 0.62 Å) [7]. The donor–acceptor N_{Cu} bond length is 2.070 Å, which is 0.140 Å longer than the sum of the covalent radii of Cu and N for $CN_{Cu} = 4$ (1.27 + 0.66 Å) [7]. These data show that the bonds between the central atom and the ligand molecule are weakened. The N(2)Cu(1)O(1) chelate angle is 81.89(10)°. The Cu–Cl(1) and Cu–Cl(2) bond lengths are 2.1974(11) and 2.2178(10) Å, respectively. The

Table 1. Crystallographic data and details of the diffraction experiment for compounds **I** and **II**

Compound	I	II
Empirical formula	$C_{11}H_{16}N_2OCl_2Cu$	$C_{23}H_{30}N_4O_2Cu$
FW	326.70	446.06
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Z	16	2
a, Å	31.748(3)	9.9647(5)
b, Å	12.425(2)	10.7340(4)
c, Å	16.5999(10)	11.0205(3)
α, deg	90	99.563(3)
β, deg	118.491(8)	102.234(4)
γ, deg	90	93.455(4)
V, Å^3	5755.11	1130.40(8)
ρ_{calcd}, g/cm^3	1.508	1.310
μ, mm^{-1}	1.875	0.990
$F(000)$	2672	470
θ, deg	2.74–31.61	2.97–31.70
Number of measured reflections	20853	12711
Number of independent reflections	8425 ($R_{int} = 0.0442$)	6400 ($R_{int} = 0.0168$)
Number of reflections with $I > 2\sigma(I)$	3428	4692
Ranges of h, k, l	$-45 \le h \le 45$, $-18 \le k \le 17$, $-21 \le l \le 24$	$-14 \le h \le 14$, $-15 \le k \le 14$, $-16 \le l \le 15$
$R1$; $wR2$ ($I > 2\sigma(I)$)	0.0342; 0.0597	0.0295; 0.0785
$R1$; $wR2$ for all data	0.1228; 0.0888	0.0449; 0.0826
GOOF for all reflections	1.000	1.000
$\Delta\rho_{max}$; $\Delta\rho_{min}$, e Å^{-3}	0.417; –0.334	0.242; –0.379

Table 2. Atomic coordinates ($\times 10^4$) and temperature parameters ($\times 10^3$, Å^2) for the $[Cu(C_6H_5CONHN(C_2H_5)_2]Cl_2$ complex (**I**)

Atom	x	y	z	U_{eq}
Cu(1)	2419(1)	6778(1)	3434(1)	39(1)
Cu(1A)	5074(1)	2175(1)	4780(1)	39(1)
Cl(1)	1972(1)	8214(1)	2846(1)	62(1)
Cl(2)	1864(1)	5544(1)	2685(1)	50(1)
Cl(1A)	5612(1)	2924(1)	6072(1)	54(1)
Cl(2A)	5541(1)	1962(1)	4148(1)	68(1)
O(1)	2850(1)	5768(2)	4365(2)	43(1)
N(1)	3423(1)	6807(2)	4359(2)	43(1)
N(1A)	4073(1)	1912(2)	3820(2)	40(1)
O(1A)	4645(1)	1897(2)	5292(2)	44(1)
C(1A)	4207(1)	1843(3)	4700(3)	36(1)
C(9A)	4376(1)	4019(3)	3537(3)	71(1)
N(2A)	4437(1)	2022(2)	3552(2)	36(1)
C(2A)	3841(1)	1719(3)	5011(2)	38(1)
C(1)	3289(1)	5958(3)	4655(2)	35(1)
N(2)	3061(1)	7518(2)	3731(2)	40(1)
C(3)	3559(1)	4679(3)	5944(2)	47(1)
C(2)	3660(1)	5251(3)	5343(2)	36(1)
C(10A)	4417(1)	1072(3)	2990(2)	47(1)
C(4)	3895(1)	3999(3)	6587(3)	53(1)
C(5A)	3192(1)	1496(3)	5658(3)	61(1)
C(10)	3138(1)	8592(3)	4174(3)	60(1)
C(8A)	4352(1)	3027(3)	3005(3)	49(1)
C(3A)	3968(1)	1221(3)	5842(3)	53(1)
C(7)	4106(1)	5116(3)	5381(3)	52(1)
C(6)	4438(1)	4421(3)	6038(3)	60(1)
C(5)	4329(1)	3877(3)	6622(3)	54(1)
C(6A)	3061(1)	2004(4)	4844(3)	75(2)
C(7A)	3386(1)	2119(3)	4505(3)	59(1)
C(9)	3014(1)	6502(4)	2402(3)	74(1)
C(8)	3092(1)	7585(3)	2861(3)	56(1)
C(4A)	3641(1)	1108(3)	6157(3)	60(1)
C(11A)	4527(1)	46(3)	3509(3)	68(1)
C(11)	3076(2)	8554(4)	5024(3)	80(2)

Cu(1)–Cl(2) and O(1)–Cu bonds are almost mutually perpendicular (the O(1)Cu(1)Cl(2) angle is 93.91(7)°), like the N(2) ⟶ Cu and Cu–Cl(2) bonds (the N(2)CuCl(1) is 95.77(8)°). The N(2)CuCl(2) and O(1)CuCl(1) angles are 150.52(9)° and 158.86(8)°, respectively. The Cl(1)Cu(1)Cl(2) angle is 98.01(4)°. The deviations of these angles from the ideal tetrahedral value (109.5°) are due to steric hindrance created by the ethyl groups. As a consequence, the arrangement of the Cl(1)CuCl(2) and O(1)CuN(2) planes differs strongly from the mutually perpendicular arrangement observed for a regular tetrahedron: the dihedral angle between these planes is ~34°. Thus, the coordination polyhedron of the copper atom is a strongly distorted tetrahedron. The distances between the chemically unbound atoms forming the tetrahedron sides are the following: Cl(1)–O(1), 4.081 Å; N(2)–Cl(1), 3.166 Å; N(2)–O(1), 2.638 Å; N(2)–Cl(2), 4.147 Å; Cl(1)–Cl(2), 3.332 Å; and O(1)–Cl(2), 3.054 Å. The distortions in the tetrahedron geometry are caused by chelation, steric hindrance created by the ethyl groups, and difference in bond lengths between the central atom and the O, N, and Cl atoms. The benzene ring is turned with respect to the chelate ring. The O(1)C(1)C(2)C(3) torsion angle is –26.91°. This turn is caused by steric hindrance created by the H(1A) atom of the NH group, because the nonbonding distance between this atom and the nearest H(3A) atom of the benzene ring is only 2.21 Å. The ethyl groups are asymmetrically located on different sides of the chelate ring: the N(1)N(2)C(8) (109.8(3)°) and N(1)N(2)C(10) (108.0(3)°) angles are approximately equal, and the CuN(2)C(8) (107.8(2)°) and CuN(2)C(10) (115.2(12)°) angles are not equal. This difference is caused by a stronger influence of the Cl(1) atom on the ethyl group with the C(10) atom because the nonbonding Cl(1)–C(10) distance (3.317 Å) is shorter than the Cl(1)–C(8) distance of another ethyl group (3.360 Å). The C–N and C–C bond lengths are 1.488–1.496 and 1.507–1.515 Å, respectively. Analysis of the crystal structure of complex **I** shows that, due to strong geometric distortions, there are considerable internal stresses decreasing its stability.

Complex **II** contains the hydrazide in the deprotonated form. Its crystal contains two crystallographically independent centrosymmetric molecules. The coordinates and temperature parameters of atoms in structure **II** are presented in Table 4. The bond lengths and bond angles are given in Table 5. The structure of a molecule of complex **II** is shown in Fig. 2. The ligands coordinate the copper atoms the chelating mode as in complex **I** through the oxygen and terminal nitrogen atoms to form a five-membered chelate ring. Complex **II** is an inner complex salt (the bond between the copper and oxygen atoms is covalent, whereas that between the copper and nitrogen atoms is donor–acceptor). In both molecules of complex **II**, the Cu–O covalent bonds (1.8854(10) ± 0.0047 Å) are the same and equal to the sum of the covalent radii of the Cu and O

Table 3. Bond lengths (*d*) and bond lengths (ω) in structure **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.954(2)	C(2A)–C(7A)	1.371(4)
Cu(1)–N(2)	2.070(3)	C(2A)–C(3A)	1.385(5)
Cu(1)–Cl(1)	2.1974(11)	C(1)–C(2)	1.476(4)
Cu(1)–Cl(2)	2.2178(10)	N(2)–C(10)	1.488(5)
Cu(1A)–O(1A)	1.950(2)	N(2)–C(8)	1.496(4)
Cu(1A)–N(2A)	2.086(3)	C(3)–C(4)	1.380(5)
Cu(1A)–Cl(1A)	2.2025(10)	C(3)–C(2)	1.380(4)
Cu(1A)–Cl(2A)	2.2107(10)	C(2)–C(7)	1.399(4)
O(1)–C(1)	1.263(3)	C(10A)–C(11A)	1.484(5)
N(1)–C(1)	1.316(4)	C(4)–C(5)	1.360(4)
N(1)–N(2)	1.430(3)	C(5A)–C(4A)	1.350(5)
N(1A)–C(1A)	1.314(4)	C(5A)–C(6A)	1.365(5)
N(1A)–N(2A)	1.429(3)	C(10)–C(11)	1.515(5)
O(1A)–C(1A)	1.266(3)	C(3A)–C(4A)	1.375(4)
C(1A)–C(2A)	1.489(4)	C(7)–C(6)	1.396(5)
C(9A)–C(8A)	1.496(5)	C(6)–C(5)	1.355(5)
N(2A)–C(10A)	1.487(4)	C(6A)–C(7A)	1.398(5)
N(2A)–C(8A)	1.491(4)	C(9)–C(8)	1.507(5)
Angle	ω, deg	Angle	ω, deg
O(1)Cu(1)N(2)	81.89(10)	C(3A)C(2A)C(1A)	119.1(3)
O(1)Cu(1)Cl(1)	158.86(8)	O(1)C(1)N(1)	120.1(3)
N(2)Cu(1)Cl(1)	95.77(8)	O(1)C(1)C(2)	120.7(3)
O(1)Cu(1)Cl(2)	93.91(7)	N(1)C(1)C(2)	119.1(3)
N(2)Cu(1)Cl(2)	150.52(9)	N(1)N(2)C(10)	108.0(3)
Cl(1)Cu(1)Cl(2)	98.01(4)	N(1)N(2)C(8)	109.8(3)
O(1A)Cu(1A)N(2A)	81.75(9)	C(10)N(2)C(8)	111.0(3)
O(1A)Cu(1A)Cl(2A)	162.75(8)	N(1)N(2)Cu(1)	104.86(18)
N(2A)Cu(1A)Cl(2A)	94.74(7)	C(10)N(2)Cu(1)	115.2(2)
O(1A)Cu(1A)Cl(1A)	91.60(7)	C(8)N(2)Cu(1)	107.8(2)
N(2A)Cu(1A)Cl(1A)	157.92(8)	C(4)C(3)C(2)	121.0(3)
Cl(2A)Cu(1A)Cl(1A)	97.45(4)	C(3)C(2)C(7)	119.0(3)
C(1)O(1)Cu(1)	114.2(2)	C(3)C(2)C(1)	119.6(3)
C(1)N(1)N(2)	118.5(2)	C(7)C(2)C(1)	121.4(3)
C(1A)N(1A)N(2A)	118.1(2)	C(11A)C(10A)N(2A)	112.9(3)
C(1A)O(1A)Cu(1A)	114.1(2)	C(5)C(4)C(3)	119.6(4)
O(1A)C(1A)N(1A)	120.9(3)	C(4A)C(5A)C(6A)	120.4(4)
O(1A)C(1A)C(2A)	119.1(3)	N(2)C(10)C(11)	111.7(3)
N(1A)C(1A)C(2A)	120.0(3)	N(2A)C(8A)C(9A)	112.7(3)
N(1A)N(2A)C(10A)	108.7(2)	C(4A)C(3A)C(2A)	120.7(3)
N(1A)N(2A)C(8A)	109.3(2)	C(6)C(7)C(2)	118.7(3)
C(10A)N(2A)C(8A)	110.0(3)	C(5)C(6)C(7)	120.8(3)
N(1A)N(2A)Cu(1A)	104.80(18)	C(6)C(5)C(4)	120.9(4)
C(10A)N(2A)Cu(1A)	114.63(19)	C(5A)C(6A)C(7A)	120.7(4)
C(8A)N(2A)Cu(1A)	109.2(2)	C(2A)C(7A)C(6A)	118.7(4)
C(7A)C(2A)C(3A)	119.6(3)	N(2)C(8)C(9)	111.5(3)
C(7A)C(2A)C(1A)	121.3(3)	C(5A)C(4A)C(3A)	119.8(4)

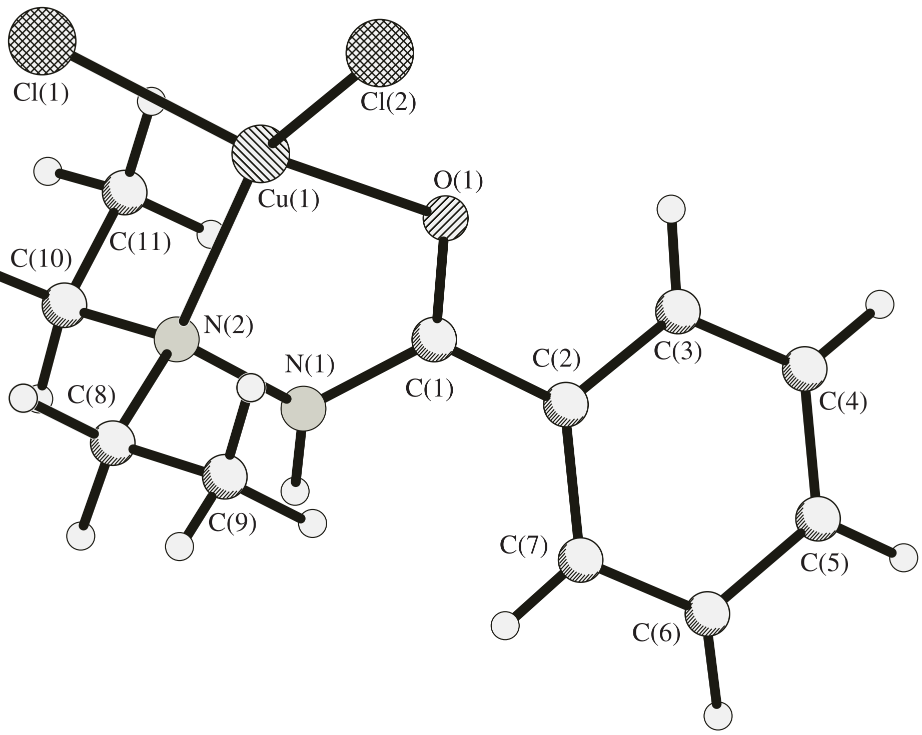


Fig. 1. General view of the $[Cu(C_6H_5CONHN(C_2H_5)_2)]Cl_2$ complex (**I**).

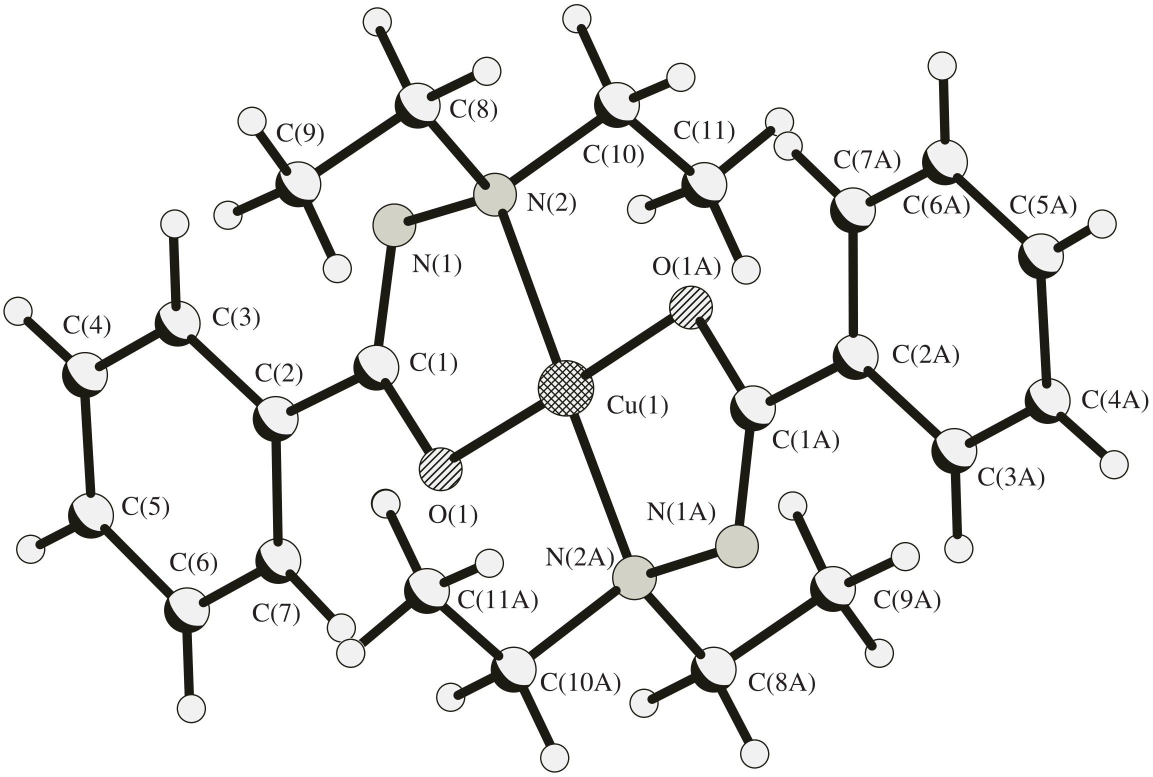


Fig. 2. General view of the $Cu(C_6H_5CONN(C_2H_5)_2)_2$ complex (**II**).

atoms for CN_{Cu} = 4[7]. The average length of the N→Cu bonds (2.0163(11) ± 0.0012 Å) is by 0.086 Å longer than the sum of the covalent radii of the Cu and N atoms for $CN_{Cu} = 4$. However, this bond in compound **II** is shorter than the N→Cu bond in complex **I**; i.e., this bond is stronger. The chelate angles are 83.70(4)° (hereinafter, the angle values and nonbonded distances are presented for the complex with the Cu(I) atom), and the interchelate angles are 96.30(4)°. The O(1)–N(2) distance between the nonbonded atoms is 2.601 Å, and the N(2)–O(1A) distance is 2.903 Å. The corresponding angle O(1)N(2)O(1A) is equal to 86.03°. The coordination polygon of the copper atom is a parallelogram. The deviations from the rectangular shape are caused by the difference between the Cu–O and N→Cu bond lengths. The planes of the benzene rings in complex **II**, like in structure **I**, are turned relatively to the planes of the chelate rings. In the molecule of the complex with the Cu(1) atom, the corresponding dihedral angle is 9.53°, and that in the complex with Cu(2) is –14.79°. Since there is no hydrogen atom at the N(1) atom, the turn of the benzene rings is, most likely, due to mutual steric hindrance between the molecules of the complexes. The minimum nonbonded distance between the hydrogen atoms of the ethyl group of the complex with the Cu(1) and the H atoms of the benzene ring in the complex with Cu(2) is 2.51 Å, and the same distance between the hydrogen atoms of the ethyl group of the complex with Cu(2) and the H atoms of the benzene ring of the complex with Cu(1) is noticeable longer (2.69 Å). Thus, steric hindrance created by the ethyl group for the benzene ring is stronger in the first case than that in the second case and, hence, the angle of rotation in the complex with Cu(2) is larger than that in the complex with Cu(1). The ethyl groups are located symmetrically with respect to the plane of the chelate ring. The N(1)N(2)C(8) and N(1)N(2)C(10) angles, as well as the C(8)N(2)Cu and C(10)N(2)Cu angles, are pairwise equal. The C–N bond lengths are 1.4778–1.490 Å, which is virtually equal to the C–C distances (1.488–1.493 Å).

The difference in the structures of the ligand molecules in complexes **I** and **II** results in differences in their geometric parameters. In complex **I**, the C–O bond is shorter than that in complex **II** (1.263(3) and 1.3003(15) Å, respectively) due to its double character. The double character of the C–N bond in complex **II** results in its shortening from 1.316(4) to 1.2947(7) Å. The N–N bond length in complex **II** is somewhat elongated compared to that in complex **I** (from 1.430(3) to 1.4608(15) Å), which is probably caused by the formation of the stronger N → Cu bond with a greater delocalization of the lone electron pair of the nitrogen atom. The O(1)C(1)N(1) bond angle in complex **I** is 120.1(3)°, and that in complex **II** is 126.28(12)°.

The thermal decomposition of complex **II** is stepwise in the temperature range 200–490°C. At 200°C,

Table 4. Atomic coordinates (×10^4) and temperature parameters (×10^3, Å^2) for the $Cu(C_6H_5CONN(C_2H_5)_2)_2$ complex (**II**)

Atom	*x*	*y*	*z*	U_{eq}
Cu(1)	5000	5000	0	34(1)
O(1)	6469(1)	3982(1)	260(1)	46(1)
C(2)	7408(1)	2380(1)	1328(1)	36(1)
N(1)	5288(1)	3176(1)	1602(1)	41(1)
N(2)	4309(1)	4080(1)	1234(1)	39(1)
C(1)	6309(1)	3241(1)	1050(1)	35(1)
C(3)	7520(2)	1752(1)	2344(1)	46(1)
C(7)	8345(2)	2201(2)	564(2)	48(1)
C(6)	9355(2)	1392(2)	798(2)	58(1)
C(4)	8549(2)	954(2)	2573(2)	60(1)
C(5)	9452(2)	760(2)	1792(2)	59(1)
C(10)	2935(2)	3350(2)	678(2)	53(1)
C(8)	4204(2)	4942(2)	2397(2)	58(1)
C(9)	5495(2)	5782(2)	3010(2)	75(1)
C(11)	2902(2)	2424(2)	–502(2)	76(1)
Cu(2)	5000	0	5000	35(1)
O(2)	3933(1)	–1559(1)	4844(1)	44(1)
C(12)	2779(1)	–1643(1)	4001(1)	36(1)
N(4)	3396(1)	322(1)	3668(1)	40(1)
N(3)	2358(1)	–778(1)	3362(1)	41(1)
C(13)	1885(1)	–2870(1)	3736(1)	38(1)
C(14)	2215(2)	–3773(1)	4479(1)	45(1)
C(21)	3808(2)	456(2)	2469(1)	50(1)
C(19)	2737(2)	1473(1)	4089(2)	49(1)
C(15)	1429(2)	–4935(2)	4214(2)	58(1)
C(18)	755(2)	–3149(2)	2716(2)	59(1)
C(16)	324(2)	–5207(2)	3207(2)	66(1)
C(22)	4593(2)	–600(2)	1997(2)	62(1)
C(20)	2123(2)	1400(2)	5207(2)	68(1)
C(17)	–11(2)	–4316(2)	2465(2)	75(1)

Table 5. Bond lengths (*d*) and bond lengths (ω) in structure **II**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.8807(10)	Cu(2)–O(2)	1.8901(9)
Cu(1)–N(2)	2.0150(11)	Cu(2)–N(4)	2.0175(11)
O(1)–C(1)	1.3003(15)	O(2)–C(12)	1.3046(15)
C(2)–C(7)	1.385(2)	C(12)–N(3)	1.2937(17)
C(2)–C(3)	1.3888(19)	C(12)–C(13)	1.4941(18)
C(2)–C(1)	1.4902(17)	N(4)–N(3)	1.4659(15)
N(1)–C(1)	1.2947(17)	N(4)–C(19)	1.4871(19)
N(1)–N(2)	1.4608(15)	N(4)–C(21)	1.4897(19)
N(2)–C(8)	1.4778(19)	C(13)–C(14)	1.382(2)
N(2)–C(10)	1.490(2)	C(13)–C(18)	1.389(2)
C(3)–C(4)	1.385(2)	C(14)–C(15)	1.385(2)
C(7)–C(6)	1.379(2)	C(21)–C(22)	1.500(3)
C(6)–C(5)	1.371(3)	C(19)–C(20)	1.498(3)
C(4)–C(5)	1.373(3)	C(15)–C(16)	1.366(3)
C(10)–C(11)	1.493(3)	C(18)–C(17)	1.382(2)
C(8)–C(9)	1.488(3)	C(16)–C(17)	1.369(3)
Angles	ω, deg	Angles	ω, deg
O(1)Cu(1)N(2)	83.70(4)	O(2)Cu(2)N(4)	83.27(4)
C(1)O(1)Cu(1)	111.09(8)	C(12)O(2)Cu(2)	111.40(8)
C(7)C(2)C(3)	118.89(13)	N(3)C(12)O(2)	126.07(12)
C(7)C(2)C(1)	119.72(12)	N(3)C(12)C(13)	117.59(12)
C(3)C(2)C(1)	121.39(13)	O(2)C(12)C(13)	116.32(12)
C(1)N(1)N(2)	110.74(10)	N(3)N(4)C(19)	108.46(11)
N(1)N(2)C(8)	107.60(11)	N(3)N(4)C(21)	106.54(11)
N(1)N(2)C(10)	107.65(10)	C(19)N(4)C(21)	108.27(11)
C(8)N(2)C(10)	107.88(12)	N(3)N(4)Cu(2)	108.62(7)
N(1)N(2)Cu(1)	108.18(7)	C(19)N(4)Cu(2)	112.65(9)
C(8)N(2)Cu(1)	112.73(10)	C(21)N(4)Cu(2)	112.07(9)
C(10)N(2)Cu(1)	112.56(9)	C(12)N(3)N(4)	110.60(10)
N(1)C(1)O(1)	126.28(12)	C(14)C(13)C(18)	118.84(13)
N(1)C(1)C(2)	117.61(11)	C(14)C(13)C(12)	119.82(13)
O(1)C(1)C(2)	116.11(11)	C(18)C(13)C(12)	121.27(13)
C(4)C(3)C(2)	120.00(15)	C(13)C(14)C(15)	120.49(15)
C(6)C(7)C(2)	120.38(15)	N(4)C(21)C(22)	113.62(13)
C(5)C(6)C(7)	120.62(16)	N(4)C(19)C(20)	113.92(12)
C(5)C(4)C(3)	120.60(15)	C(16)C(15)C(14)	120.41(16)
C(6)C(5)C(4)	119.49(15)	C(17)C(18)C(13)	119.72(16)
N(2)C(10)C(11)	113.43(13)	C(15)C(16)C(17)	119.50(15)
N(2)C(8)C(9)	113.30(14)	C(16)C(17)C(18)	121.04(17)

the DTA curve contains an endotherm without weight change due to the phase transition (melting). The first step of weight loss (200–400°C) is fast, and the weight loss is 79%. In this step, most likely, the ligand is eliminated with the partial oxidation of organic fragments and simultaneous copper oxidation to form copper(II) oxide. These processes are accompanied by two relatively small exotherms at 260 and 275°C. At temperatures above 400°C, the organic products formed by the decomposition of the ligand are oxidized. The process occurs with significant heat release (in the DTA curve) with the characteristic temperature 440°C. The weight of the residue above 490°C corresponds to the weight of copper(II) oxide formed in the reaction.

The thermal decomposition of complex **I** begins at a lower temperature (100°C) compared to the onset temperature of compound **II** (200°C). This agrees with the X-ray diffraction data showing that the bonds between the Cu atom and the ligand in complex **I** are weaker than those in structure **II**. The thermal decomposition occurs in a wider temperature range (100–880°C). In the range of relatively low temperatures (100–405°C), the ligand is presumably eliminated with the partial oxidation of the decomposition products and simultaneous formation of CuO, which is confirmed by the exotherms in the DTA curve. The weight loss is 62%. In the range 405–660°C, the weight decrease can be explained by the removal of $CuCl_2$. According to published data [8], the intense process of transition of copper(II) chloride to the gas phase is observed at 407°C. The weight loss in this temperature range is 20%, which corresponds to the loss of approximately 50% of the amount of copper(II) chloride that can form due to the complete decomposition of complex **I**. In the range 660–880°C, the weight change rate decreases to zero. Thus, the weight of the residue corresponding to copper oxide is somewhat smaller, being 50% of the theoretical value.

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