Complexation of metal salts with macrocyclic polyethers in aprotic organic solvents. Crystal structures of ionic complexes $[CuCl\cdot 15\text{-}C\text{-}5\cdot CH_3CN]_2[Cu_2Cl_6]$ and $\{[Cu\cdot 15\text{-}C\text{-}5\cdot (CH_3CN)_2][Cu_3Cl_8]\}_n$

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(Received July 25, 1990; revised December 5, 1990)

Abstract

Interaction of $CuCl_2$ and $CuCl_2\cdot 2H_2O$ with 15-C-5 in acetonitrile medium affords ionic complexes $(CuCl\cdot 15\text{-}C\text{-}5\cdot CH_3CN)_2(Cu_2Cl_6)$ (**I**) and $[(Cu\cdot 15\text{-}C\text{-}5\cdot (CH_3CN)_2(Cu_3Cl_8)]_n$ (**II**) having copper in the inner cavity of the macrocycle. The copper polyhedron in the cation of **I** is a pentagonal bipyramid with axial chloride and acetonitrile. Copper atoms in the anion are bonded with bridging and terminal chlorides located in the apices of a strongly distorted square. The axial positions of the pentagonal bipyramid of the cation of complex **II** are occupied by two acetonitrile molecules. There are only bridging chlorides in the anion $[Cu_3Cl_8]_n{}^{2-}$. The polyhedron of central copper in the anion is a square bipyramidal, that of the two terminal ones is square pyramidal. Complexes **I** and **II** decompose on heating with successive liberation of acetonitrile ligand, degradation of crown ether and reduction of copper(2+) chloride into α-CuCl.

Introduction

All structurally characterized metal complexes (excluding alkali metal complexes) with the macrocyclic polyether 15-crown-5 containing a metal ion in the inner cavity have an unexpected but similar ligand environment (pentagonal bipyramid) and the coordination number of seven (see ref. 1 and the literature cited therein). Even Cu(2+) complexes, which usually provide square-planar or octahedral species, react with 15-C-5 type ligands to give the inner complex $CuCl_2\cdot$benzo-15-C-5 [2] and the ionic complex $[Cu\cdot 15\text{-}C\text{-}5\cdot (H_2O)_2][NO_3]_2$[3] both having seven coordinated copper. At the same time the reaction of $CuCl_2$ with 12-C-4 leads to the usual donor–acceptor complex with an outer sphere copper atom with the coordination number of six [4]. Undoubtedly, this unique coordination mode in 15-C-5 complexes arises from the ligand structure and its conformational rigidity. Therefore, one can expect that under certain conditions a metal will not enter the inner cavity of 15-C-5 providing its typical ligand environment. Since the nature of the solvent is a powerful instrument for influencing the reactivity, we have studied the complex formation between $CuCl_2$ and 15-C-5 in acetonitrile medium, i.e. an aprotic donor solvent.

Results and discussion

Conductometric titrations of the $CuCl_2$–15-C-5 mixtures in acetonitrile have shown that the conductivity of solutions increases steadily on decreasing the ratio $CuCl_2$:15-C-5 from 1.60×10^{-2} to 1.94×10^{-2} S/m ($c_{CuCl_2} = 4.14 \times 10^{-3}$ M, the final ratio 1.5:1) or from 1.15×10^{-2} to 1.22×10^{-2} S/m ($c_{CuCl_2} = 2.64 \times 10^{-3}$ M, the final ratio 1.85:1). It should be mentioned however that the conductivity of solutions of $CuCl_2$ both in the presence and in the absence of 15-C-5 changes with time and does not approach the equilibrium values even after 2–3 weeks.

Absorption spectra of $CuCl_2$ in CH_3CN in the presence of 15-C-5 coincide with those in the absence of the ligand in terms of amount of peaks and positions of maxima (310 and 460 nm), but differ substantially in absorptivity at these wavelengths. This is indicative [5, 6] of simultaneous coordination of the crown ether and acetonitrile

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by a metal center. Unfortunately, the absorptivity in the visible region, as well as the conductivity, changes with time. It permanently increases at 460 nm, while at 310 nm it first increases but after 2–3 h begins to decrease. These data suggest the complicated, non-equilibrium nature of the processes taking place in the systems $CuCl_2$–CH_3CN and $CuCl_2$–15-C-5–CH_3CN which most likely arise from the co-existence of various polynuclear, differently solvated metal atoms.

If $CuCl_2$ and 15-C-5 are used in the ratio 1:1, the orange complex $2CuCl_2$·15-C-5·CN_3CN (**I**) crystallizes from the solution, while if used in the ratio 3:1 the brown complex $4CuCl_2$·15-C-5·$(CH_3CN)_2$ (**II**) is formed. At the reagent ratio 2:1 one obtains a mixture of both complexes. It is interesting to note that the same result is achieved in the reaction between $CuCl_2$·$2H_2O$ and 15-C-5 in acetonitrile medium, although in this case by analogy with hydrates of zinc chloride [1] one may except the presence of water molecules in the coordination sphere of copper.

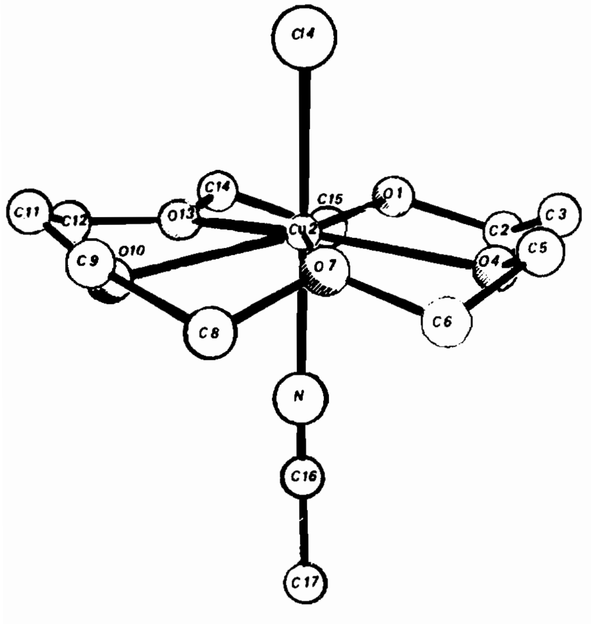

Fig. 1. The structure of the cation [CuCl·15-C-5·CH_3CN]$^+$ in **I**.

TABLE 1. Geometrical characteristics of coordinative environment of Cu1 and Cu2 atoms in complex **I**

Atoms	Bond distances (Å)
Cu1–Cl1	2.187(2)
Cu1–Cl2	2.422(2)
Cu1–Cl3	2.180(2)
Cu1–Cl2′	2.303(2)
Cu2–Cl4	2.209(2)
Cu2–O1	2.251(3)
Cu2–O4	2.277(3)
Cu2–O7	2.176(3)
Cu2–O10	2.360(3)
Cu2–O13	2.242(3)
Cu2–N	1.981(4)
Atoms	Bond angles (°)
Cl1–Cu1–Cl2	135.9(2)
Cl1–Cu1–Cl3	102.8(2)
Cl1–Cu1–Cl2′	98.7(3)
Cl2–Cu1–Cl3	100.1(2)
Cl2–Cu1–Cl2′	89.1(2)
Cl3–Cu1–Cl2′	137.1(2)
Cl4–Cu2–O1	97.6(3)
Cl4–Cu2–O4	89.3(2)
Cl4–Cu2–O7	94.4(3)
Cl4–Cu2–O10	98.0(2)
Cl4–Cu2–O13	88.0(2)
Cl4–Cu2–N	179.2(2)
O1–Cu2–O4	73.8(2)
O1–Cu2–O7	143.7(2)
O1–Cu2–O10	140.8(3)
O1–Cu2–O13	73.3(2)
O1–Cu2–N	81.9(2)
O4–Cu2–O7	72.2(3)
O4–Cu2–O10	141.9(3)
O4–Cu2–O13	146.3(3)
O4–Cu2–N	90.0(2)
O7–Cu2–O10	70.0(2)
O7–Cu2–O13	141.5(2)
O7–Cu2–N	85.7(3)
O10–Cu2–O13	71.6(3)
O10–Cu2–N	82.8(3)
O13–Cu2–N	92.3(3)

In contrast to the molecular complex $CuCl_2$·benzo-15-C-5 (**III**) obtained in chloroform [2], complexes **I** and **II** are ionic. The cation CuCl·15-C-5·CH_3CN^+ in **I** is shown in Fig. 1. The central atom has the pentagonal bipyramidal coordination, the axial sites being occupied by chloride and an acetonitrile molecule. Non-equivalence of apical substitutents leads to the departure of oxygen atoms from the plane by 0.14 Å toward chloride and decreases the Cu–Cl distance by up to 2.21 Å as compared with that in the symmetrical molecule **III** (2.25 Å) [2]. Geometrical characteristics of the polyhedron are very close to ideal (Table 1). In particular, the mean value of the bond angle OCu(2)O is equal to 72(1)°, that between the axial and equatorial ligands is equal to 90(5)°, while the bond angle ClCu(2)N is equal to 179.2°. The mean value of the Cu(2)–O bond is equal to 2.26(5) Å which, within experimental error, coincides with that found in **III** (2.28 Å [2]) and [Cu·15-C-5·$(H_2O)_2$]$(NO_3)_2$ (2.25 Å [3]).

The chain (–O–CH_2–CH_2–O–) in **I** has an ideal ap, ± sc, ap conformation (Table 2). The highest deviation of oxygen atoms from the mean plane is as high as 0.22 Å (atom C13). The polyhedron from the oxgyen atoms has a twist conformation; deviation of O(1) and O(13) oxygens from the plane of O(4), O(7) and O(13) oxygens is 0.29 and 0.31 Å. The bond lengths C–C and C–O in the crown ether vary in the range 1.49–1.52 and 1.35–1.43 Å, respectively, the mean values being 1.49(2) and 1.40(2) Å. The mean values of the bond angles COC are equal to 117(2) and

TABLE 2. Geometrical characteristics of 15-crown-5 in complex **I**

Group of atoms 1-2-3-4	Bond distance (Å) 2-3	Bond angle (°) 1-1-3	Torsion angle (°) 1-2-3-4
C15-O1-C2-C3	1.43(3)	117.4	−176.6
O1-C2-C3-O4	1.52(3)	107.7	60.6
C2-C3-O4-C5	1.42(3)	107.1	−177.5
C3-O4-C5-C6	1.41(2)	115.4	170.7
O4-C5-C6-O7	1.49(1)	107.6	−43.7
C4-C6-O7-C8	1.35(1)	112.9	−161.0
C6-O7-C8-C9	1.38(1)	120.9	−158.2
O7-C8-C9-O10	1.44(1)	111.2	−45.2
C8-C9-O10-O11	1.40(1)	109.2	173.2
C9-O10-C11-C12	1.42(1)	115.5	−168.8
O10-C11-C12-O13	1.51(2)	106.4	61.9
C11-C12-O13-C14	1.41(1)	106.6	−179.6
C12-O13-C14-C15	1.41(1)	114.5	175.2
O13-C14-C15-O1	1.52(2)	106.3	−59.3
C14-C15-O1-C2	1.40(3)	107.1	−176.5

108(2)°, respectively. All these values are quite usual for compounds of this type.

The dimeric anion $[Cu_2Cl_6]^{2-}$ is chloro-bridged. The bond lengths Cu–Cl (bridge) are equal to 2.32 and 2.30 Å. The coordination polyhedron of copper is a strongly flattened tetrahedron with bond angles varying in the range 89–137° (Table 1).

The cation $[Cu{\cdot}15\text{-}C\text{-}5{\cdot}(CH_3CN)_2]^{2+}$ is located in the center of symmetry of complex **II**. Copper is axially coordinated by two acetonitrile molecules (Fig. 2). The Cu(2)–N distance in **II** (1.95 Å) is somewhat lower than that in **I** (1.98 Å) and this is associated with the different structures of the cations. The mean bond lengths Cu(2)–O (2.23(6) Å) (Table 3) are within experimental error the same as in **I**, **III** [2] and the related nitrate complex [3]. Bond angles in the polyhedron are close to ideal ones (∢OCu(2)O–72(1)°, ∢N(1)Cu(2)O–90(4)°) (Table 3).

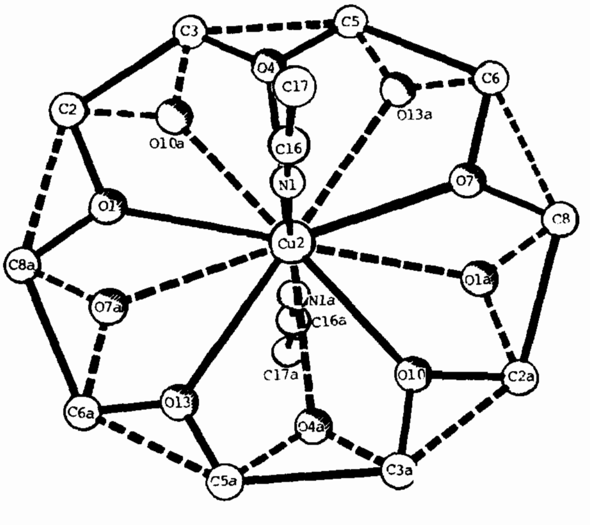

Fig. 2. The structure of the cation $[Cu{\cdot}15\text{-}C\text{-}5{\cdot}(CH_3CN)_2]$ in **II**.

As seen from Fig. 2, the macrocycle in cation **II** is disordered with respect to two equivalent positions, and this is typical of all structures where a metal is located in the center of symmetry. Hence, it is useless to discuss the geometry of the molecule. The 15-C-5 oxygens lie almost in the

TABLE 3. Bond distances and bond angles in the coordination environment of Cu2 in complex **II**

Atoms	Bond distance (Å)
Cu2–N1	1.95(1)
Cu2–O1	2.20(2)
Cu2–O4	2.24(2)
Cu2–O7	2.24(2)
Cu2–O10	2.16(2)
Cu2–O13	2.34(2)
Cu2–N1	1.95(1)
Atoms	Bond angle (°)
N1–Cu2–O1	93.7(5)
N1–Cu2–O4	86.0(5)
N1–Cu2–O7	95.7(6)
N1–Cu2–O10	88.3(5)
N1–Cu2–O13	89.9(5)
N1–Cu2–N1′	180.0
O1–Cu2–O4	70.5(7)
O1–Cu2–O7	142.4(6)
O1–Cu2–O10	143.0(7)
O1–Cu2–O13	71.2(7)
O1–Cu2–N1′	86.3(5)
O4–Cu2–O7	74.0(6)
O4–Cu2–O10	146.4(6)
O4–Cu2–O13	141.1(6)
O4–Cu2–N1′	94.5(5)
O7–Cu2–O10	73.7(7)
O7–Cu2–O13	144.9(6)
O7–Cu2–N1′	84.3(6)
O10–Cu2–O13	71.9(7)
O10–Cu2–N1′	91.7(5)
O13–Cu2–N1′	90.1(6)

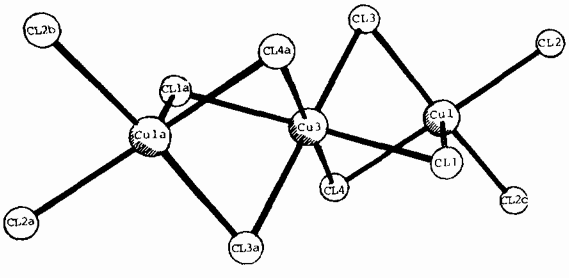

Fig. 3. The structure of the polymeric anion $\{Cu_3Cl_8\}_n^{2-}$ in **II**.

plane. Maximal deviation from the mean square plane is observed for O(7) (0.20 Å). The polygon made up of oxygen atoms has an envelope conformation with oxygen O(4) in the apex.

The anion of **II** is an infinite polymeric chain stretched along the [110] axis and consisting of $[Cu_3Cl_8]_n^{2-}$ units, rather than discrete species as in **I**. It can be seen from Fig. 3 that the polymeric anion consists of alternating fragments A and B with atoms Cu(1) and Cu(3), respectively (in the manner..ABA/ABA/ABA..), bound through bridging chlorides and having different coordination environment. The complexity of the bridging bonds affects both the interatomic distances and the degree of distortion of coordination polyhedrons (Table 4).

The coordination polyhedron of Cu(3) is close to a tetragonal bipyramid with atoms Cl(3), Cl(4), Cl(3a) and Cl(4a) in the equatorial plane. Atoms Cl(1) and Cl(1a) occupy axial positions and are closer to Cu(3). The mean value of the bond angle between axial and equatorial ligands is equal to 90(4)° (Table 4). At the same atoms Cl(1) and Cl(1a) occupy axial positions of coordination polyhedrons of copper Cu(1) and Cu(1a) (tetragonal pyramid), but the distances between the former and the latter are the highest, see Table 4. Bond angles involving Cu(1) and Cu(1a) atoms are rather strongly distorted.

The closest contact between cations and the polymeric anion (atoms Cl(1)–C(16)) is equal to 3.57 Å.

It has been noted [7, 8] that ionic complexes of the type $[MCl_2 \cdot 15\text{-}C\text{-}5][MCl_4]$ ($M = Al$ [7], Fe[8]) are characterized by high thermal stability and decompose with a mass loss at temperatures above 250 °C. In contrast, complexes **I** and **II** solvated by acetonitrile began to decompose at much lower temperatures (86 and 65 °C, respectively) and in a more complex way. Heating thermograms of both the complexes are certainly different, however, one can notice common features (Fig. 4(a), (b)). In particular, the major mass loss (57.5 and 43.3% for **I** and **II**, respectively) occurs at temperatures 50–150 °C in both cases and is due to the first four heat effects. In addition, there is an identical endothermal effect at 370 °C which is not accompanied by a mass loss.

Analytical data suggest that the first steps of decomposition of complexes **I** and **II** (<100 °C) are associated with the dissociation of the acetonitrile ligands. A cleavage of the polyether ring is observed at temperatures higher than 130 °C. This process, complete at 300–340 °C, results in practically the total decomposition of the organic part of the molecule (less than 2% carbon remains in the residue), the formation of copper (2+) chloride (150–200 °C) and its reduction into copper (1+) chloride (>200 °C). The cleavage of a cyclic polyether by Lewis acids may occur under much milder conditions for example, during the syntheses of crown ethers [9, 10]. However, this is not accompanied by a change of oxidation states of metal centers. It is possible that in the case of complexes **I** and **II** copper (2+) is reduced by

TABLE 4. Bond distances and bond angles in the anion $[Cu_3Cl_8]^{2-}$ of complex **II**

Atoms	Bond distance (Å)	Atoms	Bond angle (°)
Cu1–Cl1	2.598(3)	Cl1–Cu1–Cl2	101.6(1)
Cu1–Cl2	2.284(4)	Cl1–Cu1–Cl3	86.6(1)
Cu1–Cl3	2.262(3)	Cl1–Cu1–Cl4	89.1(2)
Cu1–Cl4	2.269(4)	Cl1–Cu1–Cl2c	104.5(1)
Cu1–Cl2c	2.276(3)	Cl2–Cu1–Cl3	92.9(1)
Cu3–Cl1	2.255(3)	Cl2–Cu1–Cl4	169.3(2)
Cu3–Cl3	2.572(5)	Cl2–Cu1–Cl2c	84.1(1)
Cu3–Cl4	2.787(4)	Cl3–Cu1–Cl4	89.1(1)
Cu3–Cl1a	2.255(3)	Cl3–Cu1–Cl2c	168.9(2)
Cu3–Cl3a	2.572(5)	Cl4–Cu1–Cl2c	92.0(1)
Cu3–Cl4a	2.787(4)	Cl1–Cu3–Cl3	87.4(1)
		Cl1–Cu3–Cl4	84.9(1)
		Cl1–Cu3–Cl3a	92.6(1)
		Cl1–Cu3–Cl4a	95.2(1)
		Cl3–Cu3–Cl4	72.6(1)
		Cl3–Cu3–Cl4a	107.4(2)

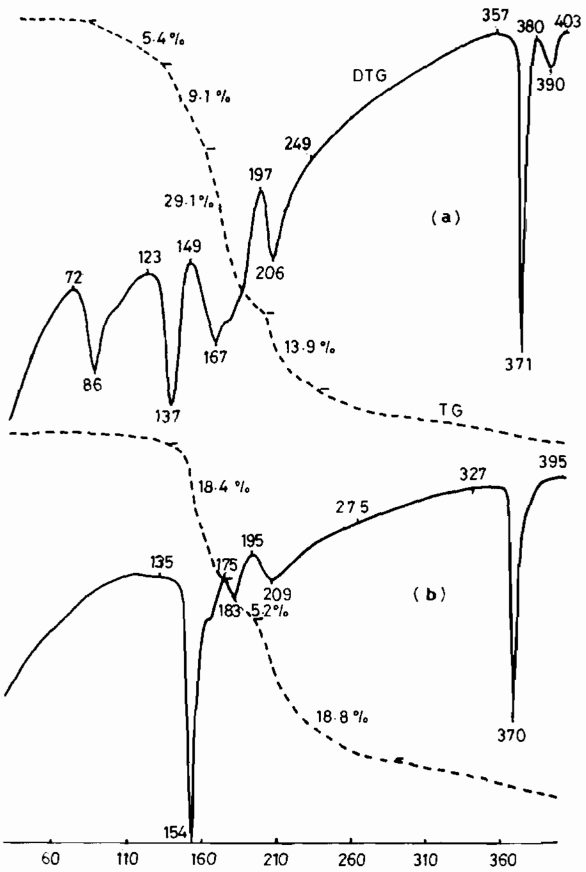

Fig. 4. Thermograms of complexes **I** (a) and **II** (b).

oxoalcohols probably formed on thermolysis of the crown ether.

The exothermal effect at 370 °C is most likely due to the phase transition of cubic CuCl into the high-temperature hexagonal modification [11].

Conclusions

Utilization of acetonitrile as a solvent of moderate donicity (donor numbers 14.1 [12]) for carrying out the complexation between $CuCl_2$ and 15-C-5 does not prevent the incorporation of the metal into the ligand inner cavity. In general, this is in accord with the previous conclusions [7, 8] that the basicity of 15-C-5 is even higher than that of Thf ($DN_{\mathrm{Thf}} = 20.0$ [12]). However, although using an inert solvent (chloroform) in this reaction provides the molecular compound **III** [2] (but the mechanism does involve ionization and dissociation of the Cu–Cl bonds [13]), donor solvents favor the formation and stabilization of complex polynuclear anions and ionization of the molecule as a whole. According to the structural data for **I** and **II**, and the corresponding spectrophotometric data obtained for the system $CuCl_2$–15-C-5–CH_3CN one can expect the formation of various compounds which differ in nuclearity of anions composed of the $[CuCl_4]_n^{2-}$ units.

Experimental

All operations involving the preparation and investigation of **I** and **II** were carried out in inert atmosphere and *in vacuo*.

Anhydrous copper chloride was prepared from $CuCl_2 \cdot 2H_2O$ on refluxing with thionyl chloride for 2 h as described in ref. 14. The presence of moisture was controlled by IR spectroscopy (1600, 3400–3500 cm^{-1}).

Acetonitrile was purified by refluxing and distillation over CaH_2.

Spectrophotometric and conductometric investigations were made according to the standard procedures. Thermograms were registered on a differential microcalorimeter Setaram DSC 111 in helium atmosphere.

Synthesis of $[CuCl \cdot 15\text{-}C\text{-}5 \cdot CH_3CN]_2[Cu_2Cl_6]$ (**I**)

Anhydrous $CuCl_2$ (1.2 g, 0.009 M) was dissolved under reflux for 30 min in 200 ml anhydrous acetonitrile. The hot solution was filtered, cooled and 15-C-5 (1.8 ml, 0.009 M) added on mixing. The orange solution was concentrated twofold *in vacuo* to initiate the precipitation of a light yellow amorphous material which was then separated. Orange crystals of complex **I** began to grow from the transparent filtrate after 1 h. These were separated and dried *in vacuo* at ambient temperature; *ca.* 0.9 g of monocrystals was obtained. *Anal.* Found: Cu, 24.0; Cl, 26.0; C, 27.1; H, 4.2; N, 2.4. Calc. for $C_{12}H_{23}O_5NCu_2Cl_4$: Cu, 24.0; Cl, 26.8; C, 27.2; H, 4.4; N, 2.6%.

The same complex was obtained when $CuCl_2 \cdot 2H_2O$ was used instead of the anhydrous salt.

Synthesis of $[Cu \cdot 15\text{-}C\text{-}5 \cdot (CH_3CN)_2][Cu_3Cl_8]$ (**II**)

Anhydrous $CuCl_2$ (1.6 g, 0.012 M) was dissolved under reflux for 30 min in 200 ml acetonitrile. The hot solution was filtered, cooled and 15-C-5 (0.8 ml, 0.004 M) added on mixing. The orange solution formed was concentrated *in vacuo* to 50–60 ml to induce rapid crystallization of the brown complex **II**. The precipitate was separated and dried *in vacuo* at ambient temperature to afford 1.1 g of monocrystals. *Anal.* Found: Cu, 31.4; Cl, 33.3; C, 19.8; H, 2.8; N, 3.1. Calc. for $C_{14}H_{26}O_5N_2Cu_4Cl_8$: Cu, 30.3; Cl, 33.7; C, 20.0; H, 3.1; N, 3.3%.

An X-ray structural investigation of monocrystals of **I** and **II** sealed in glass capillary tubes was

TABLE 5. Atom coordinates (× 10^4) and temperature factors (A^2 × 10^3) in complex **I**

Atom	*x*	*y*	*z*	U^a
Cu(1)	9262(1)	339(1)	5764(1)	56(1)
Cu(2)	6932(1)	3739(1)	4609(1)	57(1)
Cl(1)	9668(1)	1709(1)	6982(1)	75(1)
Cl(2)	9506(1)	429(20)	4065(14)	74(9)
Cl(3)	7665(1)	−424(2)	5816(2)	82(1)
Cl(4)	6617(2)	4653(2)	3281(1)	79(1)
O(1)	5922(45)	1730(50)	4266(37)	84(27)
C(2)	4926(71)	1621(87)	4309(78)	103(48)
C(3)	4792(62)	2219(88)	5258(76)	91(45)
O(4)	5439(41)	3512(55)	5231(41)	81(27)
C(5)	5519(7)	4191(8)	6119(7)	101(5)
C(6)	6343(7)	5447(8)	6002(7)	106(5)
O(7)	7137(4)	5356(5)	5571(4)	91(3)
C(8)	8049(7)	6326(7)	5657(7)	100(4)
C(9)	8694(7)	6272(8)	4871(7)	106(4)
O(10)	8617(4)	5010(5)	4751(4)	88(3)
C(11)	9127(6)	4786(10)	3931(7)	98(5)
C(12)	8783(7)	3362(10)	3824(7)	99(5)
O(13)	7771(4)	2914(5)	3632(4)	78(2)
C(14)	7319(8)	1588(8)	3517(6)	98(5)
C(15)	6227(7)	1291(7)	3406(6)	97(4)
C(16)	7274(5)	2499(6)	6542(5)	53(3)
C(17)	7356(5)	1960(7)	7503(5)	71(3)
N	7195(4)	2909(5)	5804(4)	63(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{i,j}$ tensor.

performed on a Syntex $\bar{1}$ diffractometer (MoK_α irradiation, Nb-filter, $\theta/2\theta$ scanning up to 2θ (max) = 50°).

Crystals of **I** are monoclinic: $a = 14.732(5)$, $b = 11.357(4)$, $c = 13.520(3)$ Å, $\gamma = 112.25(2)°$, $V = 2093(1)$ Å^3, space group, $P2_1/a$, $Z = 4$. A total of 1891 reflections with $I \geqslant 3\sigma(I)$ from a total of 2350 was selected for the calculation. No correction for absorption was made ($\mu = 26.2$ cm^{-1}).

Crystals of **II** are triclinic: $a = 9.762(2)$, $b = 9.644(2)$, $c = 9.353(2)$ Å, $\alpha = 95.02(2)$, $\beta = 97.80(2)$, $\gamma = 122.53(2)°$, $V = 7218(4)$ Å^3, space group, $P\bar{1}$, $Z = 1$. A total of 1637 reflections with $I \geqslant 3\sigma(I)$ from a total 2020 was selected for the calculation. No correction for absorption was made ($\mu = 17.2$ cm^{-1}).

The structure of **I** was solved by the heavy atom method; that of **II** by combination of the heavy atom and direct methods. The structures were refined by the full-matrix least-square routine in anisotropic approximation for non-hydrogen atoms (hydrogen were refined isotropically). The final values of *R* factors were: $R^{\text{I}} = 0.043$ ($R_w^{\text{I}} = 0.046$) and $R_w^{\text{II}} = 0.062$ ($R_w^{\text{II}} = 0.069$). Atomic coordinates and equivalent temperature factors for complexes **I** and **II** are shown in Tables 5 and 6.

TABLE 6. Atom coordinates (× 10^4) and temperature factors (A^2 × 10^3) in complex **II**

Atom	*x*	*y*	*z*	U^a
Cu(1)	8568(1)	2975(1)	5050(1)	44(1)
Cu(2)	5000	5000	0	38(1)
Cu(3)	5000	0	5000	40(1)
Cl(1)	5762(3)	2671(3)	5080(3)	51(1)
Cl(2)	9501(4)	4607(4)	3323(3)	67(2)
Cl(3)	7080(5)	575(4)	3346(4)	107(2)
Cl(4)	8116(6)	1427(4)	6837(4)	105(3)
N(1)	3776(12)	3918(12)	−2019(10)	44(5)
C(16)	3055(14)	3322(14)	−3194(14)	43(6)
C(17)	2060(22)	2513(23)	−4666(16)	67(10)
O(1)	6704(21)	4189(18)	−113(16)	61(10)
O(4)	3823(24)	2406(21)	470(17)	65(10)
O(7)	2784(21)	4463(20)	898(18)	66(10)
O(10)	4701(26)	7019(22)	−310(19)	77(13)
O(13)	7286(28)	7012(23)	−853(22)	75(12)
C(2)	6248(21)	2693(20)	−189(18)	109(11)
C(3)	4524(30)	1770(20)	823(16)	129(16)
C(5)	2718(27)	1903(26)	1205(26)	160(17)
C(6)	1580(23)	2982(30)	877(25)	159(15)
C(8)	2020(18)	5137(23)	550(19)	115(11)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{i,j}$ tensor.

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