

Structure of bis(triethylammonium) bromochlorocuprates(II) as a function of their composition

Z. BIELA and J. GAŽO

Department of Inorganic Chemistry, Slovak Technical University,
880 37 Bratislava

Received 19 September 1980

Compounds $[(C_2H_5)_3NH]_2CuCl_4$ (I), $[(C_2H_5)_3NH]_2CuCl_3Br$ (II), $[(C_2H_5)_3NH]_2CuCl_2Br_2$ (III), $[(C_2H_5)_3NH]_2CuClBr_3$ (IV), and $[(C_2H_5)_3NH]_2CuBr_4$ (V) were prepared by crystallization from ethanolic solutions. Changes in the composition of the complexes were accompanied by changes in the structure of the coordination polyhedron from a distorted tetrahedron of various degree of distortion up to a distorted octahedron. In consonance with this fact, the $d-d$ transition energies as well as the values of the g factors correspond to a compressed tetrahedron in the case of compounds I, II, and III, and to an elongated octahedron in the case of compounds IV and V.

Кристаллизацией из этанольного раствора были приготовлены соединения $[(C_2H_5)_3NH]_2CuCl_4$ (I), $[(C_2H_5)_3NH]_2CuCl_3Br$ (II), $[(C_2H_5)_3NH]_2CuCl_2Br_2$ (III), $[(C_2H_5)_3NH]_2CuClBr_3$ (IV), $[(C_2H_5)_3NH]_2CuBr_4$ (V). Изменения в составе комплекса приводят к изменению структуры координационного полиэдра от деформированного тетраэдра с различной степенью искажения до деформированного октаэдра. С этим согласуются также энергии $d-d$ переходов и также значения g факторов: у соединений I, II, III они принимают значения типичные для сжатого тетраэдра, а у IV и V имеют значения типичные для удлиненного октаэдра.

The symmetry of the complex anions in tetrahalocuprates(II) is strongly determined by the cation. When the cation is unable to form hydrogen bonds, the decisive factor appears to be its size. Small cations such as K^+ or NH_4^+ stabilize the D_{4h} symmetry (elongated octahedron or a square planar structure). More voluminous cations, e.g. Cs^+ , stabilize the D_{2d} symmetry (compressed tetrahedron). Cations capable to form hydrogen bonds with anions also stabilize the D_{4h} symmetry, but their size loses the decisive role. For instance, compounds $(C_nH_{2n+1}NH_3)_2CuCl_4$, having good possibility for the $NH...Cl$ hydrogen bond formation, contain complex anions of the D_{4h} symmetry in the whole interval of n

(1—18) so far examined [1, 2]. In these complex anions the axial Cu—Cl distance is proportional to the cation volume. In disubstituted alkylammonium salts which have much reduced possibility for hydrogen bond formation, the situation is more complex. For example, the changes in the structure of the complex ions in compounds $[(C_2H_5)_2NH_2]_2CuCl_4$ [3] and $[C_6H_5CH_2\overset{\oplus}{N}H_2CH_3]_2CuCl_4$ [4] induced by temperature changes are also accompanied by colour changes. An analogous phenomenon was also observed with a chlorocuprate(II) containing a monosubstituted branched alkylammonium cation — $[(CH_3)_2CHNH_3]_2CuCl_4$. X-ray analysis provided a clear evidence that the above complex kept at room temperature, contains complex anions having both tetrahedral and octahedral structures [5]. Trialkylammonium tetrachlorocuprates(II) represent complexes with a restricted possibility of hydrogen bond formation. In tetraalkylammonium salts the hydrogen bonds are out of consideration. Thus both these types of tetrachlorocuprates(II) contain, as a rule, complex anions of distorted tetrahedral structures.

The present paper describes some effects of the changes in the coordination sphere of tetrahalocuprates(II) on the structure of the coordination polyhedron. Bromine as a ligand behaves similarly as chlorine, but shows slight differences in the volume, position in the spectrochemical series, and binding ability. All bromochlorocuprates(II) studied up to the present [6, 7] did not exhibit any changes in the structure of the coordination polyhedron due to chlorine-bromine replacements. However, all these complexes contain alkylammonium cations in which the effect of hydrogen bonds is strong enough to preserve the planar structure of anions even after the ligand exchange. In the present work we investigated tetrahalocuprates(II) containing triethylammonium cation. Only weak hydrogen bonds occur in $[(C_2H_5)_3NH]_2CuCl_4$, in which the complex anion has a D_{2d} symmetry [8]. Anyway, the hydrogen bonds exist here, therefore they can contribute to certain structural changes of the complex anion after the ligand replacement.

Experimental

Chemicals and equipments

The following chemicals were used: $CuCl_2$, prepared by dehydration of the dihydrate; $CuBr_2$, prepared as described in [9]; $Et_3N \cdot HCl$ and $Et_3N \cdot HBr$ ($Et = C_2H_5$) obtained by neutralization of aqueous solution of triethylamine and subsequent recrystallization from ethanol.

X-ray powder diffraction patterns were recorded on a goniometer GON III, electronic spectra were measured in Nujol suspension in the visible spectral region with a Specord UV VIS 200 spectrophotometer and in the close infrared region ($5000—14\ 000\ cm^{-1}$) with

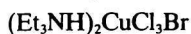
a Unicam SP 700 equipment. The e.s.r. spectra of polycrystalline samples were recorded on a Varian E-4 instrument, and the thermic measurements were done on a derivatograph MOM, Budapest.

Analytical procedures

Copper was determined complexometrically with Chelaton III and halides argentometrically using potentiometric indication.

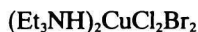
Preparation of bromochlorocuprates(II)

Preparation of $(\text{Et}_3\text{NH})_2\text{CuCl}_4$ is described elsewhere [10].



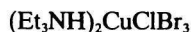
A solution of CuCl_2 (1.6 g) in ethanol (15 ml) was mixed with a solution of $\text{Et}_3\text{N}\cdot\text{HBr}$ (1.6 g) and $\text{Et}_3\text{N}\cdot\text{HCl}$ (1.3 g) in ethanol (25 ml). Crystallization at 0°C afforded bright red crystals which were washed with a small volume of anhydrous ethanol and dried with ether.

For $(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$ calculated: 13.97% Cu, 23.41% Cl, 17.59% Br; found: 14.15% Cu, 23.61% Cl, 17.68% Br.



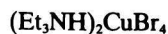
A solution of CuBr_2 (2 g) in ethanol (20 ml) was mixed with a solution of $\text{Et}_3\text{N}\cdot\text{HCl}$ (2.75 g) in ethanol (20 ml). After cooling, dark red crystals were separated, washed with anhydrous ethanol and dried with ether. The same product was obtained on mixing a CuCl_2 (1.5 g) solution in ethanol (15 ml) with a solution of $\text{Et}_3\text{N}\cdot\text{HBr}$ (3.25 g) in ethanol (25 ml).

For $(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$ calculated: 12.54% Cu, 14.42% Cl, 32.17% Br; found: 12.70% Cu, 14.31% Cl, 32.20% Br.



A solution of CuBr_2 (2 g) in ethanol (20 ml) was mixed with a solution of $\text{Et}_3\text{N}\cdot\text{HCl}$ (1.55 g) and $\text{Et}_3\text{N}\cdot\text{HBr}$ (0.9 g) in ethanol (20 ml). After crystallization at 0°C , dark red crystals were separated, washed with ethanol and dried with ether.

For $(\text{Et}_3\text{NH})_2\text{CuClBr}_3$ calculated: 11.69% Cu, 6.52% Cl, 44.14% Br; found: 11.81% Cu, 6.51% Cl, 44.49% Br.



CuBr_2 (2 g) in ethanol (20 ml) was reacted with a solution of $\text{Et}_3\text{N}\cdot\text{HBr}$ (2.5 g) in ethanol (20 ml) to give dark violet crystals, which were washed with ethanol and dried with ether.

For $(\text{Et}_3\text{NH})_2\text{CuBr}_4$ calculated: 10.81% Cu, 54.40% Br; found: 11.01% Cu, 54.42% Br.

It should be noted that by changing the ratio Cu : Cl : Br in the starting solution, compounds of the general formula $(\text{Et}_3\text{NH})_2\text{CuCl}_x\text{Br}_{4-x}$, in which x is not an integer, can be prepared.

All the prepared products are hygroscopic. Unstable are particularly the compounds with high content of bromine. Their decomposition was observed even under dry conditions.

Results and discussion

The X-ray diffraction patterns of bromochlorocuprates(II) studied in our previous works [6, 7] pointed to identity of crystal structures of complexes with varying content of chlorine and bromine (unless they had a common cation). Bromochlorocuprates(II) containing the triethylammonium cation, according to the diffraction patterns, do not appear to be isostructural. Some characteristic diffraction lines are listed in Table 1. The diffraction patterns of $(\text{Et}_3\text{NH})_2\text{CuCl}_4$ (I) and $(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$ (II) are very similar, so one may infer that both compounds possess the same crystal structure. However, the diffraction patterns of $(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$ (III), $(\text{Et}_3\text{NH})_2\text{CuClBr}_3$ (IV), and $(\text{Et}_3\text{NH})_2\text{CuBr}_4$ (V) differ in the number of characteristic lines.

The electronic absorption spectra of the compounds recorded in the visible region in Nujol suspensions are shown in Fig. 1. With increasing content of bromine in the complex, a shift of the charge-transfer bands to lower energies is observed. The resulting absorption bands arising by superposition of several bands are very wide, particularly with complexes III and IV. The spectra could not be

Table 1
Diffraction maxima of bis(triethylammonium) tetrahalocuprates(II)

Compound	2θ [°]				
$(\text{Et}_3\text{NH})_2\text{CuCl}_4$	11.3	12.4	14.5	16.6	19.8
$(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$	11.3	12.3 12.5	14.4	16.8	19.75
$(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$	11.2	11.9		16.5	20 20.7 21.4
$(\text{Et}_3\text{NH})_2\text{CuClBr}_3$		11.7		16.3	20.3
$(\text{Et}_3\text{NH})_2\text{CuBr}_4$	11.4	12.2 12.4	14.6		19.2

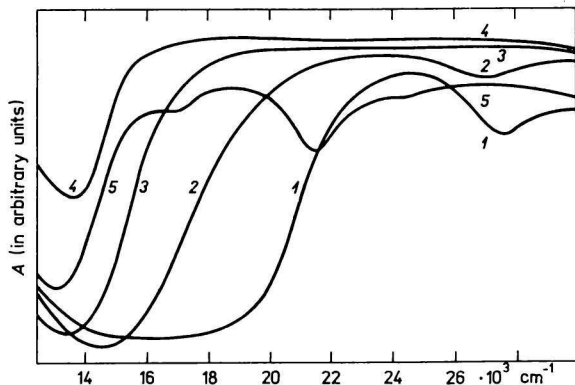


Fig. 1. Electronic absorption spectra.

1. $(\text{Et}_3\text{NH})_2\text{CuCl}_4$; 2. $(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$; 3. $(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$; 4. $(\text{Et}_3\text{NH})_2\text{CuClBr}_3$;
5. $(\text{Et}_3\text{NH})_2\text{CuBr}_4$.

Measured in Nujol suspension.

reliably resolved to Gaussian curves assignable to individual complex species. An apparent dependence of the symmetry of the coordination polyhedron on its composition is reflected in the maxima of the ligand field bands (Table 2). The spectra exhibit one common feature, a wide absorption band with a shoulder on the side of lower energies. Its maximum is influenced by substitution of chlorine by bromine.

In the tetrachlorocopper(II) complexes having the D_{2d} symmetry the energy of the highest $d-d$ transition is $\approx 9000 \text{ cm}^{-1}$ [8, 11]. In regard to the position of chlorine and bromine in the spectrochemical series one would expect that this energy will be somewhat lower in tetrabromocuprates(II) unless the same symmetry is preserved. In fact, with compound *II* a slight shift towards lower energies occurs and the value ν_{max} remains the same also in the case of compound *III*. From these facts we infer that the distortion of the tetrahedron is equal in all three cases.

Table 2

Maxima of the ligand field bands

Compound	$\nu_{\text{max}}/\text{cm}^{-1}$	
$(\text{Et}_3\text{NH})_2\text{CuCl}_4$	9100	6600 sh
$(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$	8850	6500 sh
$(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$	8900	6300 sh
$(\text{Et}_3\text{NH})_2\text{CuClBr}_3$	9800	6800 sh
$(\text{Et}_3\text{NH})_2\text{CuBr}_4$	11600	10000 sh

A clear shift of the maximum of the absorption band of *IV* indicates an increasing tetrahedral distortion, even more pronounced with *V*. The energy of the highest $d-d$ transition of tetrabromocuprates(II) of the D_{4h} symmetry was reported to be $\approx 13\,000\text{ cm}^{-1}$ [7], i.e. the structure of compound *V* is close to a planar one.

The e.s.r. spectra of polycrystalline samples were recorded in the temperature interval from -160 to 30°C . The g factors calculated from them (Table 3) are in a good correlation with the electronic spectral data. For Cs_2CuCl_4 in which CuCl_4^{2-} is of the D_{2d} symmetry, Ref. [12] gives for the g_{\perp} and g_{\parallel} values 2.08 and 2.38, respectively. These values are substantially lower for tetrachlorocuprates(II) of the D_{4h} symmetry, 2.05 (g_{\perp}) and 2.23 (g_{\parallel}) [11] and 2.27 (g_{\parallel}) [13].

Table 3
ESR data of bis(triethylammonium) tetrahalocuprates(II)

Compound	293 K			133 K		
	g_{\parallel}	g_{\perp}	g_{av}	g_{\parallel}	g_{\perp}	g_{av}
$(\text{Et}_3\text{NH})_2\text{CuCl}_4$	2.358	2.042	2.147	2.354	2.051	2.152
$(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$	2.348	2.050	2.149	2.345	2.053	2.150
$(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$			2.142	2.337	2.064	2.155
$(\text{Et}_3\text{NH})_2\text{CuClBr}_3$	2.264	2.040	2.115			2.114
$(\text{Et}_3\text{NH})_2\text{CuBr}_4$	2.238	2.038	2.105	2.228	2.038	2.102

According to the energies of the $d-d$ transitions, the tetrahalocuprate(II) anion in compounds *I*, *II*, and *III* can be considered for a distorted tetrahedron. This conclusion is supported by the g factor values obtained. A clear shift of the absorption maxima of the ligand field bands of *IV* and, particularly, of *V* towards higher energies indicates a distortion of the tetrahedron almost to a planar structure. Significant changes of the corresponding g factors are also in consonance with the above fact and their values are consistent with the D_{4h} symmetry. An interesting fact is that the character of the e.s.r. spectrum was found to be temperature-dependent only in the case of *III* and *IV*, i.e. on the boundary of the coordination polyhedral symmetry. In the interval from 0 to -20°C the spectrum of *III* was changed from an isotropical to an axial, while under the same conditions the spectrum of *IV* was changed from an axial to an isotropical. The g_{av} value was almost temperature-independent, which means that the coordination polyhedron did not undergo substantial changes.

Interesting results were obtained by studying thermal properties of the prepared complexes. The following melting points were determined on an electric stage: *I*, $71-72^\circ\text{C}$; *II*, $87-89^\circ\text{C}$; *III*, $94-95^\circ\text{C}$; *IV*, $86-88^\circ\text{C}$; *V*, $71-73^\circ\text{C}$. An

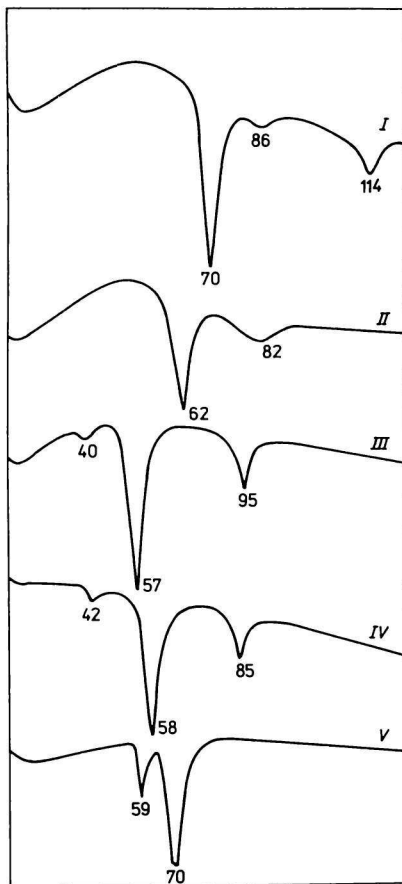


Fig. 2. DTA curves.
 I. $(\text{Et}_3\text{NH})_2\text{CuCl}_4$;
 II. $(\text{Et}_3\text{NH})_2\text{CuCl}_3\text{Br}$;
 III. $(\text{Et}_3\text{NH})_2\text{CuCl}_2\text{Br}_2$;
 IV. $(\text{Et}_3\text{NH})_2\text{CuClBr}_3$;
 V. $(\text{Et}_3\text{NH})_2\text{CuBr}_4$.

endothermic change occurring at the same temperatures is apparent from the DTA curves (Fig. 2). A striking observation is that the melting points of bromochlorocuprates(II) (II, III, and IV) do not correspond to the most pronounced thermal effect occurring much earlier, at temperatures around 60°C . Microscopic examination showed that at about 60°C the crystals significantly darken, but do not melt. We assume that this phase transition is associated with a structural change.

The presented results represent an experimental evidence that even a small change in the coordination sphere of a Cu(II) complex may bring about a considerable change in the polyhedral symmetry. In the case of halocopper(II) complexes this process can be strongly influenced by a selection of proper cations and thus compounds of a desired structure can be prepared.

References

1. Arriandiaga, M. A., Tello, M. J., Fernandez, J., Arend, H., and Roos, J., *Phys. Status Solidi* 48, 53 (1978).
2. Mischgofsky, F. H. and Delhez, R., *J. Cryst. Growth* 44, 145 (1978).
3. Willett, R. D., Haugen, J. A., Lebsack, J., and Morrey, J., *Inorg. Chem.* 13, 2510 (1974).
4. Harlow, R. L., Wells, W. J., Watt, G. W., and Simonsen, S. H., *Inorg. Chem.* 13, 2106 (1974).
5. Anderson, D. N. and Willett, R. D., *Inorg. Chim. Acta* 8, 167 (1974).
6. Biela, Z., Obert, T., Melník, M., and Gažo, J., *Chem. Zvesti* 29, 56 (1975).
7. Biela, Z. and Gažo, J., *Chem. Zvesti* 35, 21 (1981).
8. Lamotte-Brasseur, J., *Acta Crystallogr.* A30, 487 (1974).
9. Karyakin, Y. V. and Angelov, I. I., *Chistye khimicheskie reaktivy*. Goskhimizdat, Moscow, 1955.
10. Lamotte-Brasseur, J., Dideberg, O., and Dupont, L., *Cryst. Struct. Commun.* 1972, 313.
11. Willett, R. D., Liles, O. L., and Michelson, C., *Inorg. Chem.* 6, 1885 (1967).
12. Sharnoff, M., *J. Chem. Phys.* 41, 2203 (1964).
13. Drumheller, J. E., Amundson, P. H., and Emerson, K., *J. Chem. Phys.* 51, 5729 (1969).

Translated by P. Biely