

# Preparation and properties of chlorobromocopper(II) complexes of composition $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$

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Received 19 June 1974

Compounds  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  ( $x = 0-4$ ) were obtained by crystallization from ethanol solutions, by bromine oxidation of a chlorocopper(II) complex and by solid state interaction. Newly prepared substances were characterized by X-ray powder patterns, electronic crystal, nujol, and e.p.r. spectra. Chlorobromocopper(II) complexes were found to be isostructural with homogeneous halo complexes. Square-planar structure of the complex anion is preserved also in the heterogeneous coordination sphere. Regardless of the mode of preparation, no evidence has been obtained for the formation of isomers or modifications of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ .

Halocopper(II) complexes containing in the coordination sphere two different halogens were investigated in a much lesser extent than the halo complexes with homogeneous coordination sphere. Only two series of chlorobromocopper(II) complexes of the type  $\text{A}_2\text{CuX}_4$  are known:  $[(\text{CH}_3)_3\text{NH}]_2\text{CuCl}_x\text{Br}_{4-x}$  [1] and  $[\text{Li}(\text{diacetamide})_2]_2\text{CuCl}_x\text{Br}_{4-x}$  [2].  $[\text{Li}(\text{diacetamide})_2]_2\text{CuCl}_2\text{Br}_2$  was prepared by *Gentile et al.* [2] in two colour forms, green and brown, differing in the absorption spectra and in the values of magnetic moments. In addition, the complex  $[\text{Cr}(\text{NH}_3)_6]\text{CuCl}_2\text{Br}_3$  has also been described [3, 4].

In the present paper we deal with different ways of preparation of the compounds  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  ( $x = 1, 2, 3$ ) and with some of their physicochemical properties. The main purpose of this investigation was to find out how is influenced the symmetry of the complex anion by the heterogeneity of the coordination sphere. Therefore the structures of the compounds synthesized were elucidated using spectral methods. Since the ion  $\text{CuCl}_4^{2-}$  in  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  is square planar [5], there is a theoretical possibility of the formation of *cis* and *trans* isomers of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ .

## Experimental

### *Chemicals and equipments*

The following chemicals were used:  $\text{CuCl}_2$ , prepared by dehydration of the dihydrate;  $\text{CuCl}$ , prepared from  $\text{Cu}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  and  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$ , prepared by neutralization of methylamine solution and recrystallized from ethanol;  $\text{CuBr}_2$ , prepared as described in [6].

Powder diffraction patterns were recorded with a goniometer GON III, electronic crystal spectra with a CARY spectrophotometer (model 14), electronic spectra in nujol suspension with a UV-VIS 200 spectrophotometer, e.p.r. spectra with a Varian E3 spectrometer at room temperature, and frequency 9300 MHz using polycrystalline samples.

*Analytical procedures*

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

*Preparation of chlorobromocopper(II) complexes*

Chlorobromocopper(II) complexes were prepared by three procedures:

- A. crystallization from ethanol solution;
- B. bromine oxidation of chlorocopper(I) complex;
- C. solid state interaction of the components.

This type of compounds cannot be obtained by crystallization from water solutions.

*A. Preparation of chlorobromocopper(II) complexes by crystallization from ethanol solution**Preparation of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$* 

$\text{CuCl}_2$  (2 g) was dissolved in ethanol (30 ml) and  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$  (1.5 g) in ethanol (40 ml). After filtration, the solutions were mixed and left to crystallize at  $0^\circ\text{C}$ . The separated red lustrous crystals were washed with a small amount of anhydrous ethanol and finally dried with ethyl ether. The same product was isolated starting from solutions of  $\text{CuBr}_2$  (1 g) in ethanol (15 ml) and  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  (1 g) in ethanol (25 ml) processed in the same manner.

*Analysis:* 20.65% Cu, 33.95% Cl, 25.60% Br, 8.90% N.

For  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$  calculated: 20.23% Cu, 33.91% Cl, 25.47% Br, 8.92% N.

*Preparation of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$* 

A solution of  $\text{CuCl}_2$  (1 g) in ethanol (10 ml) was mixed with a solution of  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$  (6.5 g) in ethanol (90 ml). Crystallization at  $0^\circ\text{C}$  gave dark red lustrous crystals which were separated and washed with small volumes of dry ethanol and ethyl ether.

For  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$  calculated: 17.52% Cu, 19.80% Cl, 44.63% Br, 7.81% N; found: 17.40% Cu, 19.60% Cl, 44.0% Br, 7.75% N.

An attempt to prepare the complex  $(\text{CH}_3\text{NH}_3)_2\text{CuClBr}_3$  by crystallization from ethanol solution was not successful.

In addition to  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  ( $x = 1, 2$ ), it is possible to crystallize from ethanol solutions also substances in which  $x$  is not an integer.

*B. Preparation of a chlorobromocopper(II) complex by oxidation of a chlorobromocopper(I) complex*

Red powder, analysis of which corresponded to the formula  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$  was obtained after treatment of fine-ground  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3$  by bromine vapour at room temperature for 48 hrs. Starting complex  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3$  crystallized from ethanol solution containing  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  and  $\text{CuCl}$  in the molar ratio 1 : 2, in the absence of air oxygen [7].

*C. Preparation of chlorobromocopper(II) complexes by solid state interaction*

Grinding of  $\text{CuCl}_2$  or  $\text{CuBr}_2$  with  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  and/or  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$  gave rise to substances of various colours, depending on the  $\text{Cl}^- : \text{Br}^-$  molar ratio in the starting mixtures, ranging from brick red (for  $\text{Cl}^-/\text{Br}^- > 1$ ) to dark violet (for  $\text{Cl}^-/\text{Br}^- < 1$ ).

This method led to the preparation of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$ ,  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ , and  $(\text{CH}_3\text{NH}_3)_2\text{CuClBr}_3$ . However, it was possible to obtain substances with any Cl-/Br- ratio wanted.

### Results and discussion

Powder diffraction patterns pointed out the solid state interaction of  $\text{CuCl}_2$  and  $\text{CuBr}_2$  with  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  and/or  $\text{CH}_3\text{NH}_2 \cdot \text{HBr}$  does not proceed in the absence of the air moisture. In such a case, only a mechanical mixture of the starting components is obtained. When  $\text{CuCl}_2$  is replaced by its dihydrate, or when the components are ground in air, chlorobromocopper(II) complexes are gradually formed. Addition of a few drops of a solvent (*e.g.* ethanol) considerably accelerates the reaction rate. The X-ray powder diffraction patterns of the chlorobromocopper(II) complexes show great similarities. Values of the  $2\theta$  angles of individual diffraction maxima are given in Table 1. For comparison, the values for chloro- and bromocopper(II) complex prepared in an analogous way, are presented.

The number of diffraction lines remains essentially the same. Their position is slightly, but regularly, shifted to lower  $2\theta$  values with increasing amount of bromine in the substances. These results implicate that the mixed complexes are isomorphous with homogeneous halo complexes. Such mixed crystals could be formed either by substitution of chlorine by bromine or by substitution of  $\text{CuCl}_4$  group by  $\text{CuBr}_4$ . Such a phenomenon was observed by *Goldfield* and *Raymond* [4] in the case of  $[\text{Cr}(\text{NH}_3)_6]\text{CuCl}_5$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{CuCl}_2\text{Br}_3$ , and  $[\text{Cr}(\text{NH}_3)_6]\text{CuBr}_5$ . These complexes are isostructural; establishment of the structure of the chlorobromo complex showed that atoms of chlorine and bromine are statistically distributed at axial and equatorial positions.

The octahedral symmetry of ligands around the central atom is distorted in  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4 \cdot \text{Cu}$ —Cl distances at axial positions are longer than Cu—Cl distances in the plane [5]. The structure of the complex anion can be considered as approxi-

Table 1

Diffraction maxima of chloro-, bromo-, and chlorobromocopper(II) compounds

Compound	$2\theta$ [°]								
A. $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	9.8	17.8		28.9	31.1	34.7	36	38.1	38.85
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$	9.6	17.85	24.4	28.3	30.9	34.75	36	37.6	38
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$	9.5	17.8	24.3	28	30.7	34.55	35.9	37.1	37.5
$(\text{CH}_3\text{NH}_3)_2\text{CuBr}_4$	9.5	17.05		28.1	30.1	32.9	34.25	36.8	37.7
					29.7				
B. $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$	9.4	17.7	24.3	28.1	30.8	34.6	35.8	37.3	37.8
C. $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	9.4	17.6	24	28.6	30.8	34.5	35.9	37.9	38.5
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$	9.3	17.7	24.2	28	30.7	34.5	35.8	37.2	37.6
$\text{CuCl}_2 + 2\text{CH}_3\text{NH}_2 \cdot \text{HBr}$	9.3	17.7	24.3	27.9	30.6	34.5	35.7	37	37.3
$\text{CuBr}_2 + 2\text{CH}_3\text{NH}_2 \cdot \text{HCl}$	9.3	17.7	24.3	27.8	30.6	34.5	35.7	37	37.3
$(\text{CH}_3\text{NH}_3)_2\text{CuClBr}_3$	9.3	17.3	23.6	27.8	30.1	33.6	34.8	36.7	37.3
$(\text{CH}_3\text{NH}_3)_2\text{CuBr}_4$	9.1	16.9		28	29.5	32.8	34.1	36.7	37.5
					30				

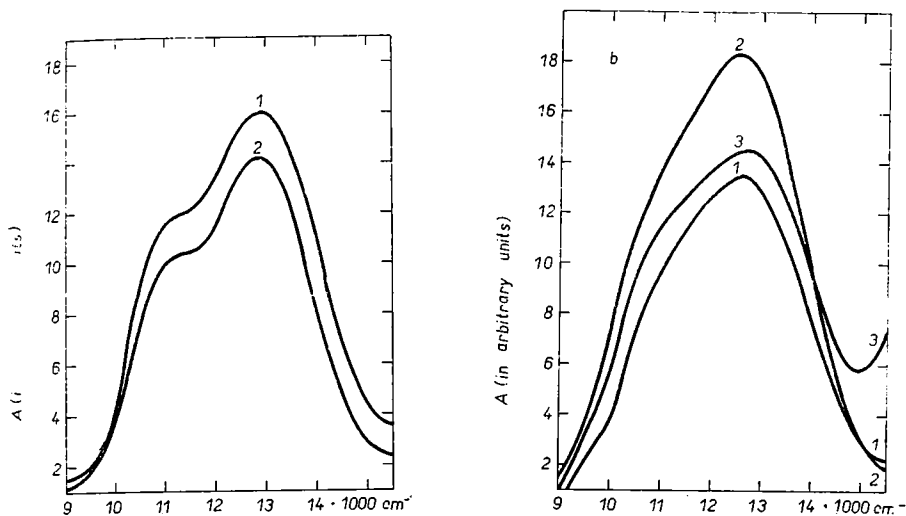


Fig. 1. Electronic absorption spectra in the infrared region.

a) at 77 K; b) at 295 K.

1.  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ ; 2.  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$ ; 3.  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ .

mately planar with weak axial perturbations. In the case of dichlorodibromocopper(II) complex, there is a theoretical possibility of the formation of two stereoisomers. However, in here described experiments, no evidence has been obtained for the existence of such isomers. As seen in Table 1, the diffraction patterns of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$  are identical regardless of the mode of its preparation. So are the reflection spectra and electronic absorption spectra in nujol.

The electronic crystal spectrum of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  shows two bands with maxima at 13 000 and 10 700  $\text{cm}^{-1}$  corresponding to  $d-d$  transitions [8]. The single crystal spectrum recorded at  $-196^\circ\text{C}$  has three maxima at 10 800, 12 200, and 13 300  $\text{cm}^{-1}$

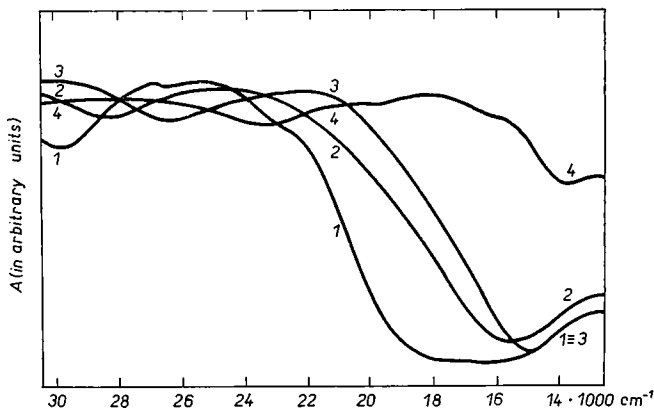


Fig. 2. Nujol absorption spectra of complexes.

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

[9]. The energies of the  $d-d$  transitions calculated for the planar complex ion  $\text{CuCl}_4^{2-}$  correspond to 10 700, 11 500, and 14 100  $\text{cm}^{-1}$  [10].

The electronic absorption spectra of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$  and  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$  (Figs. 1a and 1b) have the same character as that of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  investigated by Willett *et al.* [8]. Based on the close energy values of the ligand field bands, one can assume that the complex anions  $\text{CuCl}_3\text{Br}_2^-$  and  $\text{CuCl}_2\text{Br}_2^-$  possess the same symmetry, that means, square planar arrangement of halogens. The same is true for the character of the nujol absorption spectra in the region of the  $d-d$  transitions. All the prepared substances exhibit a broad absorption band with a maximum around 12 800  $\text{cm}^{-1}$ . The charge transfer bands show an apparent shift to lower energies with gradual substitution of chlorine by bromine (Fig. 2), which is in good agreement with their position in the spectrochemical series.

Table 2

The e.p.r. data of halocopper(II) compounds

Compound	$g_{av}$
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	2.13
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_3\text{Br}$	2.12
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$	2.13
$(\text{CH}_3\text{NH}_3)_2\text{CuBr}_4$	2.09

The e.p.r. spectra of the studied compounds are isotropic and were used for the calculation of the  $g_1$  values (Table 2) according to Kneubüll method [11]. The  $g_1$  factor which we computed for  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ , is practically identical with the value obtained by Furlani *et al.* [9]. The decrease in the  $g_1$  values with the substitution of chlorine by bromine points to a gradual decrease of orbital contribution and, at the same time, to the highest deformation of  $\text{CuBr}_4^{2-}$  in the studied complex series.

Based on the above data and in that view that substances  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  can be synthesized with  $x$  not being an integer, we suggest that here investigated chlorobromocopper(II) complexes form either mixed crystals or solid solutions.

## References

1. Ilyukevich, L. A. and Shagisultanova, G. A., *Zh. Neorg. Khim.* **8**, 2308 (1963).
2. Gentile, P. S., Shankoff, T. A., and Carlotto, J., *J. Inorg. Nucl. Chem.* **29**, 1393 (1967).
3. Raymond, K. N., *J. Chem. Soc.* **D1969**, 1294.
4. Goldfield, S. A. and Raymond, K. N., *Inorg. Chem.* **10**, 2604 (1971).
5. Willett, R. D., *J. Chem. Phys.* **41**, 2243 (1964).
6. Karyakin, Y. V. and Angelov, I. I., *Chistye Khimicheskie Reaktivy*. Goschimizdat, Moscow, 1955.
7. Remy, H. and Laves, G., *Ber.* **66**, 571 (1933).
8. Willett, R. D., Liles, O. L., Jr., and Michelson, C., *Inorg. Chem.* **6**, 1885 (1967).
9. Furlani, C., Sgamellotti, A., Magrini, F., and Cordischi, D., *J. Mol. Spectrosc.* **24**, 270 (1967).
10. Smith, D. W., *J. Chem. Soc.* **A1969**, 2529.
11. Kneubüll, F. K., *J. Chem. Phys.* **33**, 1074 (1960).

Translated by P. Biely