

*Papier u príslušnosti k*

# Preparation and Properties of Tri- and Tetrahalogenocuprates(II) with Ethanalammonium as a Cation

*do zborníku*

Z. BIELA

Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, SK-812 37 Bratislava

Received 28 May 1992

Compounds of the general formula  $(EA)_2CuCl_xBr_{4-x}$  and  $(EA)_2Cu_2Cl_xBr_{6-x}$  (EA = ethanalammonium) were prepared by crystallization from ethanol solutions. Based on spectral data and diffraction powder patterns it has been found that  $(EA)_2Cu_2Cl_xBr_{6-x}$  are isostructural and possess the same molecular structure. The energies of  $(EA)_2CuCl_xBr_{4-x}$  depend on  $x$ : for  $(EA)_2CuBr_4$  ( $\tilde{\nu} = 9000\text{ cm}^{-1}$ ), the  $d-d$  energy corresponds to a distorted tetrahedral structure, while for all other compounds ( $\tilde{\nu} = 12600\text{ cm}^{-1}$ ;  $\approx 10000\text{ cm}^{-1}$  shoulder) it corresponds to a distorted octahedral structure.  $(EA)_2CuBr_4$  is not isostructural with any of other tetrahalogenocuprates(II).

Halogenocuprates(II) exhibit a wide variety of compositions and coordination geometries. In our previous papers we dealt with the tetrahalogenocuprates(II) of the  $A_2CuCl_xBr_{4-x}$  type. Our attention was paid to those compounds in which the coordination polyhedron could be changed under the effect of  $A^+$  cation [1–3]. The most frequent changes were in the degree of tetrahedron distortion.

The ethylammonium cation  $CH_3CH_2NH_3^+$  does not belong to the mentioned group of cations. The structure of anion in the complexes  $(C_2H_5NH_3)_2CuCl_xBr_{4-x}$  was found independent of  $x$  [4]. The ethanalammonium cation  $OH-CH_2CH_2NH_3^+$  has a similar composition and structure to the ethylammonium cation. We were interested whether small changes in the cation properties will be reflected in the anion structure.

Halogenocuprates(II) the composition of which can be expressed by the general formula  $ACuCl_3$  were not so extensively investigated as tetrahalogenocuprates(II). The monomeric anion  $CuCl_3^-$  with the coordination number 3 has not been described yet. Known are the dimers  $Cu_2Cl_6^{2-}$  in both planar and nonplanar forms, as well as the chain-like structures with one, two or three bridged atoms. In these complexes the coordination number can reach values 4, 5 or 6 [5].

The salts of the  $ACuX_3$  type have not been investigated so far in our group. The literature data suggested, however, that such compounds could be an exciting objective to investigate the effect of the outer and inner coordination sphere on the structure of the anion polyhedron.

## EXPERIMENTAL

Following chemicals were used:  $CuCl_2$ , prepared by dehydration of dihydrate;  $CuBr_2$ , prepared from

$Cu(OH)_2 \cdot CuCO_3$  and HBr, crystallized from ethanol; ethanalammonium chloride (EACl) and ethanalammonium bromide (EABr), obtained on neutralization of ethanolamine by hydrohalogenic acid and recrystallized from ethanol.

Copper was determined complexometrically with Chelaton III using murexide as indicator. Halogens were determined argentometrically with potentiometric indication.

Halogenocuprates(II) were prepared by crystallization from ethanol solutions of the starting compounds mixed in appropriate ratios. Analyses, colours, and melting points of prepared crystals are given in Table 1. Most of prepared compounds, especially bromides, are hygroscopic.

Powder diffraction patterns were taken on a goniometer GON III; electronic absorption spectra were measured in nujol suspension on a UNICAM SP-700; thermal measurements were done with a derivatograph (MOM, Budapest).

## RESULTS AND DISCUSSION

### Tetrahalogenocuprates(II)

Diffraction powder patterns of  $(EA)_2CuCl_4$ ,  $(EA)_2CuCl_3Br$ ,  $(EA)_2CuCl_2Br_2$ , and  $(EA)_2CuClBr_3$  are very similar (Table 2). They exhibit relatively small number of diffraction lines displaced in periodical distances (a multiple of the first line). The diffraction powder pattern of  $(EA)_2CuBr_4$  is quite different from those of the above-mentioned compounds. Based on this one can assume that the crystal structure of  $(EA)_2CuBr_4$  is not isostructural with other bromochlorocuprates(II) of this group.

Electronic absorption spectra in the UV and VIS region of the compounds have the same shape:

**Table 1.** Colours, Analyses, and Melting Points of Prepared Bromochlorocuprates(II)

Compound	Colour	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			M.p./°C
		Cu	Cl	Br	
(EA) <sub>2</sub> CuCl <sub>4</sub>	Yellow	19.52	43.57		171
		19.20	43.17		
(EA) <sub>2</sub> CuCl <sub>3</sub> Br	Dark red	17.18	28.75	21.6	152
		17.01	28.31	21.45	
(EA) <sub>2</sub> CuCl <sub>2</sub> Br <sub>2</sub>	Violet	15.33	17.11	38.56	122
		15.15	16.50	39.42	
(EA) <sub>2</sub> CuClBr <sub>3</sub>	Violet	13.85	7.73	53.24	98
		13.52	7.17	52.32	
(EA) <sub>2</sub> CuBr <sub>4</sub>	Violet	12.63		63.50	88
		12.33		62.19	
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>6</sub>	Brick red	27.63	46.25		178
		27.60	46.02		
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>3</sub> Br <sub>3</sub>	Violet	21.26	17.80	40.16	133
		21.15	17.03	39.90	
(EA) <sub>2</sub> Cu <sub>2</sub> Br <sub>6</sub>	Violet	17.49		65.97	116
		17.48		65.57	

**Table 2.** Maxima of Diffraction Lines of Prepared Compounds

Compound	$2\theta/^\circ$								
(EA) <sub>2</sub> CuCl <sub>4</sub>	8.4	16.6	21		24.8		33.3	34.9	41.9
(EA) <sub>2</sub> CuCl <sub>3</sub> Br	8.4	16.6	20.9	23.8	24.9	29	33.3	34.9	41.0
(EA) <sub>2</sub> CuCl <sub>2</sub> Br <sub>2</sub>	8.45	16.5	21.8	24.8	28.6	33.2	34.1	41.2	41.8
(EA) <sub>2</sub> CuClBr <sub>3</sub>	8.45	16.7	21.8		24.8	28.4	33.1	41.2	42.0
(EA) <sub>2</sub> CuBr <sub>4</sub>	11.8	13	21.7	23.2	24.6	25.6	26.1	27.3	
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>6</sub>	11.6	12.2	13.5		21.9	22.8	26.4	26.9	
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>3</sub> Br <sub>3</sub>	11.3	11.9	13.2			22.6	26.2	26.5	
(EA) <sub>2</sub> Cu <sub>2</sub> Br <sub>6</sub>	11.3	11.9	13.1	17.3	21.2	23.4	25.7	26.1	

a wide absorption band, the maximum of which is shifted to lower frequencies with increasing bromine content. This bathochromic shift is in agreement with the lower electronegativity of bromine in comparison with chlorine.

The maxima of the ligand field bands are listed in Table 3. As can be seen, the spectra of the prepared tetrahalogenocuprates are very similar with the exception of that of (EA)<sub>2</sub>CuBr<sub>4</sub>. Based on the literature data, the  $d-d$  transition energies of tetrahalogenocuprates(II) are strongly influenced with their molecular structures. The highest  $d-d$  transition energy for a planar form corresponds to more than  $\tilde{\nu} = 14000 \text{ cm}^{-1}$ , while an absorption band of a distorted octahedral structure usually shows a maximum at  $\tilde{\nu}$  around  $13000 \text{ cm}^{-1}$  and a shoulder at  $\approx 11000 \text{ cm}^{-1}$ . Tetrahedrally distorted anions  $\text{CuX}_4^{2-}$  exhibit the  $d-d$  transition energies at values lower than  $\tilde{\nu} = 10000 \text{ cm}^{-1}$ , which is depending upon the degree of the distortion of the tetrahedron [6]. According to these considerations the anions in (EA)<sub>2</sub>CuCl<sub>4</sub>, (EA)<sub>2</sub>CuCl<sub>3</sub>Br, (EA)<sub>2</sub>CuCl<sub>2</sub>Br<sub>2</sub>, and (EA)<sub>2</sub>CuClBr<sub>3</sub> attain, independently of their composition, a structure of a distorted octahedron. On the other hand, the anion in (EA)<sub>2</sub>CuBr<sub>4</sub> is a distorted

tetrahedron. Similar phenomenon has been observed with di-*n*-propylammonium and diisobutylammonium tetrahalogenocuprates(II). In these complexes a significant change of the coordination polyhedron is observed when going from  $\text{CuCl}_2\text{Br}_2^{2-}$  to  $\text{CuClBr}_3^{2-}$ . In a different system, the changes were recorded in the structure of the coordination polyhedron, however, in the opposite direction [2, 3]. Based on spectral data, the structure of the anion in  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{CuClBr}_3$  is a distorted tetrahedron, while the anion in  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{CuBr}_4$  is a distorted octahedron [1]. In all these examples the decisive role

**Table 3.** Energies of  $d-d$  Transitions of Prepared Halogenocuprates(II)

Compound	$\tilde{\nu}(d-d \text{ transition energy})/\text{cm}^{-1}$	
(EA) <sub>2</sub> CuCl <sub>4</sub>	12700	11200 sh
(EA) <sub>2</sub> CuCl <sub>3</sub> Br	12700	10700 sh
(EA) <sub>2</sub> CuCl <sub>2</sub> Br <sub>2</sub>	12600	10300 sh
(EA) <sub>2</sub> CuClBr <sub>3</sub>	12600	10300 sh
(EA) <sub>2</sub> CuBr <sub>4</sub>	9000	
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>6</sub>	12000	11200 sh
(EA) <sub>2</sub> Cu <sub>2</sub> Cl <sub>3</sub> Br <sub>3</sub>	12000	10900 sh
(EA) <sub>2</sub> Cu <sub>2</sub> Br <sub>6</sub>	11500	10300 sh

for arrangement of the octahedral structures is played by hydrogen bonds as a stabilization factor.

Since ethylammonium tetrahalogenocuprates(II) do not exhibit an appreciable dependence of the structure of the anion on its composition, the observed change in the structure of  $(EA)_2CuBr_4$  is an unexpected phenomenon. The transformation leading to a distorted tetrahedral structure is a consequence of a weakening of hydrogen bonds by the hydroxyl group present in the ethanolammonium cation.

DTA curves of  $(EA)_2CuCl_xBr_{4-x}$  do not show any changes before their melting points which would correspond to a phase transition. Melting of the compounds proceeded without decomposition performed at temperatures higher than 200 °C.

### Trihalogenocuprates(II)

The positions of diffraction maxima of three investigated compounds are very similar (Table 2). There is, however, a difference in the intensity of lines which is much higher for  $(EA)_2Cu_2Cl_3Br_3$  than for  $(EA)_2Cu_2Cl_6$  and  $(EA)_2Cu_2Br_6$ . This means that all three compounds are isostructural.

In the electronic spectra of  $(EA)_2Cu_2Cl_6$ , there is a characteristic absorption band at  $\tilde{\nu} = 19100\text{ cm}^{-1}$ . On the basis of the experimental [7] and calculated [8] data, this band is an evidence for planar or nearly planar dimer  $Cu_2Cl_6^{2-}$  and can be attributed to a chlorine-to-metal charge transfer transition.

The maxima of the ligand field bands are listed in Table 3. Weak shoulders are observed on the low energy sides of those bands.

The published spectral data of trihalogenocuprates(II) are very rare. The ligand field band energies for  $KCuCl_3$  in which the coordination of Cu atom is  $4 + 2$  [9], are at  $\tilde{\nu} = 12900\text{ cm}^{-1}$  and  $10500\text{ cm}^{-1}$  (sh). For  $(4\text{-benzylpiperidinium})_2Cu_2Cl_6$ , in which the arrangement around the Cu atom is between square pyramidal and trigonal bipyramidal, the band occurs at  $\tilde{\nu} = 11100\text{ cm}^{-1}$  and the shoulder at  $9520\text{ cm}^{-1}$  [10]. Similar values of  $\tilde{\nu}$  ( $10600\text{ cm}^{-1}$  and  $7690\text{ cm}^{-1}$  at 298 K;  $11000\text{ cm}^{-1}$ ,  $9170\text{ cm}^{-1}$ , and  $7520\text{ cm}^{-1}$  at 77 K) were observed for  $(N\text{-methylphenethylam-$

monium) $_2Cu_2Cl_6$ , in which the distorted trigonal-bipyramidal structure of the dimer  $Cu_2Cl_6^{2-}$  was confirmed [11].

After publication of our preliminary results about some properties of ethanolammonium trihalogenocuprates(II) [12], structures of  $(EA)_2Cu_2Cl_6$  and  $(EA)_2Cu_2Br_6$  have been established [13]. The anions  $Cu_2X_6^{2-}$  were found to be formed by nearly planar dimers in which the Cu atom is coordinated by five halogen atoms forming a distorted square pyramid and semicoordinated by oxygen of the ethanolammonium cation. The observed values of  $d-d$  transition energies suggest somewhat smaller deviation from the planarity in  $(EA)_2Cu_2Cl_6$  than that observed in  $(4\text{-benzylpiperidinium})_2Cu_2Cl_6$ . However, the structural data do not confirm such a conclusion, since the deviation from planarity in  $(EA)_2Cu_2Cl_6$  is higher. The reason for this phenomenon may lay in the semicoordination of the Cu atom with oxygen influencing thus the energy of the  $d-d$  transition.

### REFERENCES

1. Biela, Z. and Gažo, J., *Chem. Zvesti* 35, 215 (1981).
2. Tomovič, J., Biela, Z., and Gažo, J., *Chem. Zvesti* 38, 75 (1984).
3. Biela, Z. and Siroklin, V., *Chem. Papers* 42, 29 (1988).
4. Biela, Z. and Gažo, J., *Chem. Zvesti* 35, 21 (1981).
5. Willett, R. D. and Geiser, U., *Croat. Chem. Acta* 57, 737 (1984).
6. Smith, D. W., *Coord. Chem. Rev.* 21, 93 (1976) and the literature cited therein.
7. Willett, R. D., *J. Inorg. Nucl. Chem.* 29, 2482 (1967).
8. Bencini, A. and Gatteschi, D., *J. Am. Chem. Soc.* 108, 5763 (1986).
9. Willett, R. D. and Liles, O. L., Jr., *Inorg. Chem.* 6, 1067 (1966).
10. Battaglia, L. P., Bonamartini Corradi, A., Marcotrigiano, G., Menabue, L., and Pellacani, G. C., *Inorg. Chem.* 19, 125 (1980).
11. Harlow, R. L., Wells, W. J., Watt, G. W., and Simonsen, S. H., *Inorg. Chem.* 13, 2860 (1974).
12. Biela, Z., *Proceedings of the 11th Conference on Coordination Chemistry*, Smolenice, 1987, p. 6.
13. Scott, B. and Willett, R. D., *Inorg. Chim. Acta* 141, 193 (1988).

Translated by Z. Biela