Preparation and properties of chlorobromocuprates(II) $A_2[CuCl_xBr_{4-x}]$

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Compounds $A_2[CuCl_xBr_{4-x}]$ (A = ethyl-, n-propyl- or n-butylammonium cation; $x = 0$—4) were prepared by crystallization from ethanolic solutions and by solid state interaction. Their X-ray powder diffraction patterns consisting of a small number of lines disposed in regular intervals, are identical for each series of compounds having the same cation, which means that the substances are isomorphous. The charge-transfer bands in the electronic spectra were found to be shifted to lower energies with increasing content of bromine. The character of the ligand field bands is the same for all the compounds studied. Based on the values of the energy of *d*—*d* transitions (≈13 000 and 10 800 cm^{-1}), the tetrahalocuprate(II) anion appears to have the D_{4h} symmetry. The values of the g factors calculated from the e.s.r. spectra of polycrystalline samples are also consistent with the D_{4h} symmetry of homogeneous tetrahalocuprates(II).

Соединения состава $A_2[CuCl_xBr_{4-x}]$ (A = катион этил-, н-пропил или н-бутиламмония; $x = 0$—4 были приготовлены кристаллизацией из этанольных растворов и взаимодействием в твердой фазе. Порошковые рентгенограммы соединений с одинаковым катионом состоят из малого числа линий, расположенных на одинаковых расстояниях, что свидетельствует об их изоморфизме. С повышением содержания брома полосы переноса заряда в электронных спектрах сдвигаются в сторону низких энергий. Характер полос поля лигандов одинаков у всех изученных соединений. На основании значений энергий перехода *d*—*d* (≈13 000 и 10 800 $см^{-1}$) тетрагалогенидного комплексного аниона Cu(II) он должен обладать симметрией D_{4h}. Это согласуется также со значением g фактора, рассчитанного из спектров ЭПР поликристаллических образцов.

Chlorocuprates(II) belong to the most extensively studied group of halocuprates(II). They are distinguished by great variability in composition and structure. Their interesting properties, such as thermochromism and the ability to change the structure of the complex anion with temperature and pressure conditions, have been reviewed in detail by *Smith* [1]. Bromocuprates(II) were investigated in substantially lesser extent. This fact is probably connected with their more complicated way of preparation. The properties of bromocuprates(II) are, however, in majority of known cases, analogous to those of chlorocuprates(II).

Chlorobromocuprates(II) represent the least studied group of halocuprates(II). Their investigations were initiated in our laboratories [2]. The data concerning the properties of chlorobromocuprates(II) which were reported later, are rather limited [3—8].

Complex species $CuCl_2Br^-$ and $CuClBr_2^-$ have been established in acetic acid anhydride [9] and acetone [10] solutions. Mixed halocuprates(II) $(CH_3NH_3)_2CuCl_xBr_{4-x}$ ($x = 0$—4) were prepared in solid state and characterized by spectral methods [11]. The present work is a continuation of our previous effort in studies of mixed tetrahalocuprates(II) and describes new species in which $EtNH_3^+$, $n\text{-}PrNH_3^+$, and $n\text{-}BuNH_3^+$ are present as cations.

Full X-ray analysis of $(EtNH_3)_2CuCl_4$ and $(n\text{-}PrNH_3)_2CuCl_4$ has been reported [12, 13]. These complexes, similarly as $(MeNH_3)_2CuCl_4$ [14], contain the $CuCl_6$ chromophore with four shorter (≈230 pm) and two longer (≈300 pm) Cu—Cl bonds. Their crystals have a layer structure. On the basis of great similarity in magnetic and optical properties between $(n\text{-}BuNH_3)_2CuCl_4$ [15, 16] and $(EtNH_3)_2CuCl_4$ or $(n\text{-}PrNH_3)_2CuCl_4$ [12, 13], one may infer that the structure of the anion in the n-butylammonium-containing complex will be the same. This conclusion is strengthened by the fact that n-butylamine and n-propylamine possess similar spatial arrangement and binding possibilities.

The aim of the present work was to find out to what extent the heterogeneity of the coordination sphere affects the symmetry of the complex anion. Structure of the prepared chlorobromocuprates(II) was investigated indirectly by spectral methods. The ligand arrangement in homogeneous halocuprates(II) offered a theoretical possibility of formation of stereo isomers in the case of dichlorodibromocuprates(II). Attention was also devoted to this subject.

Experimental

Chemicals and equipments

The following chemicals were used: $CuCl_2$, prepared by dehydration of the dihydrate; $CuBr_2$, prepared as described elsewhere [17]; ethyl-, n-propyl-, and n-butylchloride and -bromide prepared by neutralization of aqueous solutions of the corresponding amines followed by recrystallization from ethanol.

Powder diffraction patterns were recorded with a goniometer GON III, electronic spectra in Nujol mulls with a Specord UV VIS 200 spectrophotometer (in visible and ultraviolet region) and a Unicam SP 700 equipment (in infrared region 5 000—14 000 cm^{-1}). The e.s.r. spectra of polycrystalline samples were recorded with a Varian E-4 spectrophotometer in temperature range 113—303 K.

Analytical procedures

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

Preparation of chlorobromocuprates(II)

All studied chlorobromocuprates(II) were prepared by crystallization from ethanolic solutions. After separation, the crystals were washed with a small amount of anhydrous ethanol and dried with diethyl ether. Amounts of the starting compounds and solvent used in the synthesis of all complexes as well as the results of their analyses are given below.

$(EtNH_3)_2CuCl_3Br$

$CuCl_2$, 1 g; $EtNH_2\cdot HCl$, 0.6 g; $EtNH_2\cdot HBr$, 2.2 g; ethanol, 20 cm^3.
Calculated: 18.57% Cu, 31.09% Cl, 23.36% Br; found: 18.26% Cu, 31.58% Cl, 23.93% Br.

$(EtNH_3)_2CuCl_2Br_2$

a) $CuCl_2$, 1 g; $EtNH_2\cdot HBr$, 4.3 g; ethanol, 20 cm^3; *b*) $CuBr_2$, 3 g; $EtNH_2\cdot HCl$, 1.1 g; ethanol, 20 cm^3.
Calculated: 16.43% Cu, 18.34% Cl, 41.35% Br; found: *a*) 15.62% Cu, 18.20% Cl, 40.08% Br; *b*) 16.41% Cu, 17.99% Cl, 42.40% Br.

$(EtNH_3)_2CuClBr_3$

$CuBr_2$, 2 g; $EtNH_2\cdot HCl$, 0.4 g; $EtNH_2\cdot HBr$, 0.9 g; ethanol, 20 cm^3.
Calculated: 14.74% Cu, 8.22% Cl, 55.62% Br; found: 14.84% Cu, 8.25% Cl, 56.27% Br.

$(n\text{-}PrNH_3)_2CuCl_3Br$

$CuCl_2$, 2 g; $n\text{-}PrNH_2\cdot HBr$, 2.2 g; ethanol, 40 cm^3.
Calculated: 17.16% Cu, 28.74% Cl, 21.60% Br; found: 17.54% Cu, 29.20% Cl, 22.48% Br.

$(n\text{-}PrNH_3)_2CuCl_2Br_2$

a) $CuBr_2$, 3 g; $n\text{-}PrNH_2\cdot HCl$, 1.3 g; ethanol, 40 cm^3; *b*) $CuCl_2$, 1 g; $n\text{-}PrNH_2\cdot HBr$, 4 g; ethanol, 40 cm^3.
Calculated: 15.34% Cu, 17.10% Cl, 38.60% Br; found: *a*) 15.71% Cu, 17.35% Cl, 39.10% Br; *b*) 15.36% Cu, 17.71% Cl, 38.23% Br.

$(n\text{-PrNH}_3)_2CuClBr_3$

$CuBr_2$, 3 g; n-$PrNH_2\cdot HCl$, 0.7 g; n-$PrNH_2\cdot HBr$, 1 g; ethanol, 40 cm^3.
Calculated: 13.84% Cu, 7.72% Cl, 52.3% Br; found: 14.08% Cu, 7.97% Cl, 52.82% Br.

$(n\text{-BuNH}_3)_2CuCl_3Br$

a) $CuBr_2$, 1.3 g; n-$BuNH_2\cdot HCl$, 1.6 g; ethanol, 25 cm^3; *b*) $CuCl_2$, 0.5 g; n-$BuNH_2\cdot HBr$, 1.2 g; ethanol, 25 cm^3.
Calculated: 15.98% Cu, 26.75% Cl, 20.01% Br; found: *a*) 16.20% Cu, 26.82% Cl, 20.04% Br; *b*) 16.15% Cu, 26.29% Cl, 21.02% Br.

$(n\text{-BuNH}_3)_2CuCl_2Br_2$

$CuCl_2$, 0.5 g; n-$BuNH_2\cdot HBr$, 2.7 g; ethanol, 25 cm^3.
Calculated: 14.39% Cu, 16.01% Cl, 36.20% Br; found: 14.80% Cu, 15.71% Cl, 36.36% Br.

$(n\text{-BuNH}_3)_2CuClBr_3$

$CuBr_2$, 6.5 g; n-$BuNH_2\cdot HCl$, 1.4 g; ethanol, 25 cm^3; the solution concentrated to saturation.
Calculated: 13.05% Cu, 7.29% Cl, 49.30% Br; found: 13.50% Cu, 7.41% Cl, 49.40% Br.

All of the given compounds can also be prepared by solid state interaction of the starting components [11].

Homogeneous chloro- and bromocuprates(II) were obtained by crystallization from ethanolic solutions with the desired Cu : X ratios. By changing the Cu : Cl : Br ratio in the starting solutions or mixtures, compounds can be prepared in which x is not an integer.

Results and discussion

Powder diffraction patterns of the tetrahalocomplexes containing one type of cation are almost identical. Relatively small number of lines, displaced in regular intervals, points to a high crystal symmetry. The number of the diffraction lines is preserved, but their position is slightly shifted to lower or higher 2ϑ values with changes in the coordination sphere (Table 1). These observations together with the fact that compounds $A_2[CuCl_xBr_{4-x}]$, in which x is not an integer, can be prepared, show that the new chlorobromocuprates(II) prepared are isomorphous with homogeneous tetrahalocomplexes. The same phenomenon was observed with methylammonium tetrahalocuprates(II) [11]. This is apparently a consequence of the formation of mixed crystals like those reported in the case of $[Cr(NH_3)_6]CuCl_5$, $[Cr(NH_3)_6]CuCl_2Br_3$, and $[Cr(NH_3)_6]CuBr_5$ [6]. These compounds behave as

Table 1

Diffraction data of tetrahalocuprates(II)

Compound	2ϑ [°]					
$(EtNH_3)_2CuCl_4$	8.4	25.1	33.75	42.6		
$(EtNH_3)_2CuCl_3Br$	8.3	24.85	33.3	42.0		
$(EtNH_3)_2CuCl_2Br_2$	8.2	24.7	33.2	41.8 41.1		
$(EtNH_3)_2CuClBr_3$	8.3	24.8	33.2	41.8 41.0		
$(EtNH_3)_2CuBr_4$	8.2	24.7	33.2	41.9		
$(n\text{-}PrNH_3)_2CuCl_4$	7.5	14.7	29.3	36.8	44.4	
$(n\text{-}PrNH_3)_2CuCl_3Br$	7.4	14.6	29.2	36.7	44.3	
$(n\text{-}PrNH_3)_2CuCl_2Br_2$	7.35	15.5	29.2	36.7	44.3	
$(n\text{-}PrNH_3)_2CuClBr_3$	7.3	14.5	29.2	36.8	44.45	
$(n\text{-}PrNH_3)_2CuBr_4$	7.3	14.7	29.5	37.1	44.7	
$(n\text{-}BuNH_3)_2CuCl_4$	5.95	11.7	23.2	29.15	35.1	41.1
$(n\text{-}BuNH_3)_2CuCl_3Br$	5.95	11.7		29.2	35.2	41.2
$(n\text{-}BuNH_3)_2CuCl_2Br_2$	5.9	11.6	23.3	29.1	35.05	41.15
$(n\text{-}BuNH_3)_2CuClBr_3$	6.0	11.9	23.7	29.75	35.8	42.0
$(n\text{-}BuNH_3)_2CuBr_4$	6.15	12.2	24.35	30.5	36.7	43.0

isostructural and form mixed crystals in which the atoms of chlorine and bromine are randomly distributed between axial and equatorial positions.

Nujol absorption spectra (in the visible region) of compounds $(n\text{-}BuNH_3)_2CuCl_xBr_{4-x}$ are presented in Fig. 1. The spectra of $(n\text{-}PrNH_3)_2CuCl_xBr_{4-x}$ and $(EtNH_3)_2CuCl_xBr_{4-x}$ have the same character. Charge-transfer bands are significantly shifted to lower energies with gradual substitution of chlorine by bromine in the coordination sphere. The shift of the charge-transfer bands to the same direction was also observed with chlorobromocopper(II) complexes in acetic acid anhydride [9] and acetone [10], where the absorbing species were represented by the solvolysis products of tetrahalocuprates(II) — $[CuCl_3L]^-$, $[CuCl_2BrL]^-$, $[CuClBr_2L]^-$, and $[CuBr_3L]^-$ (L = solvent molecule). However, in this case, the sufficient distances between the absorption maxima of the respective complex species allowed to analyze the spectra into Gaussian curves and to determine thus the exact values of the absorption maxima of the above-mentioned chlorobromocuprates(II) [9]. A large number of bands with close values of absorption maxima in the Nujol spectra of mixed tetrahalocuprates(II) did not allow to make a reliable band analyses.

Nujol absorption spectra of the newly prepared substances exhibit common features in the near infrared: one broad ligand field band with maximum at about

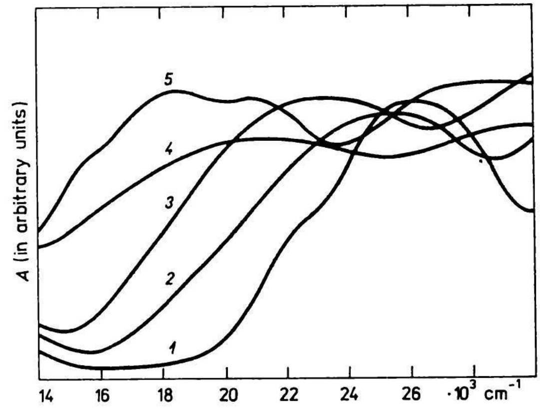

Fig. 1. Electronic absorption spectra (Nujol mull).
1. (n-BuNH$_3$)$_2$CuCl$_4$; *2.* (n-BuNH$_3$)$_2$CuCl$_3$Br; *3.* (n-BuNH$_3$)$_2$CuCl$_2$Br$_2$; *4.* (n-BuNH$_3$)$_2$CuClBr$_3$; *5.* (n-BuNH$_3$)$_2$CuBr$_4$.

12 550—13 000 cm^{-1} with evident asymmetry on the side of lower energies. The asymmetry is due to a shoulder at about 10 700—11 000 cm^{-1}. The band as well as the shoulder are shifted to higher energies with increasing content of bromine in the compounds (Table 2; for a comparison, the energies of the *d—d* transitions of

Table 2

Energies of the *d—d* transitions of chlorobromocuprates(II) measured in Nujol mull

Compound	Energy of the *d—d* bands [cm^{-1}]	
(EtNH$_3$)$_2$CuCl$_4$	12 800	10 800 sh
(EtNH$_3$)$_2$CuCl$_3$Br	12 700	10 800 sh
(EtNH$_3$)$_2$CuCl$_2$Br$_2$	12 700	10 900 sh
(EtNH$_3$)$_2$CuClBr$_3$	12 900	11 000 sh
(EtNH$_3$)$_2$CuBr$_4$	13 000	11 000 sh
(n-PrNH$_3$)$_2$CuCl$_4$	12 700	10 800 sh
(n-PrNH$_3$)$_2$CuCl$_3$Br	12 800	10 800 sh
(n-PrNH$_3$)$_2$CuCl$_2$Br$_2$	12 800	10 800 sh
(n-PrNH$_3$)$_2$CuClBr$_3$	12 900	11 000 sh
(n-PrNH$_3$)$_2$CuBr$_4$	13 000	11 000 sh
(n-BuNH$_3$)$_2$CuCl$_4$	12 550	10 700 sh
(n-BuNH$_3$)$_2$CuCl$_3$Br	12 700	10 800 sh
(n-BuNH$_3$)$_2$CuCl$_2$Br$_2$	12 700	10 700 sh
(n-BuNH$_3$)$_2$CuClBr$_3$	12 800	10 800 sh
(n-BuNH$_3$)$_2$CuBr$_4$	12 800	10 850 sh

chlorocuprates(II) and bromocuprates(II) measured under identical conditions are included). In regard to the position of chlorine and bromine in the spectrochemical series one would expect shifts to the opposite direction. The shift to higher energies points therefore to an increasing distortion of the coordination polyhedron with rising content of bromine. This phenomenon was also observed in the case of some other tetrahalocuprates(II), *e.g.* with couples Cs_2CuCl_4—Cs_2CuBr_4 and $[(CH_3)_4N]_2CuCl_4$—$[(CH_3)_4N]_2CuBr_4$, the $CuBr_4^{2-}$ anion is more distorted [18]. With our compounds the differences are extremely small, so one may conclude that bromine entering the coordination sphere does not cause any substantial change in the symmetry of the anion. The electronic spectrum of $(EtNH_3)_2CuCl_4$, measured by *Willett et al.* [19], exhibits in the infrared region a broad absorption band with maximum at 12 800 cm^{-1}, composed of two bands, corresponding to the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, and a shoulder at 10 500 cm^{-1} ascribed to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The energies of the ligand field bands are in a good consonance with the values calculated for the $CuCl_6$ chromophore (D_{4h} symmetry) [14, 20]. Since the spectra of the compounds described in this work exhibit the same character (comparable values of *d*—*d* transition energy), we presume an identical arrangement of halogens around the central atom: four halogens in a plane at shorter distance and two halogens with longer Cu—X bonds in axial positions.

Table 3

ESR data of mixed tetrahalocuprates(II)

Compound	298 K			158 K		
	g_1	g_2	g_{av}	g_1	g_2	g_{av}
$(EtNH_3)_2CuCl_4$	2.212	2.073	2.167	2.206	2.075	2.163
$(EtNH_3)_2CuCl_3Br$			2.170	2.201	2.078	2.161
$(EtNH_3)_2CuCl_2Br_2$			2.170			2.148
$(EtNH_3)_2CuClBr_3$			2.163			2.154
$(EtNH_3)_2CuBr_4$			2.174			2.181
$(n\text{-}PrNH_3)_2CuCl_4$	2.212	2.071	2.166	2.206	2.075	2.163
$(n\text{-}PrNH_3)_2CuCl_3Br$			2.165	2.196	2.075	2.156
$(n\text{-}PrNH_3)_2CuCl_2Br_2$			2.162			2.164
$(n\text{-}PrNH_3)_2CuClBr_3$			2.149			2.153
$(n\text{-}PrNH_3)_2CuBr_4$			2.182			2.178
$(n\text{-}BuNH_3)_2CuCl_4$	2.20	2.074	2.159	2.214	2.08	2.17
$(n\text{-}BuNH_3)_2CuCl_3Br$			2.166	2.197	2.083	2.159
$(n\text{-}BuNH_3)_2CuCl_2Br_2$			2.181			2.183
$(n\text{-}BuNH_3)_2CuClBr_3$			2.157			2.163
$(n\text{-}BuNH_3)_2CuBr_4$			2.161			2.161

The values of the g factors calculated from e.s.r. spectra of polycrystalline samples are given in Table 3. Axial spectra were exhibited only by tetrachlorocuprates(II) and trichlorobromocuprates(II), and were found to be reversed (Fig. 2). This observation as well as the G values ($g_1 - 2/g_2 - 2$, for all of the compounds <3) points to a considerable exchange effect in the complexes. Moreover, the low

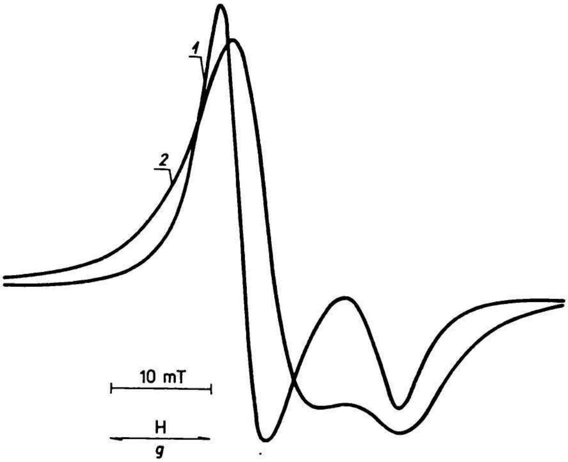

Fig. 2. ESR spectra ($T = 153$ K). *1.* $(n\text{-}PrNH_3)_2CuCl_4$; *2.* $(n\text{-}PrNH_3)_2CuCl_3Br$.

G values do not allow to correlate the e.s.r. and electronic spectra. The g_1 and g_2 values calculated for the prepared trichlorobromocuprates(II) are in a good agreement with the literature data for the compounds containing the $CuCl_6$ chromophore [19, 21], which are much lower than the values for $CuCl_4^{2-}$ of the D_{2d} symmetry [21]. The e.s.r. spectra of all remaining newly prepared compounds are pseudoisotropic and, therefore, they enable to determine the g_{av} values only. The e.s.r. lines being broad at higher temperatures, become narrower with temperature decrease.

The compounds of the formula $A_2[CuCl_2Br_2]$ prepared by two different ways (by solid state interaction of $CuCl_2$ and aminehydrobromide or $CuBr_2$ and aminehydrochloride, or by crystallization from ethanolic solutions of the starting components described in Experimental) do not differ in any of the properties examined. The theoretical possibility of the formation of stereoisomers of the given composition has not been confirmed, similarly as in the case of a number of other Cu(II) complexes.

Based upon the results of the present work one may suggest that all here described chlorobromocuprates(II) are isomorphous with homogeneous halocomplexes and form common mixed crystals. Substitution of chlorine with bromine does not bring about any substantial change of the coordination polyhedron.

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