tert-Butylammonium Halogenocuprates(II) – Preparation and Properties

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Received 15 November 1994
Accepted for publication 26 June 1995

Halogenocuprates(II) of the type $A_2Cu_2Cl_xBr_{6-x}$ (A = *tert*-butylammonium, $x = 0, 1, 3, 4, 6$) were prepared by crystallization from aqueous solutions. The prepared compounds appear to be isostructural. The energies of *d*—*d* transitions allow to propose a considerable deviation from the planarity of the dimeric anion. The compounds which could not be prepared from the studied systems include tetrahalogenocuprates(II), $A_2CuCl_xBr_{4-x}$, which are formed, however, in the case if A = n- or isobutylammonium.

In our previous papers [1, 2] we investigated the systems n-$BuNH_2 \cdot HX$—CuX_2—solvent and i-$BuNH_2 \cdot HX$—CuX_2—solvent (X = Cl, Br; solvent = ethanol, water). The following type of compounds was isolated: $A_2CuCl_xBr_{4-x}$ (A = n- or i-$BuNH_3$; $x = 0$—4). The structure of the anion in these complexes is distorted octahedral and it is not influenced by changes in x or a different geometry of the cations.

Under constant composition, the geometry of the cation may have a decisive effect on the structure of the anion in tetrahalogenocuprates(II). Examples are $(n\text{-}C_3H_7NH_3)_2CuCl_4$ (*I*) and $(i\text{-}C_3H_7NH_3)_2CuCl_4$ (*II*). The structure of $CuCl_4^{2-}$ in *I* is distorted tetrahedral [1] while three different forms of the anion were found in *II*: one is distorted octahedral and two are tetrahedral with different degree of the distortion [3]. The cation structure also influences the anion structure in $[(n\text{-}C_3H_7)_2NH_2]_2CuCl_4$ (*III*) and $[(i\text{-}C_3H_7)_2NH_2]_2CuCl_4$ (*IV*). The energies of the *d*—*d* transitions in *IV* are shifted to much lower values in comparison with those of *III*, which is a characteristic feature for the transition of the distorted octahedral structure towards a distorted tetrahedron [4].

In relation to the above observations it was of interest to examine the effect of the *tert*-butylammonium cation, which is isomeric to the n- and isobutylammonium cations, on the structure of the complex anion.

EXPERIMENTAL

The used chemicals, their preparation and analytical procedures were described in our previous paper [5]. Powder diffraction patterns were measured on a DRON equipment, electronic absorption spectra in nujol suspensions with a Specord UV VIS 200 and UNICAM SP-700 spectrophotometers, thermal measurements were taken on a MOM derivatograph, and EPR spectra on a Bruker ER 200E-SRC.

The brown-red needle crystals of $(t\text{-}BuNH_3)_2Cu_2Cl_6$ (Bu = C_4H_9) were isolated from aqueous solutions containing t-$BuNH_2$ HCl and $CuCl_2$ in the mole ratios varying from 1:1 to 2:1, acidified with HCl. A larger excess of chlorides leads to crystallization of t-$BuNH_2 \cdot HCl$ or a mixture of t-$BuNH_2 \cdot HCl$ and $(t\text{-}BuNH_3)_2Cu_2Cl_6$.

The dark-violet needle crystals of $(t\text{-}BuNH_3)_2Cu_2Br_6$ were prepared from aqueous solutions of t-$BuNH_2 \cdot HBr$ and $CuBr_2$ in the mole ratios varying from 1:1 to 2:1, in the presence of HBr. In the presence of a larger excess of bromides, t-$BuNH_2 \cdot HBr$ or its mixture with $(t\text{-}BuNH_3)_2Cu_2Br_6$ crystallize from solutions.

The violet needle crystals of $(t\text{-}BuNH_3)_2Cu_2Cl_3Br_3$ were obtained from aqueous solutions of $CuCl_2$ and t-$BuNH_2 \cdot HBr$ in the mole ratio 1:1, acidified with HBr. If HBr was substituted by HCl the crystalline violet product was $(t\text{-}BuNH_3)_2Cu_2Cl_4Br_2$. The dark-violet crystals of $(t\text{-}BuNH_3)_2Cu_2ClBr_5$ were prepared from aqueous solutions containing $CuBr_2$ and t-$BuNH_2 \cdot HCl$ in the mole ratio 1:1, in the presence of HBr. The results of analyses of the prepared compounds and their melting points are summarized in Table 1.

RESULTS AND DISCUSSION

The maxima of absorption bands in electronic spectra of all the prepared compounds are listed in Table 2. Their charge-transfer bands are very wide and probably consist of several absorption bands. The bathochromic shift of the band maximum, as a result of a lower electronegativity of bromine in

Table 1. Characterization of the Prepared Compounds

Compound	Colour	w_i(calc.)/% w_i(found)/%			M.p./°C
		Cu	Cl	Br	
$(t\text{-BuNH}_3)_2Cu_2Cl_6$	Brown-red	26.03	43.59		225
		26.26	42.89		
$(t\text{-BuNH}_3)_2Cu_2Br_6$	Dark violet	16.82		63.55	176
		16.46		63.96	
$(t\text{-BuNH}_3)_2Cu_2Cl_4Br_2$	Violet	22.01	24.58	27.72	206
		22.12	25.79	27.77	
$(t\text{-BuNH}_3)_2Cu_2Cl_3Br_3$	Violet	20.74	17.11	38.60	190
		20.06	18.02	38.16	
$(t\text{-BuNH}_3)_2Cu_2ClBr_5$	Dark violet	17.88	4.99	56.27	179
		17.36	4.20	57.94	

Table 2. Absorption Maxima in Electronic Spectra of the Prepared Compounds

Compound	$\tilde{\nu}_{max}/cm^{-1}$		
$(t\text{-BuNH}_3)_2Cu_2Cl_6$	25500	18500	9800
$(t\text{-BuNH}_3)_2Cu_2Cl_4Br_2$	23000	19000 sh	9800
$(t\text{-BuNH}_3)_2Cu_2Cl_3Br_3$	20000		9800
$(t\text{-BuNH}_3)_2Cu_2ClBr_5$	17800		9900
$(t\text{-BuNH}_3)_2Cu_2Br_6$	16900		9700

comparison with that of chlorine, was observed with all so far prepared series of bromochlorocuprates(II). $(t\text{-BuNH}_3)_2Cu_2Cl_6$ shows, in addition to the above discussed charge-transfer band, another well defined band with a maximum at $\tilde{\nu} = 18500\ cm^{-1}$ Calculations have shown that the band at 19000 cm^{-1} corresponds to the energy of the Cl—Cu charge transfer in the planar dimer Cu_2Cl_6 [6]. The shift of the maximum of this band into the region of lower energies can be considered as the evidence of a dimer with greater or less significant deviation from planarity. The presence of this band was also recorded as a shoulder on the charge-transfer band of $(t\text{-BuNH}_3)_2Cu_2Cl_4Br_2$. In the case of other prepared compounds the band is overlapped with more intense charge-transfer bands.

In the region of the *d—d* transitions the spectra of all compounds are very similar. The *d—d* transitions are reflected in a band with a maximum at 9700—9900 cm^{-1} and an asymmetry on the high-energy side. On the basis of these results we can conclude that the structure of the anion is not planar, however, we are unable to ascertain the type of the coordination polyhedron. The energies of the *d—d* transitions are very similar in the case of a distorted tetrahedron, distorted trigonal bipyramid or distorted square pyramid [7]. However, the energy of the *d—d* transition corresponding to $\tilde{\nu}$ lower than 10000 cm^{-1} suggests considerable deviation from planarity and, moreover, it is in consonance with the value of the CT transition Cl—Cu for $(t\text{-BuNH}_3)_2Cu_2Cl_6$ at $\tilde{\nu} = 18500\ cm^{-1}$, which is also much lower than the value calculated for a planar dimer.

The diffraction maxima of the prepared compounds are presented in Table 3. The most pronounced are the first two bands, the position of which practically does not change with composition. On the basis of these data one can assume that the prepared compounds are isostructural.

DTA curves of prepared compounds do not show any changes at the temperatures lower than their melting points, which would correspond to phase transitions.

Magnetic moments measured at room temperature are 1.91 μ_B for $(t\text{-BuNH}_3)_2Cu_2Cl_6$ and 1.97 μ_B for $(t\text{-BuNH}_3)_2Cu_2Br_6$. The values of μ_{eff} are high to envisage the interaction between the Cu atoms. The EPR spectrum of $(t\text{-BuNH}_3)_2Cu_2Cl_6$ at room temperature is rhombic with the values $g_1 = 2.04, g_2 = 2.155$, and $g_3 = 2.21$. According to [8], such a spectrum is typical for a distorted tetragonal pyramid, which correlates well with the electronic spectrum of $(t\text{-BuNH}_3)_2Cu_2Cl_6$. The EPR spectrum of $(t\text{-BuNH}_3)_2Cu_2Br_6$ shows in the region 0.1—0.5 T only a weak and extremely wide band. A similar phenomenon has been observed in the EPR spectrum of (ethanolammonium)$_2Cu_2Br_6$ by *Scott* and *Willett* [9]. In this compound, the configuration around the Cu atom is 4 + 1 + 1. Five bromine atoms form a distorted tetragonal pyramid and the sixth position is occupied by oxygen of ethanolammonium cation. In general, it may be concluded that the width of the band of bromocopper(II) compounds is substantially larger than that of the chlorocopper(II) ones, therefore the EPR spectra have to be measured at extremely low temperatures.

Table 3. Maxima of the Diffraction Lines of the Prepared Compounds

Compound	2Θ/°												
$(t\text{-BuNH}_3)_2Cu_2Cl_6$	10.2	10.9	14.2	18.2		20.7					27.2		
$(t\text{-BuNH}_3)_2Cu_2Cl_4Br_2$	10.3	10.8	14.1	18.2		20.8	22.1				27.8		
$(t\text{-BuNH}_3)_2Cu_2Cl_3Br_3$	10.3	10.8	14.0	18.2		20.7	22.0				27.7		
$(t\text{-BuNH}_3)_2Cu_2ClBr_5$	10.3	11.0		18.1	18.5	19.5	22.0	23.9	25.0	26.2	28.0	28.3	
$(t\text{-BuNH}_3)_2Cu_2Br_6$	10.3	10.9		18.1		19.3	21.9	23.8	25.0	26.3	27.9		29.9

CONCLUSION

We expected that in the systems t-$BuNH_2 \cdot HX$—CuX_2—HX—solvent tetrahalogenocuprates(II), $(t\text{-}BuNH_3)_2CuX_4$, would be formed. Distorted tetrahedral structures of anions in these compounds were expected, contrary to distorted octahedral anion structures observed in $(n\text{-}BuNH_3)_2CuX_4$ and $(i\text{-}BuNH_3)_2CuX_4$. However, we were not able to prepare that type of compounds. The only halogenocuprates(II), which were prepared, were $(t\text{-}BuNH_3)_2Cu_2X_6$. The main reason must be the different cation geometry. All measurements done in this work pointed out that the prepared compounds $(t\text{-}BuNH_3)_2Cu_2Cl_xBr_{6-x}$ ($x = 0, 1, 3, 4, 6$) are isostructural and a coordination polyhedron of Cu(II) is a distorted tetragonal pyramid.

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Translated by P. Biely