Effect of the cation on the anion structure in mixed bis(di-n-propylammonium) and bis(di-n-butylammonium) tetrahalocuprates(II)

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Mixed tetrahalocuprates(II) $A_2CuCl_xBr_{4-x}$ ($A = (n\text{-}C_3H_7)_2NH_2$, $(n\text{-}C_4H_9)_2NH_2$; $x = 0, 1, 2, 3, 4$) were prepared and studied. According to the energies of the d—d transitions, $\tilde{\nu} = 8100$—$8800\ cm^{-1}$, the structure of the anion in $[(n\text{-}C_4H_9)_2NH_2]_2CuCl_xBr_{4-x}$ appears to be a distorted tetrahedron. The structure of mixed tetrahalocuprates(II) having the $(n\text{-}C_3H_7)_2NH_2^+$ cation varies with x: the anion structure is tetrahedral for $x = 0$ and 1 and planar for $x = 2$, 3, and 4 (d—d transition energy; $\tilde{\nu} \approx 12\ 500\ cm^{-1}$). DTA curves of compounds with distorted tetrahedral anions show an endothermal change at a temperature lower than the melting point, suggesting a phase transition associated with a change in the molecular structure. On DTA curves of compounds having planar anions such a change was not observed.

Были получены и изучены смешанные четырехгалоидные купраты(II) $A_2CuCl_xBr_{4-x}$ ($A = (n\text{-}C_3H_7)_2NH_2$, $(n\text{-}C_4H_9)_2NH_2$; $x = 0, 1, 2, 3, 4$). По энергиям d—d переходов ($\tilde{\nu} = 8100$—$8800\ см^{-1}$) кажется, что структура аниона в $[(n\text{-}C_4H_9)_2NH_2]_2CuCl_xBr_{4-x}$ представляет искаженный тетраэдр. Строение смешанных четырехгалоидных купратов(II), содержащих $(n\text{-}C_3H_7)_2NH_2^+$ катион изменяется с x: структура аниона является тетраэдрической для $x = 0$ и 1 и планарной для $x = 2$, 3 и 4 (энергия d—d перехода; $\tilde{\nu} \approx 12\ 500\ см^{-1}$). Кривые ДТА соединений с искаженными тетраэдрическими анионами показывают эндотермические изменения при температуре ниже точки плавления, что представляет фазовый переход соединенный с изменением молекулярной структуры. На ДТА кривых соединений с анионами с планарной структурой таких изменений не наблюдалось.

The present paper is a continuation of our previous studies of mixed tetrahalocuprates(II) containing chlorine and bromine in the coordination sphere [1—3].

The structure of the CuX_4^{2-} anion in tetrahalocuprates(II) is determined mainly by cation properties, such as its size, steric arrangement, and its ability to form hydrogen bonds. With sufficiently bulky cations unable to form the hydrogen bonds N—H...X with the anion (*e.g.* Cs^+, Me_4N^+, Et_4N^+), the anions prefer a thermodynamically more convenient distorted tetrahedral structure [4, 5]. With small cations (K^+, Rb^+) or with those which have good possibilities of hydrogen bond formation (*e.g.* $R—NH_3^+$) a planar structure of the anion is stabilized [6, 7].

Substitution of chlorine by bromine in the coordination sphere does not cause considerable changes in the structure of those tetrahalocuprates(II), the $CuCl_4^{2-}$ or $CuBr_4^{2-}$ of which possess the same molecular structure [1, 2, 8]. In case the structure of these two anions is different, the substitution of chlorine by bromine can bring about a significant deformation of the coordination polyhedron [3].

In this work we investigated di-n-propyl- and di-n-butylammonium bromochlorocuprates(II). Their cations possess comparable size and the same structure. In a previous study of mixed n-propyl- and n-butylammonium tetrahalocuprates(II) we revealed a great similarity in their physical properties and structure [2]. It was of interest to find out whether the structure of the complex anion $CuCl_xBr_{4-x}^{2-}$ is influenced analogously by disubstituted alkylammonium cations which have a lowered capability of forming hydrogen bonds in comparison to the monosubstituted ones.

Experimental

Chemicals and equipments

Following chemicals were used: $CuCl_2 \cdot 2H_2O$, anal. grade; $CuBr_2$ prepared from $Cu(OH)_2 \cdot CuCO_3$ and HBr and crystallized from ethanol; $(n\text{-}C_3H_7)_2NH \cdot HCl$, $(n\text{-}C_3H_7)_2NH \cdot HBr$, $(n\text{-}C_4H_9)_2NH \cdot HCl$, and $(n\text{-}C_4H_9)_2NH \cdot HBr$, obtained on neutralization of the corresponding amine by hydrohalogenic acid and recrystallized from ethanol.

Electronic absorption spectra were measured in nujol suspensions on a Specord UV VIS 200 spectrophotometer (Zeiss, Jena) in ultraviolet and visible region, and on a Unicam SP-700 apparatus in the near infrared region. Thermal analysis was done with a Derivatograph MOM (Radelkis, Budapest). Melting points were determined on a Kofler stage at a temperature increase of 6 °C/min.

Analytical procedures

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

Preparation of bromochlorocuprates(II)

Tetrahalocuprates(II) $(DPA)_2CuCl_xBr_{4-x}$ and $(DBA)_2CuCl_xBr_{4-x}$ ($DPA = (n\text{-}C_3H_7)_2NH_2$; $DBA = (n\text{-}C_4H_9)_2NH_2$; $x = 0, 1, 2, 3, 4$) were prepared from exactly preweighed equimolar amounts of the starting compounds dissolved in ethanol. The solutions were left to evaporate to dryness. The solvent residues were removed by melting. The melts were cooled in a vacuum. The dry preparates were ground to fine powders. The analyses and melting points of the prepared compounds are given in Table 1. The temperature interval given denotes the temperatures of the beginning and of the end of melting.

The studied compounds can be also prepared by crystallization from solutions of the starting compounds in ethanol mixed in appropriate ratios. The former procedure was preferred for its simplicity.

Table 1

Analyses and melting points of di-n-propylammonium and di-n-butylammonium tetrahalocuprates(II)

Compound	*w*(Cu)/mass %	*w*(Cl)/mass %	*w*(Br)/mass %	M.p./°C
$(DPA)_2CuCl_4$	15.30	34.60		75—77
	(15.51)	(34.61)		
$(DPA)_2CuCl_3Br$	13.91	23.40	17.55	62—64
	(13.99)	(23.42)	(17.59)	
$(DPA)_2CuCl_2Br_2$	12.70	14.20	32.10	58—60
	(12.74)	(14.22)	(32.05)	
$(DPA)_2CuClBr_3$	11.68	6.50	44.13	56—58
	(11.70)	(6.52)	(44.14)	
$(DPA)_2CuBr_4$	10.75		54.34	61—64
	(10.81)		(54.38)	
$(DBA)_2CuCl_4$	13.58	30.41		88—90
	(13.63)	(30.47)		
$(DBA)_2CuCl_3Br$	12.46	20.90	15.65	85—88
	(12.45)	(20.86)	(15.67)	
$(DBA)_2CuCl_2Br_2$	11.38	12.62	28.70	64—65
	(11.45)	(12.79)	(28.82)	
$(DBA)_2CuClBr_3$	10.57	5.80	40.10	80—84
	(10.60)	(5.92)	(40.03)	
$(DBA)_2CuBr_4$	9.78		49.40	82—85
	(9.86)		(49.69)	

The data in brackets represent the calculated values.

Results and discussion

Electronic absorption spectra

Electronic absorption spectra in visible and ultraviolet region, measured in nujol suspension, are shown in Figs. 1 and 2. The spectra of both series of compounds

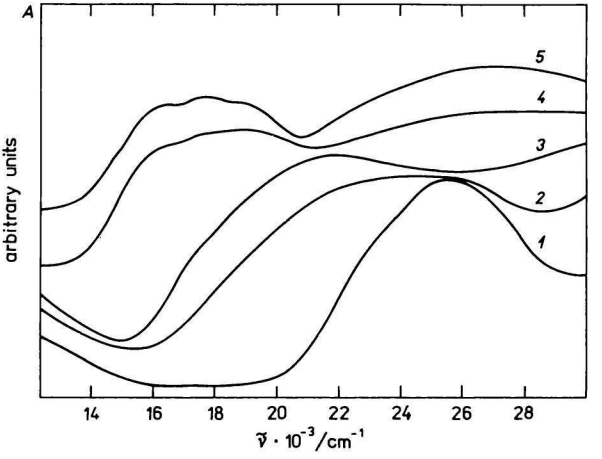

Fig. 1. Electronic absorption spectra of complexes in nujol suspension.
1. $(DPA)_2CuCl_4$; *2.* $(DPA)_2CuCl_3Br$; *3.* $(DPA)_2CuCl_2Br_2$; *4.* $(DPA)_2CuClBr_3$; *5.* $(DPA)_2CuBr_4$.

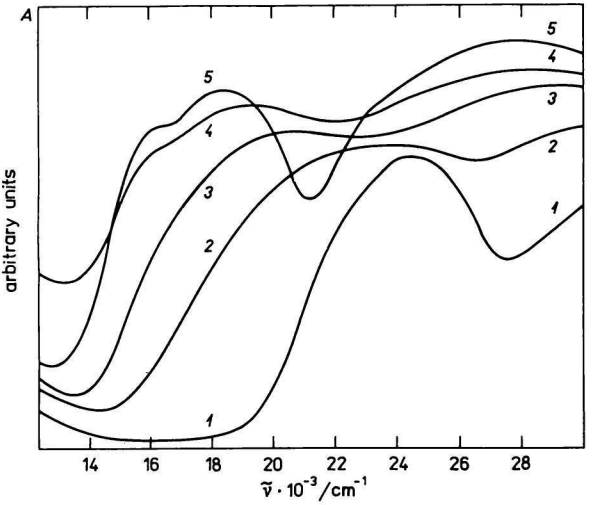

Fig. 2. Electronic absorption spectra of complexes in nujol suspension.
1. $(DBA)_2CuCl_4$; *2.* $(DBA)_2CuCl_3Br$; *3.* $(DBA)_2CuCl_2Br_2$; *4.* $(DBA)_2CuClBr_3$; *5.* $(DBA)_2CuBr_4$.

exhibit a shift of the CT bands to lower frequencies with increasing content of bromine in the complex. The bathochromic shift is in accordance with the lower electronegativity of bromine in comparison with chlorine. The absorption bands of bromochlorocuprate(II) are much broader than those of bromo- or chlorocuprate(II), due to superposition of several absorption bands. The spectra cannot be reliably analyzed to Gaussian curves corresponding to individual absorbing particles. The most significant difference occurs in the position of the absorption maxima of $(DPA)_2CuCl_4$ (Fig. 1, curve *1*) and $(DBA)_2CuCl_4$ (Fig. 2, curve *1*). The absorption spectrum of $(DPA)_2CuCl_4$ shows a maximum at 25 500 cm^{-1} and a shoulder at $\approx$22 800 cm^{-1} while the maximum of the CT band of $(DBA)_2CuCl_4$ lies at 24 500 cm^{-1} and its shoulder at $\approx$21 700 cm^{-1} The charge transfer bands of tetrahalocuprates(II) in contrast to the ligand field bands, are not so strongly dependent on their molecular structure; however, the CT transition corresponding to a distorted octahedral D_{4h} symmetry occurs at higher energies [1, 2, 9] than in the case of a distorted tetrahedral D_{2d} symmetry [3, 9—11]. Based on the electronic absorption spectra in visible and ultraviolet region one can anticipate differences between the molecular structures of $(DPA)_2CuCl_4$ and $(DBA)_2CuCl_4$; the latter complex appearing as a "more tetrahedral"

The wavenumbers corresponding to the *d—d* transitions determined from electronic absorption spectra recorded in nujol suspension in the near infrared region are presented in Table 2. With the mixed di-n-propylammonium tetrahalocopper(II) complexes the energy of the *d—d* transition is strongly dependent on their composition. The absorption spectrum of $(DPA)_2CuCl_4$ exhibits a band with a maximum at 10 000 cm^{-1} and a shoulder at $\approx$12 500 cm^{-1} Comparable values for the wavenumbers of the *d—d* transitions follow from the

Table 2

Wavenumbers corresponding to the *d—d* transitions of di-n-propylammonium and di-n-butylammonium tetrahalocuprates(II)

Compound	$\tilde{\nu}_{max}/cm^{-1}$	
$(DPA)_2CuCl_4$	10 000	12 500 sh
$(DPA)_2CuCl_3Br$	10 000	12 500 sh
$(DPA)_2CuCl_2Br_2$	9800	Shoulder overlapped by the CT band
$(DPA)_2CuClBr_3$	8300	
$(DPA)_2CuBr_4$	8200	
$(DBA)_2CuCl_4$	8100	5800 sh
$(DBA)_2CuCl_3Br$	8500	6000 sh
$(DBA)_2CuCl_2Br_2$	8700	6100 sh
$(DBA)_2CuClBr_3$	8800	6200 sh
$(DBA)_2CuBr_4$	8800	6200 sh

character of the spectra of $(DPA)_2CuCl_3Br$ and $(DPA)_2CuCl_2Br_2$. There is an essential change in the spectra of $(DPA)_2CuClBr_3$ and $(DPA)_2CuBr_4$ — the maximum is shifted to 8100—8300 cm^{-1}

The observed wavenumbers of the *d*—*d* transitions for the planar $CuCl_4^{2-}$ are 14 300, 13 100, and 10 900 cm^{-1} [12] and for a distorted octahedral chlorocuprate(II) ≈13 000 and 10 800 cm^{-1} [6, 9]. The energy of the *d*—*d* transition of tetrahalocuprates(II) of the D_{2d} symmetry depends on the degree of tetrahedral distortion and the corresponding wavenumber attains higher values than 7750 cm^{-1} This dependence (degree of tetrahedral distortion *vs.* the *d*—*d* transition) was quantitatively evaluated by *Lamotte-Brasseur* [13] and *Battaglia et al.* [14]. Based on the literature data we can assume that the anions in $(DPA)_2CuClBr_3$ and $(DPA)_2CuBr_4$ have a structure of a distorted tetrahedron. The low values of $\tilde{\nu}_{max}$ point to a lower degree of distortion, however. The interpretation of the spectra of $(DPA)_2CuCl_4$, $(DPA)_2CuCl_3Br$, and $(DPA)_2CuCl_2Br_2$ is more complicated. Chlorocuprates(II) having a distorted octahedral D_{4h} symmetry and energies of the *d*—*d* transitions comparable to the energies of the compounds discussed here, exhibit a high-energy band and a low-energy shoulder. In our case, the shoulder occurs on the side of higher energies. This fact may be due to a simultaneous existence of two forms of tetrahalocuprates(II), one form as a distorted tetrahedron and the other as a distorted octahedron. The superposition of the absorption bands of the two forms may lead to the situation that the maximum absorbance appears at 10 000 cm^{-1} A similar phenomenon has been described. X-ray analysis has established that in $[(CH_3)_2CHNH_3]_2CuCl_4$, at room temperature, the anion $CuCl_4^{2-}$ occurs in three different forms, one is planar and two are tetrahedral with different degree of distortion [15].

The character of the ligand field spectra of $(DPA)_2CuCl_4$, $(DPA)_2CuCl_3Br$, and $(DPA)_2CuCl_2Br_2$ allows considerations about the possibility of pentacoordination of the central ion. $(4\text{-Benzylpiperidinium})_2Cu_2Cl_6$, in which Cu is coordinated with five chlorine atoms (a distorted trigonal bipyramidal anion), exhibits a wide ligand field band at 11 110 cm^{-1} with a shoulder at ≈9500 cm^{-1} [16]. Cu is also pentacoordinated in the compound $[(CH_3)_2NH]CuCl_3$ (distorted square pyramid). The wavenumbers of the *d*—*d* transitions in the latter case are 10 800 cm^{-1} (shoulder) and 12 900 cm^{-1} (band) [17]. A complete solution of the problem of penta- or hexacoordination of the central atom in here studied compounds requires an X-ray analysis.

A tendency of attaining a tetrahedral structure in compounds with higher bromine content was also observed by *Marcotrigiano et al.* in studies of bromochlorocuprates(II) with morpholinium [18] and 2-methylpiperazinium cations [19]. The shift of maxima of the ligand field bands was less pronounced, from 12 500 cm^{-1} to 10 000 cm^{-1}, than in compounds studied here.

The changes in the composition of mixed di-n-butylammonium tetrahalocuprat-

es(II) are not considerably reflected in their molecular structure. The spectra have the same character, represented by a broad absorption band with a maximum at 8100—8800 cm^{-1} and by a low-energy shoulder. Such values of the *d*—*d* transitions are characteristic of tetrahalocuprates(II) having a distorted tetrahedral structure [20]. The degree of the tetrahedral distortion slightly increases with increasing content of bromine. The energies of *d*—*d* transitions would show an opposite tendency (a shift to lower values) on substitution of chlorine by bromine in complexes with preserved equal degree of distortion.

Thermal properties

Melting points of di-n-propyl- and di-n-butylammonium tetrahalocuprates(II) are listed in Table 1. All of the compounds melt without loss in their masses.

DTA records of di-n-propylammonium tetrahalocuprates(II) are shown in Fig. 3. In addition to the endothermic change corresponding to melting, the DTA curves of $(DPA)_2CuCl_4$, $(DPA)_2CuCl_3Br$, and $(DPA)_2CuCl_2Br_2$ show an endothermic change at a lower temperature. The last two compounds of the series, $(DPA)_2CuClBr_3$ and $(DPA)_2CuBr_4$, as well as di-n-butylammonium tetrahalocuprates(II) did not exhibit such a thermal change in the temperature interval

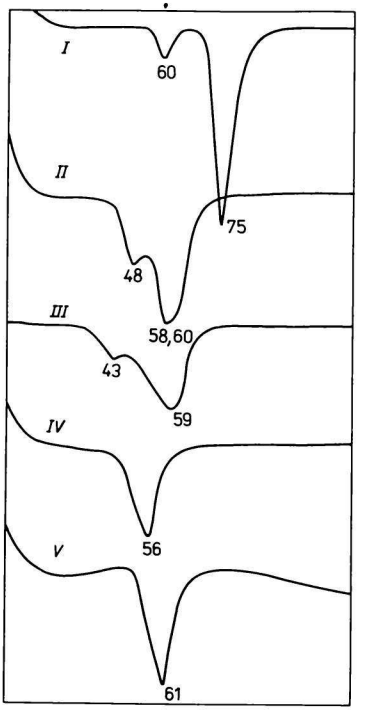

Fig. 3. DTA curves: *I.* $(DPA)_2CuCl_4$; *II.* $(DPA)_2CuCl_3Br$; *III.* $(DPA)_2CuCl_2Br_2$; *IV.* $(DPA)_2CuClBr_3$; *V.* $(DPA)_2CuBr_4$.

20—150 °C except of that corresponding to melting. Taking into consideration the fact that the anions in $(DPA)_2CuCl_4$, $(DPA)_2CuCl_3Br$, and $(DPA)_2CuCl_2Br_2$ are planar or close to planar, while the anions of all other investigated compounds are tetrahedrally distorted, *i.e.* in energetically more convenient state, one can assume that the endothermic change at a temperature lower than the melting point reflects a phase transition associated with the change of the molecular structure of the anion. An analogous phenomenon is known with $[(C_2H_5)_2NH_2]_2CuCl_4$ [21]. The green colour of this compound turns suddenly yellow at 43 °C. The colour change is accompanied by changes in the spectrum of the ligand field band. The maximum of the absorption band is shifted from 11 800 cm^{-1} to 9800 cm^{-1}, *i.e.* a tetrahedral arrangement takes place. This transition is recorded on the DTA curve of $[(C_2H_5)_2NH_2]_2CuCl_4$ as an endothermic peak at ≈ 50 °C [21].

Conclusion

Since di-n-propylammonium and di-n-butylammonium ions have very similar properties, we expected that they will affect identically also the structure of the anion in tetrahalocuprates(II). The experimental data, however, point to considerable differences in the anion structures. The reason for this is apparently a greater ability of hydrogen bond formation of $(DPA)^+$ in comparison with $(DBA)^+$ Decrease in the number of Cl ions in di-n-propylammonium tetrahalocuprates(II) leads to reduction of the N—H...Cl interactions and, consequently, the planar arrangement proposed on the basis of the energies of the *d*—*d* transitions for $(DPA)_2CuCl_4$, $(DPA)_2CuCl_3Br$, and $(DPA)_2CuCl_2Br_2$, is distorted towards the tetrahedral symmetry in $(DPA)_2CuClBr_3$ and $(DPA)_2CuBr_4$. Due to lower capability of hydrogen bonding, all di-n-butylammonium tetrahalocuprates(II) possess a distorted tetrahedral structure.

The dominant role of hydrogen bonding in the effect of cations on the anion structure also follows from the comparison of the n-propyl- and n-butylammonium salts with the di-n-propyl- and di-n-butylammonium salts. Monosubstituted alkylammonium salts having good possibilities of hydrogen bond formation have a distorted octahedral structure, or, occasionally, a planar structure. Neither substitution of chlorine by bromine in the coordination sphere, nor the changes in the cation size evoke changes in the anion structure. In disubstituted alkylammonium salts, in which the hydrogen bonding is suppressed by substitution of hydrogen with additional alkyl group, the anions occur preferably in a tetrahedral arrangement. The degree of the distortion of tetrahedron is influenced by changes in the coordination sphere and by size of the cation.

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