

Preparation and properties of bis(di-isopropylammonium) and bis(di-isobutylammonium) tetrahalocuprates(II)

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Tetrahalocuprates(II) $[(\text{iso-C}_3\text{H}_7)_2\text{NH}_2]_2\text{CuCl}_4$ and $[(\text{iso-C}_4\text{H}_9)_2\text{NH}_2]_2 \cdot \text{CuCl}_x\text{Br}_{4-x}$ ($x = 0-4$) were prepared and characterized by electronic spectra in nujol suspension, DTA and diffraction powder patterns. Three forms of $[(\text{iso-C}_4\text{H}_9)_2\text{NH}_2]_2\text{CuCl}_4$ were prepared — yellow, red, and orange. Based on the data of the $d-d$ spectra, a distorted tetrahedral structure is proposed for all complex anions. Distortion of the tetrahedron is significantly lower for $x = 0$ and 1 than for other prepared compounds. The orange form of $[(\text{iso-C}_4\text{H}_9)_2\text{NH}_2]_2\text{CuCl}_4$ differs from the red and yellow form both in the crystal and molecular structure.

Тетрагалогенкупраты $[(\text{изо-C}_3\text{H}_7)_2\text{NH}_2]_2\text{CuCl}_4$ и $[(\text{изо-C}_4\text{H}_9)_2\text{NH}_2]_2 \cdot \text{CuCl}_x\text{Br}_{4-x}$ ($x = 0-4$) были получены и охарактеризованы своими электронными спектрами в нуйоловой суспензии, методом дифференциального термического анализа и дифракционными изображениями. Были получены три формы $[(\text{изо-C}_4\text{H}_9)_2\text{NH}_2]_2\text{CuCl}_4$ — желтая, красная и оранжевая. На основании данных $d \rightarrow d$ спектров у всех комплексных анионов предполагается искаженная тетраэдрическая структура. Деформация тетраэдра существенно ниже для $x = 0$ и 1, чем для других полученных соединений. Оранжевая форма $[(\text{изо-C}_4\text{H}_9)_2\text{NH}_2]_2\text{CuCl}_4$ отличается от желтой и красной форм как кристаллической, так и молекулярной структурой.

In our previous papers we dealt with tetrahalocuprates(II) containing in the coordination sphere simultaneously chlorine and bromine [1—4]. Later we investigated mainly the effects of cations on the anion structure [3, 4]. The present contribution is a continuation of such studies.

The anion structure in tetrahalocuprates(II) A_2CuX_4 can vary from planar through distorted octahedral to tetrahedral with various degree of tetrahedral distortion. The planar structure of the anion is typical mainly for bulky organic cations having possibilities to form hydrogen bonds with X, e.g. for creatinium cation $\text{C}_4\text{H}_8\text{N}_3\text{O}^+$ [5] or *N*-(2-ammonioethylmorpholinium) $\text{C}_6\text{H}_{16}\text{N}_2\text{O}^+$ cation [6]. The distorted octahedral structure is typical for smaller cations, also with good capabilities of hydrogen bond formation, e.g. R-NH_3^+ [7]. There is

a large number of tetrahalocuprates(II) with distorted tetrahedral structure of anion. This group includes almost all compounds with cations unable to form hydrogen bonds [7, 8]. The tetrahedral distortion varies in a relatively wide interval — with the flattening angle ranging from 129° in Cs_2CuCl_4 [9] to 159° in $(\text{iso-C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ [10].

The most interesting cation forms are those which form only weak hydrogen bonds $\text{N—H}\cdots\text{X}$ that do not stabilize distorted octahedral, eventually planar structures. This fact makes the distorted tetrahedral structure not very rigid and definitive. In the case of such cations, there is a possibility to influence the anion structure by changing external factors, *e.g.* temperature. Small changes in the composition of the coordination sphere of the $\text{A}_2\text{CuCl}_x\text{Br}_{4-x}$ compounds can be induced by changing x .

Study of the effect of cations on anion structure in bis(di-*n*-propylammonium) and bis(di-*n*-butylammonium) tetrahalocuprates(II) showed that by changing the chlorine to bromine ratio in the coordination sphere, changes in the anion structure occur only in the case of di-*n*-propylammonium salts. The distorted tetrahedral structure of anion in di-*n*-butylammonium salts was found to be independent of the coordination sphere changes [4]. These results stimulated us to study the influence of cation stereochemistry on the anion structure in bis(di-isopropylammonium) and bis(di-isobutylammonium) tetrahalocuprates(II).

Experimental

Chemicals and equipments

Following chemicals were used: CuCl_2 , prepared by dehydration of dihydrate; CuBr_2 , prepared as described in [11]; DiPACl , DiPABr , DiBACl , DiBABr ($\text{DiPA} = (\text{iso-C}_3\text{H}_7)_2\text{NH}_3^+$, $\text{DiBA} = (\text{iso-C}_4\text{H}_9)_2\text{NH}_3^+$), prepared by neutralization of the corresponding amine by hydrohalic acid and recrystallization from ethanol.

Powder diffraction patterns were taken on goniometer GON III using cathode of the lamp $\text{CuK}\alpha$ ($\lambda = 1.5405 \times 10^{-10}$ m); electronic absorption spectra were measured in nujol suspension in UV and VIS region on a Specord UV VIS 200 (Zeiss, Jena) spectrophotometer, and on a UNICAM SP-700 apparatus in the near IR region; thermal measurements were done with a Derivatograph MOM (Radelkis, Budapest).

Analytical procedures

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

Preparation of halocuprates(II)

Chlorocuprates(II), bromocuprates(II), and bromochlorocuprates(II) were prepared by crystallization from ethanolic or methanolic solutions containing the starting compounds in desired ratios. Crystals obtained by cooling the solution to 0°C were separated, washed by a small amount of dry alcohol and dried by diethyl ether.

Preparation of (DiPA)₂CuCl₄

The orange crystals were prepared from a solution containing 1 g CuCl₂ and 2 g DiPACl (mole ratio = 1 : 1.95) in 13 cm³ of ethanol. Analysis: $w_i(\text{calc.})$: 15.51 % Cu, 34.61 % Cl; $w_i(\text{found})$: 15.48 % Cu, 34.44 % Cl. Attempts to prepare (DiPA)₂CuBr₄ and (DiPA)₂CuCl_xBr_{4-x} from ethanolic or methanolic solutions were not successful. The solubility of DiPABr is very low and mixtures crystallize from solutions.

Preparation of (DiBA)₂CuCl₄

Depending on conditions of preparation, three forms differing in colour and partly in crystal shape were obtained:

a) light-yellow needles were prepared from a solution containing 1.03 g CuCl₂ and 2.53 g DiBACl (mole ratio = 1 : 2) in 23 cm³ of ethanol by cooling at 0°C. Analysis: $w_i(\text{calc.})$: 13.61 % Cu, 30.44 % Cl; $w_i(\text{found})$: 13.30 % Cu, 30.48 % Cl.

b) brick-red needles, similar in shape to the above-mentioned substance, but strongly distinct in colour, were obtained from a solution containing 0.96 g CuCl₂ and 2.31 g DiBACl (mole ratio = 1 : 2) in 6.5 cm³ of methanol after 4 days of crystallization at 0°C. The same substance was also prepared from a diluted ethanolic solution after long-time crystallization at 0°C. Analysis: $w_i(\text{found})$: 13.50 % Cu, 29.97 % Cl.

c) orange cubic crystals, strongly distinct in shape from the two above-mentioned forms, were separated from a solution containing 1.09 g CuCl₂ and 2.69 g DiBACl (mole ratio = 1 : 2) in 14 cm³ of ethanol at 20°C. Analysis: $w_i(\text{found})$: 13.64 % Cu, 30.57 % Cl.

Preparation of (DiBA)₂CuCl₃Br

Light-red needles were obtained on cooling of a solution containing 1.35 g CuCl₂, 1.1 g DiBACl, and 2.1 g DiBABr (mole ratio = 1 : 0.65 : 1) in 17 cm³ of ethanol. Analysis: $w_i(\text{calc.})$: 12.45 % Cu, 20.84 % Cl, 15.66 % Br; $w_i(\text{found})$: 12.43 % Cu, 20.81 % Cl, 15.21 % Br.

Preparation of (DiBA)₂CuCl₂Br₂

Dark-red crystals were obtained after 4 days of crystallization from a solution containing 1.02 g CuBr₂, 1.1 g DiBACl (mole ratio = 1 : 1.45) in 8 cm³ of methanol. Analysis: $w_i(\text{calc.})$: 11.45 % Cu, 12.78 % Cl, 28.81 % Br; $w_i(\text{found})$: 11.21 % Cu, 12.45 % Cl, 29.01 % Br.

Preparation of (DiBA)₂CuClBr₃

Dark-violet product crystallized from a solution containing 1.6 g CuBr₂, 1.36 g DiBABr, and 1.08 g DiBACl (mole ratio = 1 : 0.95 : 0.95) in 9 cm³ of methanol. Analysis: $w_i(\text{calc.})$: 10.60 % Cu, 5.92 % Cl, 40.00 % Br; $w_i(\text{found})$: 10.45 % Cu, 5.47 % Cl, 40.64 % Br.

Preparation of (DiBA)₂CuBr₄

Dark-violet crystals were obtained by cooling a solution containing 1.5 g CuBr₂ and 2.8 g DiBABr (mole ratio = 1 : 2) in 11 cm³ of methanol. Analysis: $w_i(\text{calc.})$: 9.87 % Cu, 49.66 % Br; $w_i(\text{found})$: 9.88 % Cu, 49.68 % Br.

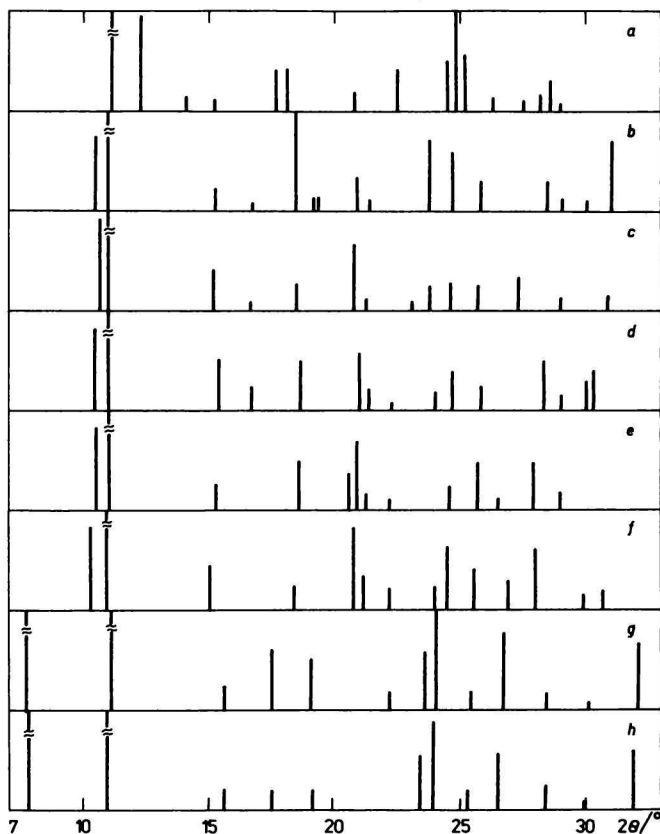


Fig. 1. Diffraction powder patterns of tetrahalocuprates(II).

a) (DiPA)₂CuCl₄; b) (DiBA)₂CuCl₄ — orange form; c) (DiBA)₂CuCl₄ — red form; d) (DiBA)₂CuCl₄ — yellow form; e) (DiBA)₂CuCl₃Br; f) (DiBA)₂CuCl₂Br₂; g) (DiBA)₂CuClBr₃; h) (DiBA)₂CuBr₄.

Results and discussion

Diffraction powder patterns

On the basis of diffraction powder patterns we can divide the studied compounds into four groups:

1. (DiPA)₂CuCl₄ (Fig. 1a);
2. orange form of (DiBA)₂CuCl₄ (Fig. 1b);
3. yellow and red forms of (DiBA)₂CuCl₄; (DiBA)₂CuCl₃Br, (DiBA)₂CuCl₂Br₂ (Fig. 1c—f);
4. (DiBA)₂CuClBr₃, (DiBA)₂CuBr₄ (Fig. 1g, h).

Tetrahalocuprates(II) with DiBA⁺ cation are not isostructural compounds. Tribromochloro- and tetrabromocuprates(II) are isostructural and their diffraction powder patterns differ considerably from diffraction powder patterns of all other compounds. Dichlorodibromo-, trichlorobromo-, and the yellow and red forms of tetrachlorocuprates(II) (Fig. 1c—f) can be considered to be isostructural. Not great, but significant are the changes in the diffraction powder pattern of the orange form, where a marked difference was observed in the intensity of some lines, specially at $2\Theta = 18.5^\circ$, 23.8° , and 31° , in comparison with those of the yellow and the red form.

Electronic absorption spectra

The charge transfer bands of tetrachlorocuprates(II) are not strongly dependent on their molecular structure. With a distorted octahedral symmetry, maximum of the CT band lies usually in the region $\tilde{\nu} = 25\,000$ — $26\,000\text{ cm}^{-1}$, while with the distorted tetrahedral symmetry it lies a little bit lower, usually at about $\tilde{\nu} = 24\,000\text{ cm}^{-1}$ [12]. Electronic absorption spectrum of (DiPA)₂CuCl₄, measured in nujol suspension, shows in the visible region of the spectrum an absorption band with maximum at $\tilde{\nu} = 24\,400\text{ cm}^{-1}$, which points to the D_{2d} anion symmetry. In the near infrared region, the spectrum of (DiPA)₂CuCl₄ shows a broad, almost symmetrical d — d transition band due to superposition of at least two absorption bands. Approximate values of $\tilde{\nu}_{\text{max}}$ are 7200 cm^{-1} and $10\,200\text{ cm}^{-1}$, which corresponds to the D_{2d} symmetry with a highly distorted tetrahedron. This supports our assumption done on the basis of the CT band position.

Mixed di-isopropylammonium tetrahalocuprates(II) were not prepared, so we could compare the (DiPA)₂CuCl₄ spectrum only with that of (DPA)₂CuCl₄ (DPA = (n-C₃H₇)₂NH₂) discussed in our previous paper [4]. The cation influence is evident: a shift of the maximum of the CT band takes place from $\tilde{\nu} = 25\,500\text{ cm}^{-1}$ for (DPA)₂CuCl₄ to $\tilde{\nu} = 24\,400\text{ cm}^{-1}$ for (DiPA)₂CuCl₄ and a

Table 1

Maxima of the charge transfer bands in the visible region of the spectra and maxima of the ligand field bands

Compound	$\tilde{\nu}_{\max}/\text{cm}^{-1}$		
(DiPA) ₂ CuCl ₄	24 400	10 200,	7 200
(DiBA) ₂ CuCl ₄ red form	21 000 sh, 24 600	10 100 sh,	7 200
(DiBA) ₂ CuCl ₄ yellow form	24 600	10 100 sh,	7 200
(DiBA) ₂ CuCl ₄ orange form	24 600	11 800,	9 800,
		8 000,	6 600 sh
(DiBA) ₂ CuCl ₃ Br	23 500	9 600 sh,	7 100
(DiBA) ₂ CuCl ₂ Br ₂	29 000, 20 400	9 600 sh,	7 100
(DiBA) ₂ CuClBr ₃	28 000, 19 200, 17 000 sh	8 950,	5 950
(DiBA) ₂ CuBr ₄	27 000, 18 600, 17 000 sh	8 950,	5 800

shift of maxima of the ligand field bands from $\tilde{\nu} = 10\,000\text{ cm}^{-1}$ and $\tilde{\nu} = 12\,500\text{ cm}^{-1}$ for (DPA)₂CuCl₄ to $\tilde{\nu} = 7\,200\text{ cm}^{-1}$ and $\tilde{\nu} = 10\,200\text{ cm}^{-1}$ for (DiPA)₂CuCl₄. On the basis of these data we can assume an essential change in the CuCl₄²⁻ structure: the structure changes from nearly a planar arrangement in (DPA)₂CuCl₄ to a distorted tetrahedral structure in (DiPA)₂CuCl₄. Regarding the fact that DiPA is more branched than DPA and that it could block the hydrogen bond formation between the cation and the anion, the effect of DiPA on CuCl₄²⁻ structure is understandable. A similar phenomenon was observed for (n-C₃H₇NH₃)₂CuCl₄ and (iso-C₃H₇NH₃)₂CuCl₄. In the first case, the structure of the anion is distorted octahedral, typical for almost all tetrahalocuprates(II) with R—NH₃⁺ cations [7]. In the second case, two thirds of anions showed the tetrahedral distortion [10].

The charge transfer spectra of the three in colour distinct forms of (DiBA)₂CuCl₄ exhibit in the visible region an absorption band at $\tilde{\nu}_{\max} = 24\,600\text{ cm}^{-1}$. The band of the yellow and the orange form is symmetrical. The absorption band of the red form is asymmetrical with a slight shoulder on the low-energy side, at about $\tilde{\nu} = 21\,000\text{ cm}^{-1}$. With increasing content of bromine in the complex, the CT bands of the remaining compounds shift to lower energies (Table 1). Due to a superposition of several bands, the resulting bands are very broad. It was not possible to make a reliable spectral analysis into Gaussian curves and their assignment to individual complex species. Data given in Table 1 give only the absorbance maxima.

The ligand field spectra of mixed di-isobutylammonium tetrahalocuprates(II) may be divided on the basis of their similarity, as the diffraction powder patterns, into three groups (Table 1). The *d*—*d* spectra of the yellow and red

(DiBA)₂CuCl₄, (DiBA)₂CuCl₃Br, and (DiBA)₂CuCl₂Br₂ show the same character: an absorption band at $\tilde{\nu} = 7100\text{--}7200\text{ cm}^{-1}$ with a clear shoulder in the $\tilde{\nu} = 10\,000\text{ cm}^{-1}$ region. On the basis of these data we assume a highly distorted tetrahedral structure of CuCl₄²⁻, CuCl₃Br²⁻, and CuCl₂Br₂²⁻ anions. The values of the flattening angles Θ in the tetrahedra calculated by the empirical equation of Harlow *et al.* [13] $E = (144.5\{\Theta\} - 9784)\text{ cm}^{-1}$ (E corresponds to the highest $d\text{--}d$ transition) approach 135° . The substantial differences are observed in the ligand field spectra of (DiBA)₂CuClBr₃ and (DiBA)₂CuBr₄. A shoulder becomes separated and two absorptior bands appear with a lower $\tilde{\nu}_{\text{max}}$. The value calculated for the flattening angle is 129° . Transition to a less distorted tetrahedron is easy to understand, under condition that a stepwise substitution of chlorine by bromine leads to a decrease in the hydrogen bond energies N—H...X. It is of interest, however, that the change in the structure takes place suddenly after substitution of the third chlorine atom. An analogous phenomenon was observed with (DPA)₂CuCl₂Br₂ and (DPA)₂CuClBr₃. Maximum of the $d\text{--}d$ transition band was shifted from $\tilde{\nu} = 9800\text{ cm}^{-1}$ for CuCl₂Br₂²⁻ to $\tilde{\nu} = 8300\text{ cm}^{-1}$ for CuClBr₃²⁻ [4]. This means that the distortion of the tetrahedron also decreases with the substitution of the third chlorine by bromine. The ligand field spectrum of the orange (DiBA)₂CuCl₄ shows three separated absorption bands with maxima at $\tilde{\nu} = 11\,800\text{ cm}^{-1}$, 9800 cm^{-1} , and 8000 cm^{-1} and a shoulder at $\tilde{\nu} = 6600\text{ cm}^{-1}$. The bands at $\tilde{\nu} = 9800\text{ cm}^{-1}$ and $\tilde{\nu} = 8000\text{ cm}^{-1}$ are more pronounced than that at $\tilde{\nu} = 11\,800\text{ cm}^{-1}$ and the shoulder. Only small differences were observed in the diffraction powder patterns of the three (DiBA)₂CuCl₄ forms (Fig. 1*b*—*d*). These results suggest that there are no striking differences in their molecular structures. The most probable explanation might be the fact that the orange (DiBA)₂CuCl₄ contains, in addition to the tetrahedral CuCl₄²⁻ with the flattening angle $\Theta = 135^\circ$ (discussed at the interpretation of the yellow and red (DiBA)₂CuCl₄), at least one, considerably more distorted tetrahedral form. Characteristic absorption of this form lies at $\tilde{\nu} = 11\,800\text{ cm}^{-1}$ and is not observed in the spectra of the yellow and red form. The absorption band at $\tilde{\nu} = 9800\text{ cm}^{-1}$ was observed in the spectra of all three forms. Discrepancies concerning the position of other bands (at $\tilde{\nu} = 7200\text{ cm}^{-1}$ for the yellow and red forms and $\tilde{\nu} = 8000\text{ cm}^{-1}$ and 6600 cm^{-1} for the orange form) could be due to a change in the ratio of intensity of the absorption band and the shoulder and their superposition, resulting in a broader absorption band with the observed maximum at $\tilde{\nu} = 7200\text{ cm}^{-1}$.

Comparison of the ligand field spectra of (DiBA)₂CuCl_{*x*}Br_{4-*x*} with the spectra of the previously studied complexes (DPA)₂CuCl_{*x*}Br_{4-*x*} and (DBA)₂CuCl_{*x*}Br_{4-*x*} points to some similarities between DiBA and DPA compounds. The substitution of chlorine by bromine in the coordination sphere of DPA tetrahalocuprates(II) leads to a transition of the anion structure from a

nearly planar to a distorted tetrahedral; a significant change of the degree of tetrahedral distortion was observed under the same conditions with DiBA tetrahalocuprates(II). The pattern of the ligand field spectra of DBA tetrahalocuprates(II) was preserved with changes in the coordination sphere, e.g. the $\text{CuCl}_x\text{Br}_{4-x}^{2-}$ anions possess the distorted tetrahedral structure with approximately equal degree of distortion regardless x .

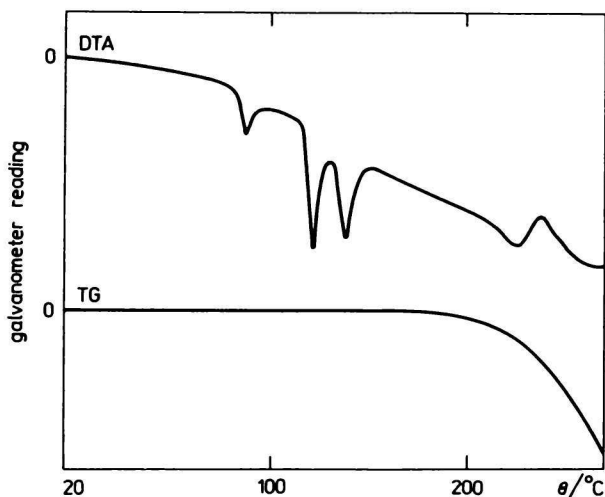


Fig. 2. TG and DTA curves of $(\text{DiPA})_2\text{CuCl}_4$.

Thermal properties

TG and DTA curves of $(\text{DiPA})_2\text{CuCl}_4$ are shown in Fig. 2. Melting takes place without loss in the mass at 135°C . In addition to the endothermic change corresponding to the melting, the DTA curve shows two other endothermic deviations at 88°C and 119°C . We propose they correspond to phase transitions associated with the structural change of CuCl_4^{2-} .

$(\text{DiBA})_2\text{CuCl}_x\text{Br}_{4-x}$ for $x = 0-4$ melt without decomposition. The DTA curves of the yellow, orange, and red forms of $(\text{DiBA})_2\text{CuCl}_4$ are identical. In addition to the endothermic deviation connected with melting of the compound (155°C), another endothermic change is observed at 142°C with the yellow and red forms and at 146°C with the orange form. The DTA curves are depicted in Fig. 3. In the studied temperature interval $20-250^\circ\text{C}$ endothermic deviations

other than meltings were also observed in the case of $(\text{DiBA})_2\text{CuCl}_3\text{Br}$ and $(\text{DiBA})_2\text{CuCl}_2\text{Br}_2$. In contrast, only melting was registered with $(\text{DiBA})_2\text{CuClBr}_3$ and $(\text{DiBA})_2\text{CuBr}_4$, which suggests that these compounds do not undergo reversible phase transition as the former two compounds do. The phase transition is associated with a structural change. We suppose a tetrahedral arrangement with the lowest degree of distortion. The temperature of the phase transition decreases with increasing content of bromine: 142°C or 146°C for CuCl_4^{2-} , 117°C for $\text{CuCl}_3\text{Br}^{2-}$, 92°C for CuCl_2Br_2 . The last two compounds do not exhibit phase transition. Their stable form, even at room temperature is a tetrahedron with a lower distortion degree than in the former compounds.

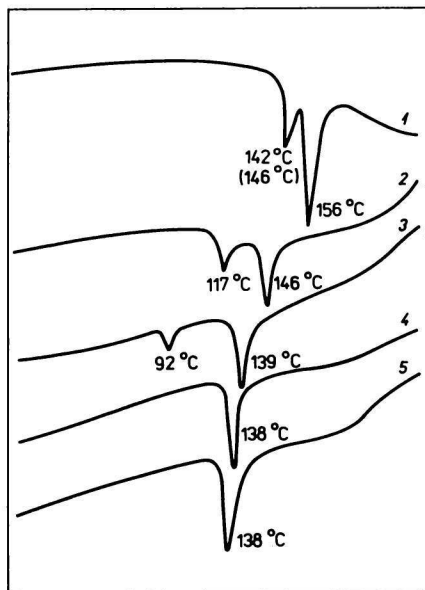
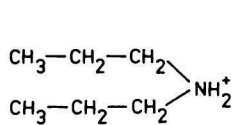


Fig. 3. DTA curves of: 1. $(\text{DiBA})_2\text{CuCl}_4$, 2. $(\text{DiBA})_2\text{CuCl}_3\text{Br}$, 3. $(\text{DiBA})_2\text{CuCl}_2\text{Br}_2$, 4. $(\text{DiBA})_2\text{CuClBr}_3$, 5. $(\text{DiBA})_2\text{CuBr}_4$.

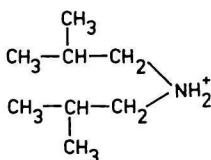
Conclusion

We expected that different steric arrangement of cation would strongly affect the anion structure in the way that the di-isopropyl- and di-isobutylammonium tetrahalocuprates(II) would be "more tetrahedral" than their di-n-analogues. These assumptions have been confirmed only partially. Based on the electronic spectra, CuCl_4^{2-} in $(\text{DiPA})_2\text{CuCl}_4$ may be considered indeed a tetrahedron with much lower degree of distortion than that occurring in $(\text{DPA})_2\text{CuCl}_4$. On the other hand, di-isobutylammonium tetrahalocuprates(II) show greater similarity

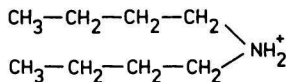
with di-n-propylammonium salts than with di-n-butylammonium salts. The structure of the cations is following:



DPA



DiBA



DBA

From these results we may propose that in limited case, a decisive effect on the strength of hydrogen bonds and, consequently, on the degree of tetrahedral distortion, has the length and not the branching of the cation.

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