

# Preparation and spectral and EPR properties of $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$

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Compounds of the general formula  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  were prepared and studied by means of EPR, electronic absorption spectroscopy and powder diffraction methods. Ligand field bands energies point to the typical layer structure of complex anions independent of  $x$ . The form of the EPR spectra and the  $g$ -values evidence the antiferrodistortional ordering of the elongated anion octahedra in the layers. Below 50 K, temperature dependence of the microwave resonance fields and a linewidth typical for layer ferromagnets was observed.

Получены соединения общей формулы  $(\text{изо-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$ . Проведено изучение полученных соединений с помощью ЭПР, электронной абсорбционной спектроскопии и метода порошковой дифракции. Значения энергий полос поля лиганда указывают на типично слоистую структуру комплексных анионов, независимо от  $x$ . Вид спектров ЭПР и  $g$ -величины свидетельствуют об антиферродеформированном упорядочении удлиненных анионных октаэдров в слоях. При температурах ниже 50 К наблюдалась температурная зависимость полей микроволнового резонанса и ширина полос, типичная для слоистых ферромагнетиков.

It is known that copper compounds of the general formula  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$  ( $n = 1-10$ ) consist of two-dimensional ferromagnetic  $\text{Cu}^{2+}$  layers, separated by two layers of nonmagnetic alkylammonium groups. The results obtained by an extensive study of the magnetic properties of these two-dimensional magnets (the characteristic behaviour in the paramagnetic temperature region, in the vicinity of the critical point, in the temperature region near 0 K) are reviewed in detail by *deJongh* and *Miedema* [1]. According to the literature data, the anion structure in *n*-propylammonium tetrachlorocuprate(II) differs substantially from that in iso-propylammonium tetrachlorocuprate(II): the cation influence in this case is very expressive.  $(\text{iso-PropylNH}_3)_2\text{CuCl}_4$

undergoes a first-order phase transition at 59 °C [2]. Its low-temperature structure contains discrete  $\text{CuCl}_4^{2-}$  ions packed in infinite ribbons parallel to the *a* crystal axis. It has been supposed that the tilting of the iso-propyl groups prevents the transformation of the ribbons into two-dimensional layers found in  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  and related compounds with *n*-alkylammonium groups [3–5].

In this connection it appears to be interesting to study the structure and properties of compounds with some other iso-alkylammonium cation. The anion structure in  $(n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  is distorted octahedral and remains unchanged even upon the substitution of  $\text{Cl} \rightarrow \text{Br}$  [6]. The aim of the present work was to study the peculiarities of tetrahalocuprates(II) containing the cation  $\text{iso-C}_4\text{H}_9\text{NH}_3^+$ .

## Experimental

### *Chemicals and equipments*

The following chemicals were used:  $\text{CuCl}_2$ , prepared by dehydration of the dihydrate;  $\text{CuBr}_2$ , prepared by [7]; iso-butylammonium chloride and bromide, prepared by neutralization of aqueous solution of iso-butylamine followed by recrystallization from ethanol.

Powder diffraction patterns were recorded with a GON III goniometer, electronic absorption spectra in Nujol mulls with a Specord M 40 spectrophotometer, the EPR spectra of polycrystalline samples were measured with ESR 230 spectrometer in the temperature range (4.2–300.0) K.

### *Analytical procedures*

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

### *Preparation of chlorobromocuprates(II)*

All studied chlorobromocuprates(II) were prepared from ethanolic solutions which were allowed to crystallize at 0 °C. Amounts of the starting compounds solved in 25 cm<sup>3</sup> of ethanol as well as the results of their analyses are given below.



$\text{CuCl}_2$ , 1 g;  $\text{iso-C}_4\text{H}_9\text{NH}_2 \cdot \text{HCl}$ , 2 g.

$w_i(\text{calc.})$ : 17.97 % Cu, 41.10 % Cl;  $w_i(\text{found})$ : 17.99 % Cu, 41.04 % Cl.



$\text{CuBr}_2$ , 1.3 g;  $\text{iso-C}_4\text{H}_9\text{NH}_2 \cdot \text{HCl}$ , 1.7 g.

$w_i(\text{calc.})$ : 15.98 % Cu, 26.75 % Cl, 20.01 % Br;  $w_i(\text{found})$ : 16.17 % Cu, 26.77 % Cl, 21.50 % Br.



$\text{CuCl}_2$ , 0.5 g;  $\text{iso-C}_4\text{H}_9\text{NH}_2 \cdot \text{HBr}$ , 2.6 g.

$w_i(\text{calc.})$ : 14.39 % Cu, 16.01 % Cl, 36.20 % Br;  $w_i(\text{found})$ : 15.35 % Cu, 17.12 % Cl, 37.41 % Br.



$\text{CuBr}_2$ , 5 g;  $\text{iso-C}_4\text{H}_9\text{NH}_2 \cdot \text{HCl}$ , 1.7 g.

$w_i(\text{calc.})$ : 13.05 % Cu, 7.29 % Cl, 49.30 % Br;  $w_i(\text{found})$ : 13.53 % Cu, 7.52 % Cl, 51.29 % Br.



$\text{CuBr}_2$ , 2 g;  $\text{iso-C}_4\text{H}_9\text{NH}_2 \cdot \text{HBr}$ , 3 g.

$w_i(\text{calc.})$ : 11.95 % Cu, 60.20 % Br;  $w_i(\text{found})$ : 12.13 % Cu, 62.74 % Br.

## Results and discussion

The powder diffraction patterns of all studied complexes are almost identical. A relatively small number of lines displaced in regular intervals points to a high crystal symmetry. The position of the lines remains practically the same independent of  $x$  (Table 1). We assume that the mixed chlorobromocuprates(II) are isomorphous with the homogeneous tetrahalo complexes, similarly as it was observed in the case of  $n\text{-C}_4\text{H}_9\text{NH}_3^+$  salts [6].

Table 1

Powder diffraction data of  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$

Compound	$2\theta^\circ$						
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_4$	6.3	12.8	19.25	25.6	32.15	38.8	45.6
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_3\text{Br}$	6.2	12.6	19.0	25.5	32.0	38.65	45.45
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$	6.2	12.65	19.1	25.6	32.1	38.8	45.5
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuClBr}_3$	6.2	12.6	19.0	25.5	32.0	38.7	45.5
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuBr}_4$	6.3	12.6	19.1	25.6	32.2	38.9	45.65

Nujol absorption spectra in the visible region are presented in Fig. 1. Charge transfer bands are shifted to lower energies on substitution of chlorine by bromine in the coordination sphere. In the near infrared region, spectra of

newly prepared substances exhibit one broad ligand field band with maximum at  $\tilde{\nu} \approx 13\,000\text{ cm}^{-1}$  and a slight asymmetry on the low-energy side. The asymmetry may be assigned to a shoulder at  $\tilde{\nu} \approx 10\,800\text{ cm}^{-1}$ . These ligand field bands energies are typical for compounds with pseudooctahedral structure [8].

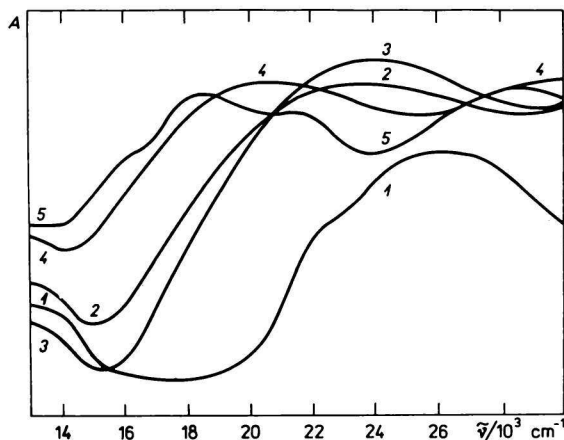


Fig. 1. Electronic absorption spectra of 1.  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_4$ , 2.  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_3\text{Br}$ , 3.  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$ , 4.  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuClBr}_3$ , 5.  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuBr}_4$ .

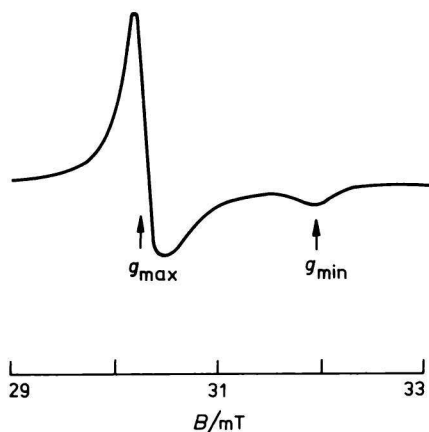


Fig. 2. EPR spectrum of  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_4$  at 77 K,  $\tilde{\nu} = 9.3\text{ GHz}$ .

The EPR spectra are typical for polycrystalline samples with  $S = 1/2$  centres of one type in the case of the axial symmetry of the  $g$ -tensor with  $g_{\perp} > g_{\parallel}$  (Fig. 2). The  $g$ -values at  $T = 77\text{ K}$  and  $300\text{ K}$  are given in Table 2. The form of

Table 2

EPR data of  $(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$ 

Compound	77 K		300 K	
	$g_{\max}$	$g_{\min}$	$g_{\max}$	$g_{\min}$
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_4$	2.160	2.044	2.160	2.048
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_3\text{Br}$	2.127	2.036*	$g_{\text{av}} = 2.095$	$\Delta B = 3.12 \text{ mT}$
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$	2.145	2.051	2.101	2.20 mT
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuClBr}_3$	2.113	2.041	2.075	5.00 mT
$(\text{iso-C}_4\text{H}_9\text{NH}_3)_2\text{CuBr}_4$	2.094	2.055	2.058	5.00 mT

\* The anisotropy is resolved at 45 K.

the EPR spectra and the  $g$ -values are close to those characteristic of the layer ferromagnets  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$  ( $x = 2$  and  $4$ ) [8, 9] and evidence the antiferrodistortional ordering of the elongated anion octahedra in the layers.  $g_{\max}$  and  $g_{\min}$  are the  $g$ -values obtained when the external magnetic field is parallel and perpendicular, respectively, to the magnetic plane. It should be noted that only crystal  $g$ -values are determined from the EPR spectra. For this layer structure crystal ( $g_{\text{cr}}$ ) and molecular ( $g_{\text{mol}}$ )  $g$ -values are related by the following approximate expression

$$(g_{\text{cr}})_{\min} = (g_{\text{mol}})_y$$

$$(g_{\text{cr}})_{\max} = \frac{(g_{\text{mol}})_z + (g_{\text{mol}})_x}{2}$$

A successive substitution of  $\text{Cl} \rightarrow \text{Br}$  leads to a decrease of the  $g$ -values, apparently evidencing some increase of the crystal field strength and of the distortion degree of the coordination polyhedron. All these facts as well as the similarity of the EPR spectra enable us to suppose that in the layer structures with  $x = 2$  and  $3$ , bromine preferably occupies out-of-plane positions. This behaviour of bromine in  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$  has been confirmed [10].

With lowering the temperature to the range 50–300 K the  $g$ -values are practically unchanged evidencing that also the coordination polyhedron and the  $D_{4h}$  symmetry remain unchanged. In the temperature range 13–50 K, a temperature dependence of the microwave resonance fields and of the linewidth is observed. The resonance signal corresponding to  $g_{\min}$  shifts to the high field side, while that corresponding to  $g_{\max}$  shifts to the low field side when the temperature is lowered. The effective  $g$ -values at 13 K are approximately 2.20 for  $g_{\max}$  and 1.90 for  $g_{\min}$ . The linewidth is somewhat reduced with decreasing temperature, but it increases again with further decrease of temperature. All compounds

under investigation behave — in the presence of a relatively weak external field — as two-dimensional ferromagnets. An analogous behaviour had been observed in the case of  $(C_2H_5NH_3)_2CuCl_4$  [11] and some other related compounds [10]. This fact serves as an additional evidence in favour of the layer structure of the studied compounds.

The above experimental results suggest that the structure of the anion in iso-butylammonium tetrahalocuprates(II) is the same as in n-butylammonium tetrahalocuprates(II), *i.e.* a distorted octahedron. The degree of distortion is independent of the  $N(Cl) : N(Br)$  ratio in the coordination sphere. The structure of the anion is not significantly affected by the steric arrangement of the cation, as it was observed in the case of n-propylammonium and iso-propylammonium salts.

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