# Magnetic Properties of Different Modifications of Dihalide Diammine Copper(II) Complexes

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The magnetic susceptibilities of dihalide diammine copper(II) complexes of the type $CuX_2(NH_3)_2$ (X = Cl or Br), which differ as regards their distortion of octahedral configuration of ligands, were measured over the temperature range $77-293\ °K$. The magnetic data were then interpreted on the basis of the known crystal structures of these compounds.

It is well known that the most salient feature of the stereochemistry of the copper(II) complexes is their tetragonally distorted structure [1] in which, the coordination number being 6, the central atom is linked with two ligands in the direction of the axis $z$ by bonds differing in their lengths from those of the remaining four ligands in the plane $xy$. That means that the octahedral field is distorted by a certain participation of lower symmetry component $D_{4h}$ and the spectroscopic ground state $^2D$ is split in the manner shown in Fig. 1.
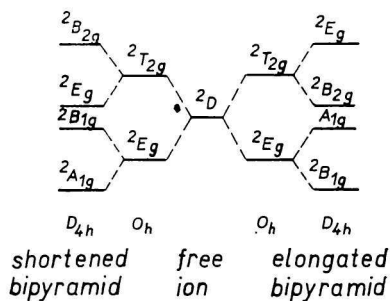


Fig. 1. Splitting of the $^2D$-term of the $Cu^{2+}$ ion in the octahedral ($O_h$) and tetragonal ($D_{4h}$) ligand field in case of the elongation and shortening along the axis $z$.

The ground term $^2E_g$ in the symmetry $O_h$ is a „non-magnetic" doublet which by itself can not produce any orbital contribution to the magnetic moment. In spite of this, by the interaction of the ground term $^2E_g$ with the excited term $^2T_{2g}$, which is an orbital triplet, a certain orbital component is introduced into the magnetic moment. Similar situation arises in the case of tetragonally distorted octahedral system, the magnetic moment of which can be calculated using the formula [2]:

$$\mu_{\text{eff.}} = \mu_0 \left(1 - \frac{2\,k\lambda}{\Delta}\right),$$

where $\mu_0$ denotes the spin-only value of the magnetic moment for the compounds of Cu(II), which is 1.73 B. M., $k$ is the orbital reduction factor, $\lambda$ is the spin-orbit coupling constant, $\Delta$ is the separation between the ground term $^2B_{1g}$ and $^2A_{1g}$ respectively, and the components of the term $^2T_{2g}$. Hence we can expect that the values of the magnetic moments of copper(II) complexes will be influenced by the field strength of the participating ligands, by the degree of the distortion of the „octahedral" coordination and also by the extent of the expansion of the electron cloud of the unpaired electron from the central atom towards the ligands.

In order to get experimental data by which the theoretical assumptions on magnetic properties of copper(II) complexes could be verified, we measured at different temperatures over the range $77-293$ °K the magnetic susceptibilities of dihalide diammine copper(II) complexes of the type $CuX_2(NH_3)_2$, where X = Cl or Br. These complexes are known [3—8] in different modifications which use to be designated as $\alpha$ and $\beta$*. The structures of these modifications differ in that in the former the ligands are arranged around the central copper atom in the form of an elongated bipyramid, in the latter in the form of a shortened tetragonal bipyramid (Fig. 2). Recently, by the study of IR spectra, it has been found [9] that $\alpha$- and $\beta$-modifications of $CuBr_2(NH_3)_2$, apart from belonging to two different types of structure geometry, are various chemical individuals with different bond strengths. With regard to this it seems advisable to find if, as a consequence of these differences in the chemical structure, the complexes $CuBr_2(NH_3)_2$ would have different physical properties, especially magnetic moments. Since, according to the ligand field theory, the magnetic moments depend on the splitting parameter value $\Delta$, we may expect that as a consequence of differently distorted arrangement and of different bond strength, even indentical ligands will show moments varying to a certain degree. Apart from this, in the halide complexes

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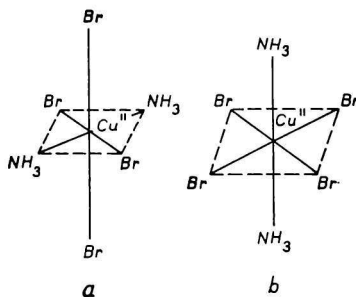* $\beta$-Modification of $CuBr_2(NH_3)_2$ exists in crystalline and powder form.



Fig. 2. The coordination polyhedron of copper in a) $\alpha$-CuBr$_2$(NH$_3$)$_2$; b) $\beta$-CuBr$_2$(NH$_3$)$_2$.

$CuX_2(NH_3)_2$ there is, owing to their polymeric structure with halide bridges, the possibility of antiferromagnetic interaction between the copper ions, similarly as it has been observed [10] for many halide complexes of Cu(II) with analogous structure. Taking into account the above said, the research of magnetic properties of this type of copper(II) complexes would be useful and would improve upon the actual knowledge of the influence of structure factors on magnetic properties of copper(II) complexes.

## Experimental

### Reagents

Copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$, analytical-reagent grade from Lachema, was recrystallized from the water solution. Lithium bromide was prepared by the reaction between the lithium carbonate $Li_2CO_3$ pss. and pure hydrobromic acid, both from Lachema. Then it was three times recrystallized from the water solution. Gaseous ammonia was prepared from aqueous ammonia by the action of solid potassium hydroxide and before using it was dried by solid potassium hydroxide. All remaining reagents used were Czechoslovak products of analytical-reagent grade.

### Analytical methods

The composition of the individual specimens was determined by estimation of copper, ammonia and halogen content. The copper content was determined gravimetrically by transforming the sample to bis(oxinate) copper(II) chelate. Halogen was determined by the potentiometric titration carried out with the standard solution of silver nitrate and with silver and calomel electrodes. Ammonia was determined by titration after previous destillation.

### Preparation of compounds

$\alpha$-$CuBr_2(NH_3)_2$ was prepared from the acetone solution of copper nitrate and lithium bromide, in which $[Br^-] : [Cu^{2+}] \approx 6 : 1$, by introducing gaseous ammonia into it according to the procedure described in [3]. $\alpha$-$CuCl_2(NH_3)_2$ was prepared in an analogous way [3]. $\beta$-$CuBr_2(NH_3)_2$ was prepared by treating $\alpha$-$CuBr_2(NH_3)_2$ with gaseous ammonia and by subsequent thermic decomposition of the formed higher ammoniacate [3]. The crystalline $CuX_2(NH_3)_2$ were obtained by recrystallization of the powder substances from saturated water solutions of ammonium halogenides by the procedure described in [3].

For $\alpha$-$CuCl_2(NH_3)_2$ $(M = 168.54)$
      Calculated:   37.71 % Cu,   42.08 % Cl,   20.21 % $NH_3$;
      Determined:   37.37 % Cu,   41.95 % Cl,   19.90 % $NH_3$.

For $\alpha$-$CuBr_2(NH_3)_2$ $(M = 257.46)$
      Calculated:   24.68 % Cu,   62.08 % Br,   13.23 % $NH_3$;
      Determined:   24.81 % Cu,   62.18 % Br,   13.39 % $NH_3$.

For $\beta$-$CuBr_2(NH_3)_2$ $(M = 257.46)$
      Calculated:   24.68 % Cu,   62.08 % Br,   13,23 % $NH_3$;
      Determined:   24.80 % Cu,   61.91 % Br,   13.04 % $NH_3$.

For the crystalline $CuCl_2(NH_3)_2$

     Determined: 37.43 % Cu, 41.45 % Cl, 19.87 % $NH_3$.

For the crystalline $\beta$-$CuBr_2(NH_3)_2$

     Determined: 19.11 % Cu, 65.27 % Br, 13.82 % $NH_3$.

From the analysis results it follows that the compounds $\alpha$- and $\beta$-$CuX_2(NH_3)_2$, as well as the crystalline $CuCl_2(NH_3)_2$, have stoichiometric composition whereas the crystalline compound $\beta$-$CuBr_2(NH_3)_2$ contains about 21 weight % ammonium bromide; its varying content being dependent on the crystallization conditions.

## X-Ray diffraction diagrams

The identity of the modifications of $CuBr_2(NH_3)_2$ was determined by X-ray diffraction diagrams. These diagrams were made with the aid of the powder goniometer GON with $CuK_\alpha$ radiation; the speed of rotation was 1°/min., the time constant 4.

The diffraction diagrams of the individual $CuBr_2(NH_3)_2$ samples are shown in Fig. 3. It is evident that the diffraction diagram of $\alpha$-$CuBr_2(NH_3)_2$ exhibits patterns characteristical for this modification [3] whereas the diagram of the powdered $\beta$-$CuBr_2(NH_3)_2$ seems to indicate [3, 4] — owing to slight splitting of the characteristic lines — that there is a very small amount of $\alpha$-modification in the sample, which admixture can not be entirely avoided when the sample is prepared by dry reaction [4]. The diffraction diagram of the crystalline $\beta$-$CuBr_2(NH_3)_2$ is, according to [3], very similar to that of the powdered sample $\beta$-$CuBr_2(NH_3)_2$.
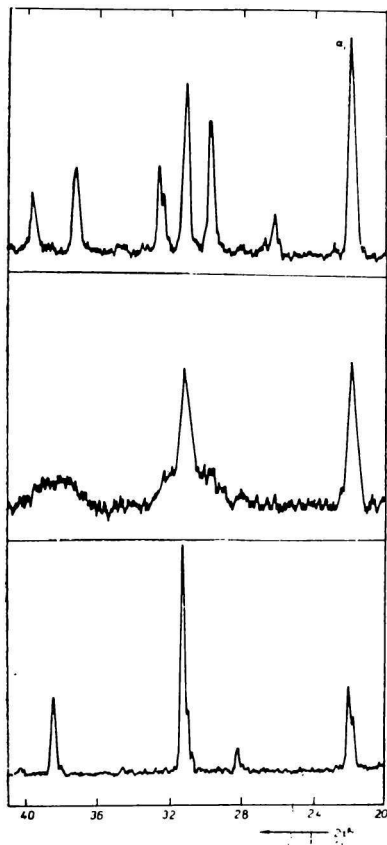


Fig. 3. X-ray diffraction diagrams of
a) $\alpha$-$CuBr_2(NH_3)_2$;
b) powdered $\beta$-$CuBr_2(NH_3)_2$;
c) crystalline $\beta$-$CuBr_2(NH_3)_2$.

## Magnetic measurements

The magnetic measurements of the prepared complexes were performed much in the same way as it has been described in [11]. The effective magnetic moments were calculated from the relation $\mu_{\text{eff.}} = 2.84 \sqrt{(\chi'_M - N\alpha)T}$, where for the temperature independent paramagnetism $N\alpha$ the value of $60 \cdot 10^{-6}$ abs. units was substituted, which is the usual value for the tetragonal complexes of Cu(II). The results of magnetic measurements are presented in Tab. 1.

### Table 1

Specific, molar and corrected molar susceptibilities (absolute units) and magnetic moments (B. M.) at individual temperatures

| Complex | Temperature (°K) | $\chi \cdot 10^6$ | $\chi_M \cdot 10^6$ | $\chi'_M \cdot 10^6$ | $\mu_{\text{eff.}}$ (B.M.) | $\Theta$ (°K) |
|---|---|---|---|---|---|---|
| $\alpha$-CuCl$_2$(NH$_3$)$_2$ | 293 | 7.21 | 1215 | 1307 | 1.72 | |
| | 273 | 7.85 | 1323 | 1415 | 1.73 | 77 |
| | 201 | 9.77 | 1646 | 1738 | 1.65 | |
| | 77 | 18.37 | 3095 | 3187 | 1.39 | |
| $\alpha$-CuBr$_2$(NH$_3$)$_2$ | 293 | 4.46 | 1148 | 1260 | 1.68 | |
| | 273 | 4.80 | 1235 | 1347 | 1.68 | 117 |
| | 201 | 5.82 | 1498 | 1610 | 1.59 | |
| | 87 | 9.59 | 2469 | 2581 | 1.33 | |
| powdered $\beta$-CuBr$_2$(NH$_3$)$_2$ | 293.4 | 4.53 | 1166 | 1278 | 1.70 | |
| | 273 | 4.84 | 1246 | 1358 | 1.69 | 87 |
| | 201 | 6.22 | 1601 | 1713 | 1.64 | |
| | 84 | 11.29 | 2906 | 3018 | 1.42 | |

## Discussion

The investigated dihalide diammine copper(II) complexes have at room temperature magnetic moments slightly lower than the spin-only value for the compounds of bivalent copper (1.73 B. M.): these magnetic moments are temperature dependent and with lowering temperature their values markedly decrease (Fig. 4). Though the inverse values of their corrected molar susceptibilities exhibit a linear dependence on the absolute temperature, the corresponding straight lines intercept very long intervals on the temperature axis in the range of the negative values (Fig. 5). The susceptibility dependence on the outer magnetic field over the range 1700—8200 Oe has not been observed. Hence it follows that the magnetic behaviour of these complexes obeys the Curie—Weiss law in the form $\chi'_M \alpha(T + \Theta)^{-1}$, the Weiss constants $\Theta$ acquiring rather high positive values over the range 77—117 °K. These

experimental results are indicative of the antiferromagnetic character of the investigated complexes and the explanation of this behaviour must of necessity be based on their lattice structure.
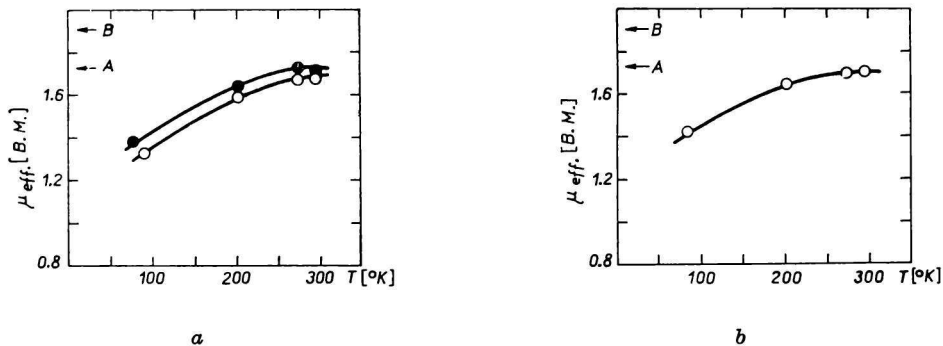


a                                                                          b

Fig. 4. $\mu_{eff.}$ vs. $T$ for a) $\alpha$-CuCl$_2$(NH$_3$)$_2$ and $\alpha$-CuBr$_2$(NH$_3$)$_2$; b) powdered $\beta$-CuBr$_2$(NH$_3$)$_2$.
A. spin only value for copper(II) compounds; B. value found for CuSO$_4$ . 5H$_2$O.
a) ● $\alpha$-CuCl$_2$(NH$_3$)$_2$;  ○ $\alpha$-CuBr$_2$(NH$_3$)$_2$.



a                                                                          b
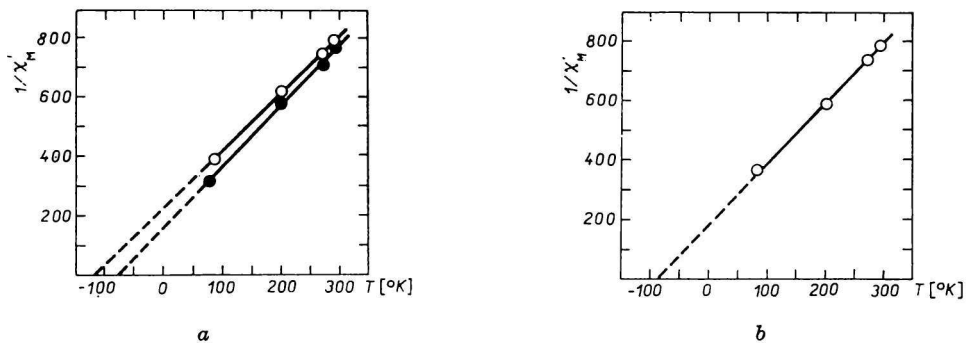
Fig. 5. $1/\chi'_M$ vs. $T$ for a) $\alpha$-CuCl$_2$(NH$_3$)$_2$ and $\alpha$-CuBr$_2$(NH$_3$)$_2$; b) powdered $\beta$-CuBr$_2$(NH$_3$)$_2$.
a) ● $\alpha$-CuCl$_2$(NH$_3$)$_2$;  ○ $\alpha$-CuBr$_2$(NH$_3$)$_2$.
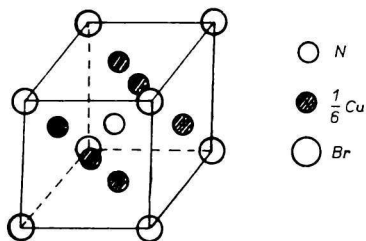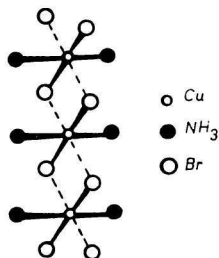


Fig. 6.  Chains in the crystal lattice of          Fig. 7.  Elementary cell of $\beta$-CuBr$_2$(NH$_3$)$_2$.
$\alpha$-CuBr$_2$(NH$_3$)$_2$.

The crystal structure of the $\alpha$-dibromo-diammine copper(II) complex is formed [7] by the planar molecules $CuBr_2(NH_3)_2$, in which the ammonia molecules are in *trans*-positions and the coordination number of copper is completed from 4 to 6 by polymerization in the course of which the bridges of bromide ions joining the copper ions form infinite linear chains (Fig. 6). To each copper atom two $Br^-$ ions and two ammonia molecules, always in *trans*-positions, are bonded on the „short" coordinates and further two $Br^-$ ions are bonded on the „long" coordinates, forming thus an elongated tetragonal bipyramid configuration round the central copper ion (Fig. 2*a*). The structure of the crystalline $\beta$-dibromo-diammine copper(II) complex may be described [6] as a structure of $NH_4Br$ in which the $NH_4^+$ ions are substituted by $NH_3$ molecules, the centre of one of the six faces of the elementary cell is statistically occupied by one copper ion, the $Br^-$ ions remaining in their original positions (Fig. 7). With regard to the isomorphous substitution of ammonium bromide in this substance, a certain part of the elementary cells consists merely of $NH_4^+$ and $Br^-$ ions. The bond between copper and bromine can be considered to be ionic [6] since its length is 2.87 Å, whereas the sum of ionic radii of copper and bromine is 2.72 Å. Owing to the chain formation, also in this case the coordination number is completed to 6, the $Br^-$ ions being bonded on the „long" coordinates and two ammonia molecules on the „short" coordinates, so that each copper ion is coordinated in the manner of a shortened tetragonal bipyramid (Fig. 2*b*). This modification, however, is a statistical structure in which the octahedral complexes $CuBr_4(NH_3)_2$ may be oriented in the direction of all three crystallographic axes. For this reason, the interatomic distances $Cu-Br$ are but the average values of the real bond lengths which actually may be statistically shorter or longer and the real bond lengths $Cu-N$ can be systematically shorter than the distances between the centre of the elementary cell faces and the point 1/2, 1/2, 1/2 [12]. Up to now, the structure of powder $\beta$-modification which does not contain $NH_4^+$ ions has not been investigated in details, but from analogy with the X-ray diagrams [3] it may be assumed that the structure of this modification is analogous with that of the crystalline $\beta$-modification [6, 7]. The structure of $\alpha$-dichloro--diammine copper(II) complex is closely related [8] to the above structure of the $\beta$-bromocomplex and the main difference is that the copper ions are not distributed statistically but their positions are exactly defined. As to the coordination of copper, there holds the same as has been stated for $\beta$-$CuBr_2(NH_3)_2$. A review of the main structure parameters of the complexes $CuX_2(NH_3)_2$ is presented in Tab. 2.

The found magnetic properties of the dihalide diammine copper(II) complexes show beyond any doubt that in their crystal structures a magnetic interaction between the copper ions occurs. Since the distance between the

Table 2

Basic structure parameters of the complexes $CuX_2(NH_3)_2$

| Complex | Distance (Å) | | |
|---|---|---|---|
| $\alpha$-$CuBr_2(NH_3)_2$ | Cu—2NH$_3$ <br> 1.93 | Cu—2Br <br> 2.54 | Cu—2Br <br> 3.08 |
| crystalline <br> $\beta$-$CuBr_2(NH_3)_2$ | Cu—2NH$_3$ <br> 2.034 | Cu—4Br <br> 2.876 | — |

neighbouring copper ions [Cu—Cu = 4.05 Å in $\alpha$-$CuBr_2(NH_3)_2$] is fairly great, we hardly can expect a direct copper—copper interaction which occurs e. g. in the copper(II) acetate monohydrate and in higher copper(II) alkanoates [13, 14]. Nevertheless, the polymeric structure of these complexes leading to linear chains, in which the copper ions are bridged by the halide ions, allows for a superexchange interaction [15] between the copper ions along the chains via halide bridges. A similar exchange mechanism is supposed to exist [16] in the case of copper(II) bromide and chloride, whose crystal lattices are also formed [17, 18] by infinite linear chains of copper ions linked by the bridging halide ions. The copper bromide and chloride have at room temperature magnetic moments of 1.61 and 1.33 B. M., respectively [19, 20] and the temperature dependence of their susceptibilities is in good agreement [16] with the assumed linear antiferromagnetism which is due to the interaction of electron spins along the infinite copper atom chains.

Generally, the antiferromagnetic substances are characterized by a maximum on their susceptibility — temperature plot, as well as by the fact that, at temperatures sufficiently above the temperature of this maximum, their susceptibilities obey the Curie—Weiss law. The constant $\Theta$ of this law is related to the interaction energy $J$ in a manner depending upon the structure of the substance. Below the temperature of the maximum of the susceptibility there is a widegoing orientation of electron spins which brings about a spontaneous antiferromagnetism in a definite direction [21]; above this temperature, the electron spins are randomly oriented. The maximum susceptibility temperatures are usually lower than the values $\Theta$, so that for the halide complexes under investigation, these temperatures will be lower than the lowest temperatures of the measurements. In order to verify this assumption of the antiferromagnetism of these complexes* it would be advisable to carry out

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* Some preliminary calculations performed on the basis of the one-dimensional Ising model of antiferromagnetism [22] seem to confirm this assumption. It has not been possible to make more precise calculations of the dependence $\chi'_M$ -- $T$ as we do not know the accurate values of the pertinent parameters and these can not be determined from the available experimental data.

a series of susceptibility measurements in this low-temperature range so as to find the maximum susceptibility temperatures and to examine the magnetic behaviour under these temperatures. In this range, the temperature dependence of susceptibilities have a qualitatively different course and some anomalies could occur in connection with the character of the exchange mechanism.

Essentially, there are two manner in which the migration of the unpaired electron on copper ion on the way $Cu-X-Cu$ can take place, either through $\sigma$- or $\pi$-orbitals of the bridged halide ions and this migration is responsible for the assumed antiferromagnetic behaviour. In case of the binary compound $KCuF_3$, which is known to have a strong antiferromagnetic interaction [23, 24], this interaction evidently takes place along the linear chains $Cu-F-Cu-F$ in the crystal lattice [25] through the $2p_\sigma$-orbitals of the fluoride ions. The bond angle $Cu-X-Cu$ in our halide complexes is nearly rectangular and this almost precludes the use of the $p_\sigma$-orbitals for the superexchange interaction. On the other hand, a $\sigma$-pathway set up by using $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals of the copper ion and $s$-orbital of the halide ion as well as a $\pi$-pathway mediated by $3d_{xz}$ or $3d_{yz}$ orbitals of the copper ion and $p_z$ orbitals of the halide ion are possible. The choice between these two pathways for the superexchange depends on whether the transition of the unpaired electron from $3d_{x^2-y^2}$ or $3d_{z^2}$ to $3d_{xz}$ or $3d_{yz}$ which is inevitable for the $\pi$-path, or the delocalization from a lower $s$-orbital of the halide ion which is necessary for the $\sigma$-path, is more favourable from the energetical point of view.

The values of the magnetic moments of the halide complexes at room temperature prove that the exchange interaction between the copper ions is considerably lower than that of the chloride or bromide itself. Most probably this is due to greater $Cu-X$ distances in the chains of the complexes $CuX_2(NH_3)_2$. Whereas in $CuBr_2$ the distances $Cu-Br$ in the chains are 2.40 Å [18], it may be seen from the Tab. 2 that these bonds occuring in both modifications of $CuBr_2(NH_3)_2$ are so much longer that this accounts for the observed decrease of magnetic exchange. It is as well evident that the differences in the magnetic properties of both chloro- and bromocomplexes are relatively very small. This is interesting since it has been found [10] that as to the copper(II) compounds with halide bridges, the exchange interaction in bromides is considerably stronger than that in chlorides. This may be accounted for in such a way that, on the more voluminous and more easily polarizable bromide ion the electrons of the outer shell are rather weakly fastened and their mobility, responsible for the magnetic interaction between the copper ions by superexchange, is energetically more accessible. Anyway there is a possibility to establish a hypothesis that these magnetic properties of chloro- and bromocomplexes are due to the bonding of ammonia molecules to the copper ions. Ammonia has a very strong ligand field owing to which the energy difference

between $e_g$ and $t_{2g}$ orbitals of copper ions becomes much greater and consequently the electron transition $3d_{x^2-y^2} (3d_{z^2}) \rightarrow 3d_{xz}; 3d_{yz}$ connected with the $\pi$-pathway is much more difficult. As a result of this, the influence of different fixing strength of the outer electrons on the bromide and chloride ions is mostly eliminated so that the superexchange effect is very similar for both the chloro- and bromocomplexes. Taking this into account, the $\pi$-path in the superexchange seems to be more probable.

Similarly, the differences of the magnetic properties of the $\alpha$- and powdered $\beta$-modification of $CuBr_2(NH_3)_2$ are rather small and only at lower temperatures they are slightly more pronounced. It can be stated that the powdered $\beta$-$CuBr_2(NH_3)_2$ represents, as to its magnetic properties, a transition between the $\alpha$-$CuBr_2(NH_3)_2$ and the $\alpha$-$CuCl_2(NH_3)_2$ approaching especially at lower temperatures the latter complex. It is evident that under these circumstances, when the magnetic behaviour of both modifications is complicated by the antiferromagnetic interaction, it is rather difficult to estimate the influence of different distortions of the octahedral field on the magnetic moment of each modification. The fact that the magnetic behaviour of the powdered $\beta$-$CuBr_2(NH_3)_2$ is very similar to that of $\alpha$-$CuCl_2(NH_3)_2$ is in a good agreement with the closely related structures of both complexes. A slightly smaller exchange interaction copper—copper may be expected in the case of $\beta$-$CuBr_2(NH_3)_2$ since the statistical mean distance Cu—Br in the chains of the crystalline $\beta$-modification (see Tab. 2) are by 0.07 Å greater than the average of the two different distances Cu—Br in the chains of $\alpha$-$CuBr_2(NH_3)_2$.

The crystalline specimen $\beta$-$CuBr_2(NH_3)_2$ contains according to the analysis, 0.59 molar fractions of the complex itself, in which the magnetic moment of the copper ion is 1.79 B. M. at room temperature. This is in good agreement with the fact that, by the formation of mixed crystals of the complex $\beta$-$CuBr_2(NH_3)_2$ with ammonium bromide with which it is isostructural, the possibility of magnetic interaction between the copper ions in crystal lattice decreases. In a part of the elementary cells of $\beta$-$CuBr_2(NH_3)_2$ (Fig. 7), the molecules $NH_3$ are substituted by $NH_4^+$ ions and the ions $Cu^{2+}$ which statistically occupy one of the six faces of each cell, are left out. Consequently there is an intermittence in the bromide-bridged chains and as a result of this, the magnetic connection between the copper ions is interrupted to a certain degree, the magnetic moment thus approaching the value of a magnetically shielded copper ion in the given ligand field. The magnetic moment of the crystalline $CuCl_2(NH_3)_2$, the composition of which is practically stoichiometric, was found to be 1.71 B. M. at room temperature which does not greatly differ from that of the powdered specimen (1.72 B. M.).

## MAGNETICKÉ VLASTNOSTI DIHALOGENO-DIAMOMĚDNATÝCH KOMPLEXŮ VYSKYTUJÍCÍCH SE V RŮZNÝCH MODIFIKACÍCH

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Změřily se magnetické susceptibility dihalogeno-diamomědnatých komplexů typu $CuX_2(NH_3)_2$, kde X = Cl nebo Br, a to při různých teplotách v rozmezí 77—293 °K. Zjistilo se, že tyto komplexy mají při pokojové teplotě magnetické momenty nižší než čistě spinová hodnota pro Cu(II) a s klesající teplotou se tyto momenty výrazně snižují. Magnetické susceptibility těchto komplexů se řídí Curie—Weissovým zákonem při vysokých kladných hodnotách konstanty $\Theta$. Z tohoto chování se usuzuje na antiferromagnetickou povahu a předpokládá se, že magnetická interakce nastává supervýměnou v nekonečných lineárních řetězcích iontů mědi prostřednictvím můstkových halogenidových aniontů. Diskutují se možné způsoby, jimiž se supervýměnná interakce může uskutečňovat, a hodnotí se vliv některých činitelů, ktoré tuto interakci mohou ovlivňovat. Zjišťuje se, že magnetické momenty $\alpha$- a $\beta$-modifikace $CuBr_2(NH_3)_2$ se při obyčejné teplotě liší jen velmi málo a poněkud větší rozdíly se objevují až při nízkých teplotách, při čemž magnetické chování $\beta$-$CuBr_2(NH_3)_2$ se blíží spíše chování $\alpha$-$CuCl_2(NH_3)_2$ v souhlase s velmi blízkou strukturou obou těchto látek. V krystalickém $CuBr_2(NH_3)_2$ má ion mědi při pokojové teplotě magnetický moment znatelně vyšší, což zřejmě vyplývá ze skutečnosti, že tvorbou směsných krystalů bromokomplexu s bromidem amonným se možnost magnetické interakce mezi ionty mědi zmenšuje.

## МАГНИТНЫЕ СВОЙСТВА ДИГАЛОГЕНО-ДИАММОКОМПЛЕКСОВ ДВУХВАЛЕНТНОЙ МЕДИ, СУЩЕСТВУЮЩИХ В РАЗЛИЧНЫХ МОДИФИКАЦИЯХ

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Братислава

При различных температурах в интервале 77—293 °К были измерены магнитные восприимчивости дигалогено-диаммокомплексов двухвалентной меди типа $CuX_2(NH_3)_2$, где X = Cl или Br. Нашли, что магнитные моменты этих комплексов при комнатной температуре ниже, чем только спиновое значение для Cu(II), а с понижением температуры эти моменты значительно понижаются. Магнитные восприимчивости этих комплексов подчиняются закону Кюри—Вайса при высоких положительных значениях константы $\Theta$. На основе такого поведения предполагается антиферромагнитная природа и предполагается, что магнитное взаимодействие происходит суперобменом в бесконечных линейных цепях ионов меди с помощью мостиковых галогеновых ионов. Об-

суждаются возможные способы, которыми суперобменное взаимодействие может осуществляться и оценивается влияние некоторых обстоятельств, которые бы на это взаимодействие могли влиять. Определили, что магнитные моменты α- и порошковых β-модификаций $CuBr_2(NH_3)_2$ при обычной температуре очень мало отличаются и это различие увеличивается только при низких температурах, причем магнитное поведение порошкового β-$CuBr_2(NH_3)_2$ более похоже поведению α-$CuCl_2(NH_3)_2$, что находится в согласии с очень близкой структурой обоих этих веществ. В кристаллическом $CuBr_2(NH_3)_2$ магнитный момент иона меди при комнатной температуре заметно выше, что, очевидно, вытекает из того обстоятельства, что при образовании смешанных кристаллов бромокомплекса с бромидом аммония возможность магнитного взаимодействия между ионами меди понижается.

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