Copper(II) Complexes with Organic Ligands (VII)
Magnetic Properties of Copper(II) Acetate and Copper(II) Salicylate Complexes of Pyridine and Quinoline N-Oxides

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Copper(II) acetate and copper(II) salicylate complexes of pyridine and quinoline N-oxides were prepared. Magnetic susceptibilities between 77—294 °K have been measured and on the basis of the determined magnetic properties the structures of these compounds is discussed.

It is well known that copper(II) acetate monohydrate has a binuclear bridged structure [1, 2] in which two copper atoms are bonded by four acetate groups and the water molecules are linked to copper atoms in axial terminal positions (Fig. 1). The salient feature of this structure is the close approach of the neighbouring copper atoms Cu—Cu = 2.64 Å, owing to which there is direct copper—copper bonding, arising most likely [3—7] from the lateral overlap of $3d_{x^2-y^2}$ orbitals on each copper atom. Owing to this bonding, the magnetic moment is depressed below the spin-only value 1.73 B. M. for one unpaired electron of $3d^9$ configuration of the copper(II) ion to the value 1.40 B. M. at room temperature [3]. Simultaneously a remarkable temperature dependence of the susceptibility is observed [3, 8, 9] which does not obey the Curie—Weiss law but which is compatible with the anti-ferromagnetic behaviour. The exchange energy $|2J|$ determined from this dependence is about 300 cm^{-1}.

The water molecules in the terminal positions in the copper(II) acetate monohydrate structure may be substituted [10—12] by other neutral ligands of available field strength so that the binuclear structure with magnetic interaction between the copper atoms is maintained. Similarly the anions of other carboxylic acids
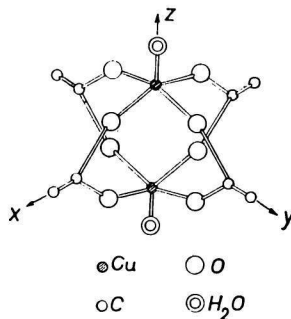

Fig. 1. Structure of copper(II) acetate monohydrate.

[13—20] may take over the function of bridges in binuclear structures supposing they are able to keep the positively charged copper ions at sufficiently short distances [10, 16, 18], which is indispensable for the structure of this type.

Naturally we may expect that the type of the neutral ligands and of the anions of the carboxylic acids will exert considerable influence on the possibility of the formation of the binuclear bridged structures and — if such structures are formed — on the degree of overlap between $3d_\delta$-orbitals. This will further influence the magnetic interaction and consequently the magnetic moments of these complexes. In order to study in greater details these interesting theoretical problems we have prepared the copper(II) acetate and copper(II) salicylate complexes of pyridine N-oxide (Pyox) and quinoline N-oxide (Quinox) and we measured their magnetic susceptibilities at different temperatures between 77—294 °K.

Experimental

Reagents

Copper(II) acetate monohydrate made by Lachema (without designation of the purity degree) was recrystallized twice from the water solution that had been acidified by a few drops of acetic acid. Bis(salicylato)diaquocopper(II) dihydrate has been prepared by the procedure discussed in [21]. Pyridine N-oxide and quinoline N-oxide were prepared and purified by the procedure [22]. All other chemicals were of Czechoslovak make, analytically pure.

Reaction of copper(II) acetate monohydrate with pyridine N-oxide and quinoline N-oxide

A suspension of finely powdered copper(II) acetate monohydrate in ethanol solution of pyridine N-oxide or quinoline N-oxide was heated. Several drops of acetic acid were added to the reacting substances. After 20—30 minutes of boiling, the undissolved particles were removed by filtration and the clean filtrate was cooled to 0 °C. The precipitated green crystalline products were sucked off, then washed with cooled ethanol and freely dried in the air to constant weight.

We used:

a) A suspension of 5 g copper(II) acetate monohydrate ($1.25 . 10^{-2}$ M) in a solution of 7.1 g pyridine N-oxide ($7.50 . 10^{-2}$ M) in 100 ml of 96 % ethanol. We isolated 5.5 g of the resulting substance.

b) A suspension of 5 g copper(II) acetate monohydrate ($1.25 . 10^{-2}$ M) in a solution of 9.1 g quinoline N-oxide ($6.27 . 10^{-2}$ M) in 100 ml of 96 % ethanol. We isolated 4.6 g of the final product. Copper and nitrogen were determined in the isolated substances. Copper was determined after the sample had been burnt and the ashes were converted into copper(II) nitrate by titration with Chelaton III using murexide as indicator. Nitrogen was determined by the Dumas method.

a) For $Cu(CH_3 . COO)_2 . C_5H_5NO$ ($M = 276.73$)

Calculated: 22.96 % Cu,   5.06 % N;
Found: 22.82 % Cu,   4.95 % N.

b) For Cu(CH₃ . COO)₂ . C₉H₇NO (*M* = 326.79)

Calculated:	19.44 % Cu,	4.29 % N;
Found:	19.48 % Cu,	4.11 % N.

Reaction of bis(salicylato)diaquocopper(II) dihydrate with pyridine N-oxide

The reaction was achieved by mixing the acetone solutions of the initial reactants in the molar ratio 1 : 4 (in favour of pyridine *N*-oxide) with the salicylic acid in the molar ratio 0.5 : 1 (referred to Cu^{II}). This reaction system was heated to boiling point and after filtering it was allowed to cool to 0 °C in a refrigerator. The precipitated blue-green crystalline product was sucked off, thoroughly washed with cooled acetone and was left to dry freely at room temperature.

c) The solution of 10 g of bis(salicylato)diaquocopper(II) dihydrate (2.44 . 10⁻² M) and of 1.7 g of salicylic acid (1 . 3 . 10⁻²M) in 40 ml acetone and the solution of 9.3 g of pyridine *N*-oxide (9.76 . 10⁻² M) in 40 ml of the above solvent were used. Finally 10.7 g of the resulting product was obtained.

Reaction of bis(salicylato)diaquocopper(II) dihydrate with quinoline N-oxide ako

The reaction was performed by mixing ethanol solutions of the initial reactants in the molar ratio 1 : 4 (in favour of quinoline *N*-oxide) at room temperature. Salicylic acid — in molar ratio 0.5 : 1 (referred to Cu^{II}) was added to the reacting substances. A green microcrystalline substance, the final product, started precipitating spontaneously after several minutes. This substance was then sucked off, washed first with a small quantity of ethanol, then washed thoroughly with ether and finally dried at room temperature.

d) The solution of 5 g of bis(salicylato)diaquocopper(II) dihydrate (1.22 . 10⁻² M) and of 0.8 g of salicylic acid (6.1 . 10⁻³ M) in 50 ml 96 % ethanol and the solution of 7.1 g of quinoline *N*-oxide (4.9 . 10⁻² M) in 30 ml of the latter solvent were taken. Then the final product in the amount of 5 g was isolated.

Copper and nitrogen were estimated in the isolated substances by the above procedures.

c) For Cu(C₆H₄ . OH . COO)₂(C₅H₅NO)₂ (*M* = 527.97)

Calculated:	12.03 % Cu,	5.30 % N;
Found:	11.98 % Cu,	5.39 % N.

d) For Cu(C₆H₄ . OH . COO)₂ . C₉H₇NO (*M* = 482.99)

Calculated:	13.16 % Cu,	2.90 % N;
Found:	13.10 % Cu,	3.01 % N.

Magnetic measurements

Magnetic susceptibilities of the above complexes were measured by the Gouy method with the currently available apparatus. Measurements were carried out at room temperature and at temperatures of 273, 201 and 77 °K. The room temperature was maintained with the aid of a thermostat and the temperatures of 273, 201 and 77 °K were attained with the help of melting ice, of the mixture of solid carbon dioxide with ethanol and of the boiling liquid nitrogen. In order to prevent the interference of possible ferromagnetic impurities we always made the measurements at several magnetic field strengths ranging between 1700—3700 Oe. The forces exerted on the specimen in the magnetic field were

Table 1

Gram, molar and corrected molar susceptibilities (c. g. s. u.) and magnetic moments (B. M.) at individual temperatures

a) $Cu(CH_3COO)_2(Pyox)$; b) $Cu(CH_3COO_2)(Quinox)$;

c) $Cu(C_6H_4 . OH . COO)_2(Pyox)_2$; d) $Cu(C_6H_4 . OH . COO)_2(Quinox)$

	Temperature (°K)	$\chi_g . 10^6$	$\chi_M . 10^6$	$\chi'_M . 10^6$	μ_{eff} (B . M.)
a	294.4	2.63	728	848	1.37
	273	2.68	742	862	1.33
	201	2.29	634	754	1.06
	77	—0.022	—6	114	0.18
b	294.4	2.15	703	860	1.38
	273	2.18	712	869	1.33
	201	1.87	611	768	1.07
	77	—0.181	—59	98	0.15
	294	2.55	1408	1665	1.95
	273	2.69	1485	1742	1.92
	201	3.82	2109	2366	1.93
	77	10.31	5691	5948	1.91
d	294	1.41	681	922	1.43
	273	1.47	710	951	1.40
	201	1.26	609	850	1.13
	77	—0.234	—113	128	0.20

determined by means of a semimicrobalance MP 57. Mercury tetrathiocyanatocobaltate(II) was used as the standard substance [23] whose gram susceptibility is 16.44 . 10⁻⁶ c. g. s. units at 293 °K. The molar susceptibilities χ_M calculated from the obtained gram susceptibilities χ_g were corrected for the diamagnetism of the constituent atoms by means of Pascal's constants [24]. From these corrected molar susceptibilities χ_M we then calculated the effective magnetic moments by use of the formula $\mu_{eff} = 2.84 \sqrt{(\chi_M - N\alpha)T}$, where $N\alpha$ is the temperature independent contribution to the paramagnetism per gram-ion of copper. For this contribution the value of 60 . 10⁻⁶ c. g. s. units was substituted which was first calculated theoretically [25] for the $[Cu(H_2O)_6]^{2+}$ ion and later also for cop-

per(II) acetate monohydrate [26] assuming tetragonal ligand field splitting. The results of magnetic measurements of the studied Cu(II) complexes are summarized in Tab. 1.

Discussion

The complexes $Cu(CH_3 . COO)_2(Pyox)$ and $Cu(CH_3 . COO)_2(Quinox)$ have subnormal magnetic moments at room temperature and their susceptibilities exhibit temperature dependence which is characteristic for antiferromagnetism. This fact and the composition of both complexes allow us to assume that these complexes have binuclear bridged structure similar to that of copper(II) acetate monohydrate (Fig. 1). The water molecules in the terminal positions are substituted by pyridine N-oxide or quinoline N-oxide molecules. This may be checked by comparing the measured susceptibilities with the calculated ones on the basis of the formula derived for the copper(II) acetate monohydrate [3, 26]:

$$\chi'_M = \frac{g^2 N \beta^2}{3kT} \frac{1}{1 + 1/3 \exp(-2J/kT)} + N\alpha, \tag{1}$$

where $-2J$ is the energy separation between a singlet and a triplet state level and it may be derived from the equation $|2J| = 8/5 \, kT_m$, where T_m is the temperature at which the susceptibility reaches its maximum. Using for the spectroscopic splitting factor g the value 2.16, which involves the orbital contribution to the magnetic moment of the Cu^{2+} ion in a tetragonal field, we may calculate the energy difference $|2J|$ by inserting the experimental susceptibility values into the equation (1). The calculations were carried out — with regard to increased inaccuracy of the susceptibility determination at 77 °K — only at three higher temperatures 201, 273, 294.4 °K and the average values are:

a) $|2J| = 311$ cm$^{-1} = 0.89$ kcal mol^{-1}; $T_m = 280$ °K,
b) $|2J| = 307$ cm$^{-1} = 0.88$ kcal mol^{-1}; $T_m = 276$ °K.

We can write the equations for the susceptibility calculations in this definitive form:

$$Cu(CH_3 . COO)_2(Pyox) \qquad \chi'_M = \frac{0.585}{T} \frac{1}{1 + 1/3 \exp(447/T)} + 60 . 10^{-6}, \tag{2}$$

Fig. 2. Experimental and calculated values of magnetic susceptibilities and of magnetic moments for $[Cu_2(CH_3 . COO)_4(Pyox)_2]$.

○ experimental values $\chi'_M . 10^6$; ● experimental values μ_{eff}; —— calculated by use of the equation (2).

$$\text{Cu}(\text{CH}_3 . \text{COO})_2(\text{Quinox}) \qquad \chi'_M = \frac{0.585}{T} \frac{1}{1 + 1/3 \exp(442/T)} + 60 . 10^{-6}. \qquad (3)$$
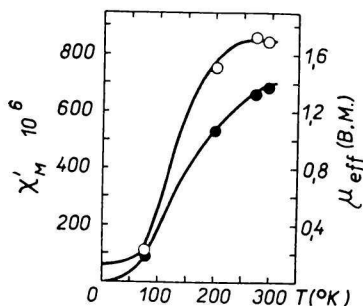
In Figs. 2 and 3 both theoretical $\chi'_M - T$ and $\mu_{\text{eff}} - T$ curves and the experimental values of χ'_M and μ_{eff} for the two complexes under investigation are plotted. There is very good agreement between the experimental values and the calculated curves, especially if we consider that we had no possibility to calculate the splitting factor g for each complex and we did not take into account possible temperature changes of the energy $|2J|$.
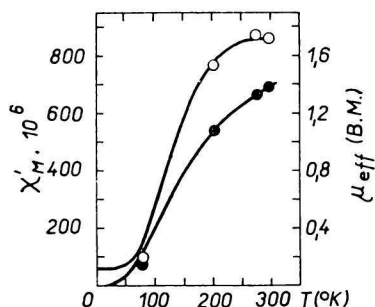

Fig. 3. Experimental and calculated values of magnetic susceptibilities and of magnetic moments for $[\text{Cu}_2(\text{CH}_3 \quad \text{COO})_4 (\text{Quinox})_2]$.

○ experimental values $\chi'_M . 10^6$; ● experimental values μ_{eff}; ——— calculated by use of the equation (3).

In Tab. 2 there are the values of singlet-triplet interval $|2J|$ and the temperature of the maximum susceptibility T_m calculated for three higher temperatures at which measurements were performed.

The attained experimental results prove beyond any doubt that in both discussed complexes the magnetic interaction between copper ions is of the same origin as in copper(II) acetate monohydrate and the differences are but quantitative as regards the quantities which characterize this interaction. First it should be stated

Table 2

Calculated values of $|2J|$ and T_m at 201, 273 and 294.4 °K
a) $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{Pyox})_2]$; b) $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{Quinox})_2]$

	Temperature (°K)	$|2J|$		T_m (°K)
		cm^{-1}	kcal mol^{-1}	
	201	316	0.90	284
a	273	306	0.88	275
	294.4	311	0.89	280
	201	312	0.89	281
b	273	303	0.87	273
	294.4	306	0.88	275

that through the substitution of two terminal water molecules by two pyridine N-oxide or quinoline N-oxide molecules the overlap $3d_\delta - 3d_\delta$ increases, which brings about the increase of the energy $|2J|$ (309 and 307 cm^{-1} respectively) when compared with the value of $|2J|$ found for the copper(II) acetate monohydrate [3] (286 cm^{-1}). This may easily be explained if we consider that a negatively charged oxygen atom from the pyridine N-oxide or quinoline N-oxide molecules is more inclined to the σ electron density transfer towards the central copper atom than an oxygen atom from the water molecule would be. The greater electron transfer causes that the $3d_\delta$ orbitals of the copper ion become larger and consequently their overlapping is easier. Further we assumed that there might be some differences in the magnetic behaviour of both complexes owing to different electron-donation powers of pyridine N-oxide and quinoline N-oxide. These differences, however, were not proved experimentally and we can not rule out that they occur within the range of experimental errors.

The complex [Cu(Sal)$_2$(Pyox)$_2$] (Sal is the anion of the salicylic acid) shows the magnetic moment of 1.95 B. M. at room temperature, which value corresponds to the magnetically diluted complexes of copper(II) [27]. The dependence of the inverse of the corrected molar susceptibility on the absolute temperature, which is plotted in Fig. 4, is linear and the magnetic behaviour of this complex obeys the Curie—Weiss law when the constant Θ equals 4 °K. With regard to these facts it may be stated that in the complex [Cu(Sal)$_2$(Pyox)$_2$] the central copper atom is octahedrally coordinated with the oxygen atoms with a certain tetragonal distortion. Using the Polder formula [25], $\mu_{eff} = 1.73(1 - 2\lambda/10$ Dq) and substituting for the spin-orbit coupling constant the value which is valid for the free Cu^{2+} ion, and for the parameter 10 Dq the value given in [28] for the ligand field in the complex [Cu(H$_2$O)$_6$]$^{2+}$, we get the above value of 1.95 B. M. for the magnetic moment. F. Hanic [29] determined the crystal structure of copper(II) salicylate tetrahydrate whose magnetic moment has been lately found to be 1.92 B. M. [30].

The schematic diagram of this structure is shown in Fig. 5a and it seems probable that the complex [Cu(Sal)$_2$(Pyox)$_2$] has an analogous structure, which is illustrated
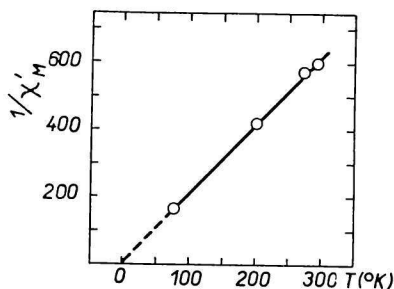

Fig. 4. Inverse of corrected molar susceptibility versus temperature for Cu(Sal)$_2$(Pyox)$_2$.

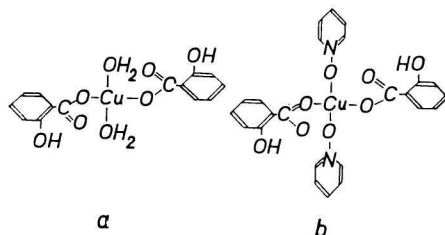(The broken line designates the extrapolation $1/\chi'_M$ to zero absolute temperature.)

Fig. 5. Structure of the complexes [Cu(Sal)$_2$(H$_2$O)$_2$] and [Cu(Sal)$_2$(Pyox)$_2$].

in Fig. 5*b*. The fifth and sixth coordination position of the copper ion are evidently occupied by oxygen atoms placed in greater distances in axial positions and belonging to different structure units of [Cu(Sal)$_2$(Pyox)$_2$], similarly as it has been proved [29] in the case of the complex [Cu(Sal)$_2$(H$_2$O)$_2$] . 2H$_2$O.

Table 3

Calculated values of $|2J|$ and T_m at 201, 273 and 294 °K
for [Cu$_2$(Sal)$_4$(Quinox)$_2$]

Temperature (°K)	$|2J|$		T_m (°K)
	cm^{-1}	kcal mol^{-1}	
201	291	0.83	262
273	273	0.78	245
294	279	0.80	251

In contrast, the complex Cu(Sal)$_2$(Quinox) represents with regard to its composition and magnetic behaviour another structure type. Its magnetic moment at room temperature is 1.43 B. M., this being indicative of a strong magnetic interaction between the neighbouring copper atoms. This is a conspicuously close value to the magnetic moment of copper(II) acetate monohydrate, 1.40 B. M. [3], and it also depends strongly on temperature. For better understanding of the magnetic properties of this complex we used the singlet-triplet equation (*1*), from which, similarly as in case of copper(II) acetate complexes, we calculated the energy difference $|2J|$. Using the values of $|2J|$ we found then the values of T_m at the corresponding temperatures. The results of these calculations are listed in Tab. 3. The mean values of the foregoing quantities are $|2J| = 281$ cm^{-1} = 0.80 kcal mol^{-1} and $T_m = 253$ °K. The previous value of $|2J|$ was then used for the calculation of theoretical values of the susceptibility of the discussed complex:

$$\chi'_M = \frac{0.585}{T} \frac{1}{1 + 1/3 \exp(404/T)} + 60 . 10^{-6}. \qquad (4)$$

In Fig. 6 the curve of the theoretical dependence of $\chi'_M - T$ and $\mu_{eff} - T$, as well as

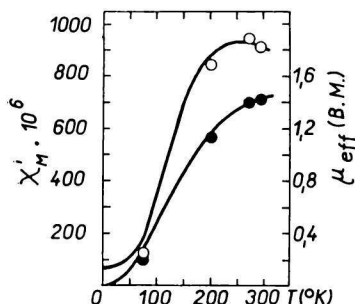*Fig. 6.* Experimental and calculated values of magnetic susceptibilities and of magnetic moments for [Cu$_2$(Sal)$_4$(Quinox)$_2$].

○ experimental values $\chi'_M . 10^6$; ● experimental values μ_{eff}; —— calculated by use of the equation (*4*).

the experimental values of χ'_M and μ_{eff} are plotted. The experimental data are evidently in good agreement with the calculated curves, especially if we take into account that at lower temperatures there is a certain increase of the value $|2J|$.
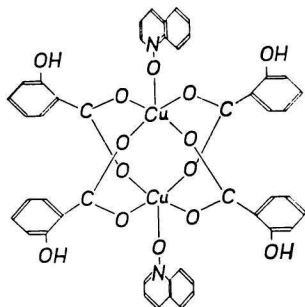

Fig. 7. Assumed structure of the complex [Cu$_2$(Sal)$_4$(Quinox)$_2$].

From this agreement we may conclude that the investigated copper(II) salicylate complex of quinoline N-oxide forms a binuclear species in which the salicylate anions act as bridges between two copper ions and the quinoline N-oxide molecules are bonded in the axial positions as it may be seen in Fig. 7. Hence it is correct to assume that the formula of this complex is [Cu$_2$(Sal)$_4$(Quinox)$_2$]. The singlet-triplet separation of 281 cm^{-1} is but slightly smaller than that found for the copper(II) acetate and its monohydrate [3], where it is 302 and 286 cm^{-1} respectively. This proves that the exchange interaction between the neighbouring copper atoms is about identical with that of copper(II) complexes of the acetate series. The salicylic acid (pK_a = 2.97) is considerably stronger than the acetic acid (pK_a = 4.75) so that the electron density transfer from oxygen atoms of the carboxylate group to copper ions is smaller in the case of the salicylate anion — and this should bring about a distinct decrease of the assumed overlap $3d_\delta$—$3d_\delta$ — when compared with the acetate complex. Apparently this effect is mostly compensated by a reverse effect owing to the transfer of the σ charge from the oxygen atoms of the quinoline N-oxide molecules to the copper ions and as a consequence of this, the overlap of d_δ orbitals should be increased. These atoms, with regard to their negative charge, are more inclined to delocalisation of the electron cloud favouring so the formation of stronger δ bonds than in the case of the water molecules. This accounts for the fact that the magnetic properties of the complex [Cu$_2$(Sal)$_4$(Quinox)$_2$] are very close to those found [3] for the complex [Cu$_2$(CH$_3$. COO)$_4$(H$_2$O)$_2$] which is structurally similar.

C. M. Harris et al. [31] prepared copper(II) complexes of quinoline N-oxide having the composition CuCl$_2$(Quinox) and CuBr$_2$(Quinox) as well as analogous Cu(II) complexes of pyridine N-oxide. With regard to the magnetic properties of the latter complexes, these are supposed to have binuclear structure in which the oxygen atoms from the molecules of the N-oxides bridge two copper atoms and mediate the superexchange interaction between them. The correctness of this assumption was proved by a complet X-ray analysis of the single crystals of the copper(II) chloride monopyridine N-oxide [32]. The fact that the complexes Cu(CH$_3$. COO)$_2$(Pyox) and Cu(CH$_3$ COO)$_2$(Quinox) as well as the complex Cu(Sal)$_2$(Quinox) do not have this structure may be accounted for by rather dif-

fering properties of carboxylate and chloride or bromide anions. The acetate or salicylate anion may, with regard to its stereochemistry and coordination properties, bond the copper ions in the binuclear bridged structure with direct copper-to-copper interaction and, on the other hand, the oxygen atoms of the N-oxide molecules owing to their electronegativity, would rather bond to the copper ions in the terminal positions than act as bridges between these ions. Thus, the occurence of the structure of the copper(II) acetate in the above complexes may be accounted for by mutual influence of both kinds of ligands which form these complexes.

Preparation of further Cu(II) complexes with anomalous magnetic properties and the research into the influence of the anion and neutral ligands on their magnetic properties will be the next stage of our investigations.

KOMPLEXNÍ SLOUČENINY MĚĎNATÉ
S ORGANICKÝMI LIGANDY (VII)

MAGNETICKÉ VLASTNOSTI ACETÁTOMĚĎNATÝCH A SALICYLÁTOMĚĎNATÝCH KOMPLEXŮ S PYRIDINOXIDEM A CHINOLINOXIDEM

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Připravily se acetátoměďnaté a salicylátoměďnaté komplexy s pyridinoxidem a chinolinoxidem a změřily se jejich magnetické susceptibility při různých teplotách. Zjistilo se, že komplex Cu(sal)$_2$(pyox)$_2$ má chování magneticky zředěných komplexů měďnatých, zatím co komplexy Cu(CH$_3$COO)$_2$(pyox), Cu(CH$_3$COO)$_2$(chinox) a Cu(sal)$_2$(chinox) vykazují za pokojové teploty vesměs anomálně nízké magnetické momenty a teplotní závislosti jejich susceptibilit nasvědčují na antiferromagnetismus. Na základě toho se usoudilo, že v Cu(sal)$_2$(pyox)$_2$ má ion Cu^{2+} deformovanou oktaedrickou koordinaci obdobně jako v Cu(sal)$_2$(H$_2$O)$_2$, kdežto komplexy s jednou molekulou N-oxidu mají dvojjádrovou strukturu typu monohydrátu octanu měďnatého s přímou vazbou měď——měď. Z naměřených susceptibilit se pro jednotlivé komplexy tohoto typu vypočítaly singlet-tripletové separace $|2J|$ a teploty přechodu T_m. Diskutují se činitelé podmiňující velikost magnetické interakce mezi ionty mědi ve zkoumaných komplexech dvojjádrové struktury.

КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ ДВУХВАЛЕНТНОЙ МЕДИ С ОРГАНИЧЕСКИМИ ЛИГАНДАМИ (VII)

МАГНИТНЫЕ СВОЙСТВА УКСУСНОКИСЛЫХ И САЛИЦИЛОВЫХ КОМПЛЕКСОВ ДВУХВАЛЕНТНОЙ МЕДИ С ОКИСЬЮ ПИРИДИНА И С ОКИСЬЮ ХИНОЛИНА

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Были получены уксуснокислые и салициловые комплексы двухвалентной меди с окисью пиридина (=окпи) и с окисью хинолина (=окхин) и измерены их магнитные восприимчивости при различных температурах. Нашли, что комплекс Cu(сал)$_2$(окпи)$_2$ ведет себя, как магнитно разбавленные комплексы двухвалентной меди, в то время как комплексы Cu(CH$_3$COO)$_2$(окпи), Cu(CH$_3$COO)$_2$(окхин) и Cu(сал)$_2$(окхин) проявляют при комнатной температуре в общем аномально низкий магнитный момент, а зависимость их магнитной восприимчивости от температуры указывает на антиферромагнетизм. На основе этого сделался вывод, что в Cu(сал)$_2$(окпи)$_2$ ион Cu^{2+} обладает деформированной октаэдрической координацией аналогично, как в Cu(сал)$_2$(H$_2$O)$_2$, в то время как комплексы с одной молекулой N-окиси обладают двухъядерной структурой типа моногидрата уксуснокислой двухвалентной меди с прямой связью медь—медь. Из полученных величин магнитных восприимчивостей были для отдельных комплексов этого типа рассчитаны сингулет-триплетные расщепления $|2J|$ и температуры перехода T_m. Обсуждаются факторы, обусловливающие величину магнитного взаимодействия между ионами меди в исследуемых комплексах двухъядерной структуры.

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