

Copper(II) Complexes with Organic Ligands (X) Magnetic Properties of Copper(II) Salicylate Complexes with Nitrogen Containing Ligands of the Pyridine and Aniline Group

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Magnetic susceptibilities of the modifications of bis(salicylato)dipyridine copper(II) complex over the temperature range 77—293 °K, and of some complexes of the type $\text{Cu}(\text{sal})_2\text{L}_2$, where sal is the anion of the salicylic acid and L is the unidentate nitrogen ligand, were measured. On the basis of the magnetic data the structures of the complexes under investigation are discussed.

Adjusting conveniently the conditions of the syntheses, we succeeded to prepare [1—5] different modifications of the compounds of the type CuX_2L_2 , where X is the anionic and L the neutral ligand, which have been characterized on the basis of differently arranged X-ray diffraction patterns. In some cases [2, 3, 5—7] we prepared several of these so-called transition specimens which represent transition from one modification to the other. It is natural that for better understanding of this type of isomerism physico-chemical study is indispensable, the results of which could be interpreted in terms of the existing notions. Lately [8], magnetochemical research of α - and β -isomer $\text{CuX}_2(\text{NH}_3)_2$ (X = Cl, Br) has been performed; the structure of these isomers was determined by X-ray structure analysis [9—11]. Interpretation of magnetic data from the standpoint of isomerism is rather difficult owing to complications caused by antiferromagnetic properties. In the present work, the magnetic properties of those isomer forms of bis(salicylato)dipyridine copper(II) complex are investigated which have different relative intensities of certain maxima [5] in X-ray diffraction patterns. These changes evidently indicate certain differences in the structure of individual forms and it is interesting to find out how these differences would influence the magnetic behaviour of these compounds. We also performed magnetochemical studies of some further salicylate copper(II) complexes of the type $\text{Cu}(\text{sal})_2\text{L}_2$, where L is the unidentate ligand of the pyridine and aniline group [12], in order to find out in which way the changes of the ligand L would influence the magnetic properties of individual complexes.

Experimental

Preparation

Specimens of bis(salicylato)dipyridine copper(II) complex prepared by [5] and designated as α (V), β (I) and transition preparations (III)* were used for our investigations. The analyses and X-ray diffraction patterns are given in [5]. From among the complexes $\text{Cu}(\text{sal})_2\text{L}_2$, where L can be either α -, β -, or γ -picoline, 4-acetylpyridine, aniline and *p*-toluidine, those prepared by [12] were taken.

Magnetic measurements

Magnetic measurements of specimens of bis(salicylato)dipyridine copper(II) complex were performed similarly as it has been described in the paper [13]. The complexes $\text{Cu}(\text{sal})_2\text{L}_2$ were treated alike except that measurements were taken at room temperature. The magnetic moments of the investigated complexes were calculated by the equation $\mu_{\text{eff}} = 2.84 \sqrt{(\chi'_M - N\alpha)T}$, in which for the temperature independent paramagnetism $N\alpha$, the value $60 \cdot 10^{-6}$ a. was inserted, which is usual for the tetragonal copper(II) complexes. The results of magnetic measurements are shown in Tab. 1 and 2.

Discussion

The magnetic moments of the investigated specimens of bis(salicylato)dipyridine copper(II) complex are 1.88–1.91 B. M. at room temperature, which corresponds [14] to the magnetically diluted complexes of Cu(II) the octahedral ligand arrangement of which around the central atom exhibit a certain

Table 1

Specific, molar and corrected molar susceptibilities (a. u.) and magnetic moments (B. M.) of the specimens of bis(salicylato)dipyridine copper(II) complex

| Complex* | Temperature °K | $\chi_g \cdot 10^6$ | $\chi_M \cdot 10^6$ | $\chi'_M \cdot 10^6$ | μ_{eff} (B. M.) |
|--|-------------------|---------------------|---------------------|----------------------|-------------------------------|
| α -Cu(sal) ₂ (py) ₂ | 293 | 2.52 | 1310 | 1558 | 1.88 |
| | 273 | 2.67 | 1388 | 1636 | 1.86 |
| | 201 | 3.79 | 1971 | 2219 | 1.87 |
| | 77 | 10.24 | 5325 | 5573 | 1.85 |
| β -Cu(sal) ₂ (py) ₂ | 293 | 2.59 | 1347 | 1595 | 1.91 |
| | 273 | 2.78 | 1446 | 1694 | 1.90 |
| | 201 | 3.86 | 2007 | 2255 | 1.89 |
| | 77 | 10.46 | 5439 | 5687 | 1.87 |
| Cu(sal) ₂ (py) ₂ t. p. | 293 | 2.59 | 1347 | 1595 | 1.91 |
| | 273 | 2.78 | 1446 | 1694 | 1.90 |
| | 201 | 3.93 | 2044 | 2292 | 1.90 |
| | 77 | 10.33 | 5372 | 5620 | 1.86 |

* py = pyridine, t. p. = transition preparation.

* Designations in brackets were introduced in [5].

Table 2

Specific, molar and corrected molar susceptibilities (a. u.) and magnetic moments (B. M.) of the complexes $\text{Cu}(\text{sal})_2\text{L}_2$ (L = unidentate nitrogen ligand) at room temperature

| Complex* | Temperature °K | $\chi_g \cdot 10^6$ | $\chi_M \cdot 10^6$ | $\chi'_M \cdot 10^6$ | μ^{eff} (B. M.) |
|--|-------------------|---------------------|---------------------|----------------------|-------------------------------|
| $\text{Cu}(\text{sal})_2(\alpha\text{-pic})_2$ | 293.2 | 2.39 | 1276 | 1548 | 1.87 |
| $\text{Cu}(\text{sal})_2(\beta\text{-pic})_2$ | 293.6 | 2.37 | 1266 | 1538 | 1.87 |
| $\text{Cu}(\text{sal})_2(\gamma\text{-pic})_2$ | 293.2 | 2.39 | 1276 | 1548 | 1.87 |
| $\text{Cu}(\text{sal})_2(4\text{-acpy})_2$ | 293.2 | 2.16 | 1305 | 1595 | 1.91 |
| $\text{Cu}(\text{sal})_2(\text{an})_2$ | 293.2 | 2.38 | 1271 | 1540 | 1.87 |
| $\text{Cu}(\text{sal})_2(p\text{-tol})_2$ | 293.2 | 2.23 | 1253 | 1546 | 1.87 |

* pic = picoline, 4-acpy = 4-acetylpyridine, an = aniline, *p*-tol = *p*-toluidine.

tetragonal distortion. The magnetic moments of these complexes are practically temperature independent and the dependence of the inverted values of their corrected molar susceptibilities on temperature is linear, whereat the intercepts on the temperature axis are very small (Fig. 1).

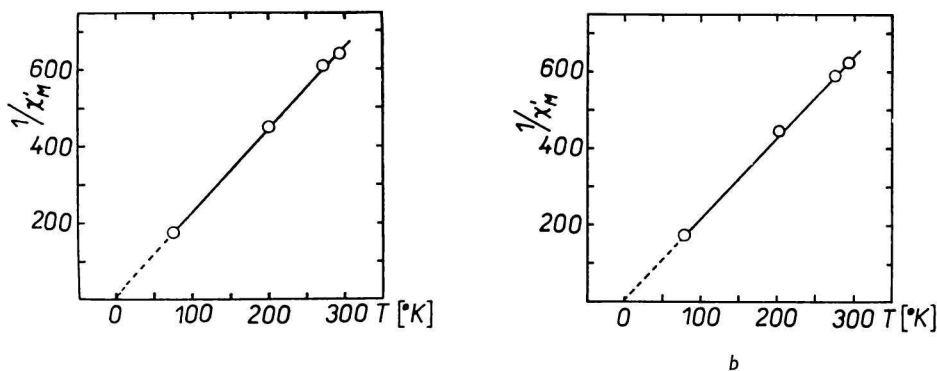


Fig. 1. The curve $1/\chi'_M$ versus T for a) $\alpha\text{-Cu}(\text{sal})_2(\text{py})_2$ and b) $\beta\text{-Cu}(\text{sal})_2(\text{py})_2$.

That means that their magnetic behaviour obeys the Curie-Weiss law $\chi'_M \propto (T + \Theta)^{-1}$, in which, however, the Weiss constants Θ have but very low value of 3 °K. Hence it may be stated that there are the usual paramagnetic „octahedral“ complexes of Cu(II) with a rather low separation between the interacting ligand states. The dihydrate of the bis(salicylato)diaquocopper(II) complex, which has been used for the preparation of complexes under investigation, has the magnetic moment of 1.92 B. M. at room temperature [15]. This complex, whose X-ray structure has been elucidated by F. Hanic and J. Michalov [16], consists of structure units of $[\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2]$.

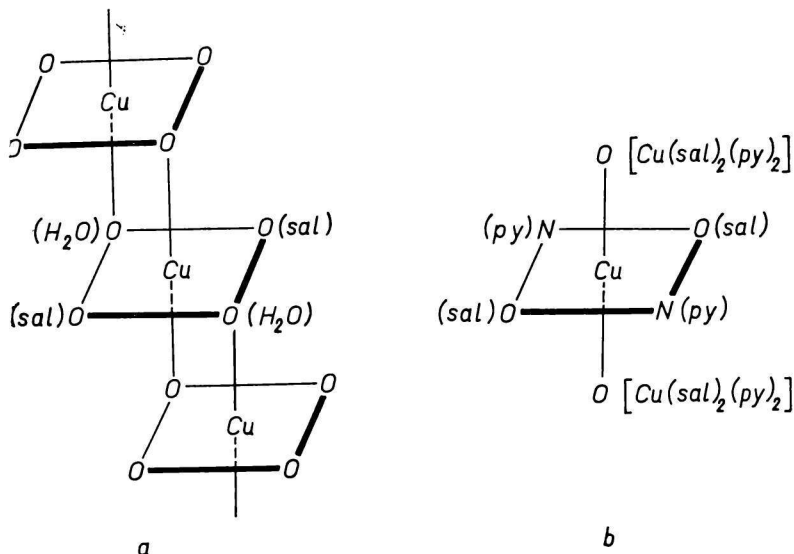


Fig. 2. Schematic representation of the structure of the complex $\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2$ according to [16] (a); the assumed structure of the complex $\text{Cu}(\text{sal})_2(\text{py})_2$ (b).

in which the copper ion is square planar coordinated by the oxygen atoms of the carboxyl groups of the anions sal^- and of the water molecules (Fig. 2a); the coordination number of copper is completed from 4 to 6 by oxygen atoms belonging to other similar structure units. We may assume that the structure of the complexes $\text{Cu}(\text{sal})_2(\text{py})_2$ is similar to that of the above complex and that they are formed from this substituting the water molecules in the structure units by the pyridine molecules (Fig. 2b). The very close values of the magnetic moments of the complexes $\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2$ and $\text{Cu}(\text{sal})_2(\text{py})_2$ seem to corroborate this assumption. The observed slight lowering of the magnetic moment to 1.91 and 1.88 B. M. respectively, is evidently caused by the stronger field of pyridine if compared with that of water, and by a certain perturbation of the ligand field influencing upon of the copper ion.

It has been found that the magnetic moments of both extreme modifications of $\text{Cu}(\text{sal})_2(\text{py})_2$ designated as α and β differ by 0.03 B. M. at room temperature; the magnetic moment of a transition specimen is identical with that of β -modification. As the measurements performed at room temperature with a sample of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ yielded at repeated runs with different loads of the measuring tube the value $\mu_{\text{eff}} = 1.92 \pm 0.01$ B. M., we may consider the determined difference 0.03 B. M. to be correct. Apart from this, a certain difference between the magnetic moments of α - and β -modifications were found at all temperatures of measurements. This difference is rather small

and indicates that the modifications of $\text{Cu}(\text{sal})_2(\text{py})_2$ with lattice structure differ but slightly, which besides is evident from the changes of the diffraction patterns. This difference might be due e. g. to different bond lengths in the coordination polyhedron of copper, which means its different distortion [1] or different orientation of planar ligands, or of whole complex molecules [5]; this eventually can bring about small changes in the forces which act upon the copper ion in the crystal field to which it belongs and as a consequence of this, slight energy changes of its ligand states.

All complexes $\text{Cu}(\text{sal})_2\text{L}_2$, where L is the unidentate ligand of the pyridine or aniline groups, have at room temperature, except the complex $\text{Cu}(\text{sal})_2(4\text{-acpy})_2$, the magnetic moment of 1.87 B. M. As to their structure, these complexes are most probably analogous to the complex $\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2$ from which they have been formed [12] probably by substitution of water molecules in the complex units by the nitrogen containing bases, similarly as it has been done with the complex $\text{Cu}(\text{sal})_2(\text{py})_2$. We assume that the differences in the field strengths of the individual ligands L, coordinated according to the above said to the copper ion in a plane with the anions sal^- , could influence the values of the magnetic moments of the complexes $\text{Cu}(\text{sal})_2\text{L}_2$, similarly, as they no doubt are responsible for different colouring of these complexes. This assumption, however, has not been experimentally proved and we can not rule out that these differences will not be established for because of limited sensitivity of experimental measurement methods. From among the investigated complexes, the complex $\text{Cu}(\text{sal})_2(4\text{-acpy})_2$ behaves slightly differently, its magnetic moment being 1.91 B. M. at room temperature. It is hardly possible to ascribe a greater importance to this fact, especially since it was observed that the specimen displayed, though small but still discernible dependence of the susceptibility on the intensity of the magnetic field.

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KOMPLEXNÍ SLOUČENINY MĚDNATÉ S ORGANICKÝMI LIGANDY (X)
MAGNETICKÉ VLASTNOSTI SALICYLÁTOMĚDNATÝCH KOMPLEXŮ
S NĚKTERÝMI DUSÍKATÝMI LIGANDY
SKUPINY PYRIDINU A ANILINU

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Změřily se při různých teplotách magnetické susceptibility isomerních forem bis(salicyláto)dipyridinmědnatého komplexu a při pokojové teplotě magnetické susceptibility

některých komplexů typu $\text{Cu}(\text{sal})_2\text{L}_2$, kde L značí jednofunkční ligand skupiny pyridinu příp. anilinu. Komplexy $\text{Cu}(\text{sal})_2(\text{py})_2$ mají při pokojové teplotě magnetické momenty obvykle nalézané pro deformované oktaedrické komplexy $\text{Cu}(\text{II})$ a jejich susceptibilita se řídí Curie—Weissovým zákonem při velmi malých hodnotách konstanty Θ . Blízké hodnoty magnetických momentů nasvědčují tomu, že tyto komplexy mají v podstatě obdobnou strukturu jako komplex $\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2$ a vznikají z něho substitucí molekul vody molekulami pyridinu. Rozdíly mezi modifikací α a β , třebaže se projevují při všech teplotách měření, jsou velmi malé a nasvědčují, že se tyto modifikace strukturálně jen málo liší. Komplexy $\text{Cu}(\text{sal})_2\text{L}_2$ mají při pokojové teplotě magnetické momenty velmi blízké momentům komplexů $\text{Cu}(\text{sal})_2(\text{py})_2$ a předpokládaný vliv rozdílů v síle polí jednotlivých ligandů L na velikost magnetických momentů příslušných komplexů se experimentálně neprojevil.

КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ ДВУХВАЛЕНТНОЙ МЕДИ
С ОРГАНИЧЕСКИМИ ЛИГАНДАМИ (X)
МАГНИТНЫЕ СВОЙСТВА САЛИЦИЛАТОМЕДНЫХ КОМПЛЕКСОВ
С НЕКОТОРЫМИ АЗОТСОДЕРЖАЩИМИ ЛИГАНДАМИ ГРУППЫ
ПИРИДИНА И АНИЛИНА

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Измерились магнитные восприимчивости модификаций бис(салицилато)дипиридин-комплекса двухвалентной меди в температурном диапазоне 77—293 °K и некоторых комплексов типа $\text{Cu}(\text{sal})_2\text{L}_2$, где sal обозначает анион салициловой кислоты и L монофункциональный азотсодержащий лиганд при обыкновенной температуре. На основании полученных магнитных моментов обсуждается строение изучаемых комплексов.

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