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Copper (II) Complexes with a Subnormal Magnetic Moment

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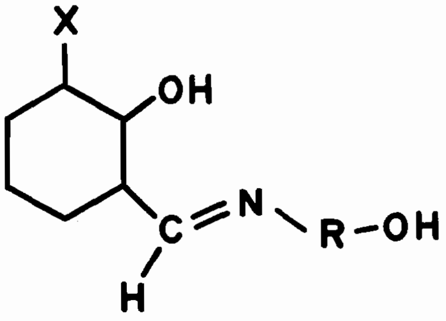
In the course of the study about copper(II) complexes of Schiff bases of type I[1] obtained from salicylaldehyde derivatives and alkanol amines, we have isolated some interesting compounds, which have a subnormal magnetic moment.



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A typical preparation method was as follows. To a solution of N-γ-hydroxypropyl-salicylideneimine (0.1 mole) in ethanol (10 ml.) were slowly added an aqueous solution of copper(II) nitrate (0.05 mole in 25 ml.) and sodium hydroxide (0.025 mole). The solution was warmed at 60° for one hour, filtered while it was warm, and kept at 5° overnight. The crystals separated were filtered, and recrystallized from chloroform. Grey-violet crystals with a formula of $Cu(sal.\,CH_2CH_2CH_2O)$ were obtained (Table I).

A similar procedure, using 3-methoxysalicylaldehyde instead of salicylaldehyde, yielded olive-green crystals with a formula of $Cu(3\text{-}CH_3O.sal.CH_2CH_2CH_2OH)_2$. In a similar way, $Cu(sal.C(CH_3)_2CH_2O)$ and $Cu(3\text{-}CH_3O.sal.C(CH_3)_2CH_2O)$ were obtained as olive-green and green crystals, respectively. Analytical data of these complexes are shown in Table I, together with magnetic moments at room temperature, which were determined by the Gouy method.

The moments for the compounds (1), (3) and (4) are much smaller than those expected for one unpaired electron. The subnormal magnetic moments of these complexes are considered to be due to an interaction between copper ions. It is most likely that these three copper(II) complexes have a binuclear structure shown in Fig. 1, as was also proposed for a series of copper(II) complexes with a subnormal magnetic moment.[2] The molecular weight of the compound (1) in chloroform, determined with a Hitachi Model-115 osmometer, was

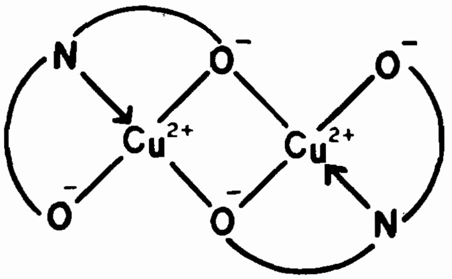

Figure 1. A proposed structure for Cu(X-sal.RO) with a subnormal magnetic moment.

Table I. Analytical data

Compound	mag. moment*	Elemental analysis			
(1) $Cu(sal.(CH_2)_3O)$	0.39	Anal.	49.66	4.58	5.73
		Calcd.	49.89	4.98	5.77
(2) $Cu(3\text{-}CH_3O.sal.(CH_2)_3OH)_2$	1.88	Anal.	55.03	5.92	5.74
		Calcd.	55.02	5.88	5.82
(3) $Cu(sal.C(CH_3)_2CH_2O)$	0.67	Anal.	52.24	5.25	5.28
		Calcd.	51.86	5.14	5.49
(4) $Cu(3\text{-}CH_3O.sal.C(CH_3)_2CH_2O)$	0.64	Anal.	49.84	5.43	4.65
		Calcd.	50.61	5.31	4.92

* In B. M., at room temperature.

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(1) The salicylideneiminate anions derived from compounds of type I are abbreviated in this communication as X-sal.ROH.

(2) See, for example, G. A. Barclay, C. M. Harris, B. F. Hopkins and E. Kokot, *Proc. Chem. Soc.*, 264 (1961); M. Kishita and M. Kubo, *Bull. Chem. Soc. Japan*, 35, 1241 (1962); J. Fanning and H. Jonassen, *J. Inorg. Nucl. Chem.*, 25, 29 (1963).

460, in agreement with the binuclear structure (mol. wt. 481.5). It is interesting to note that the compound (2) has a normal magnetic moment. The difference between the compounds (1) and (2) indicates a significant effect of the substituent, CH_3O. The effect of the substituent, however, causes no apparent difference between the compounds (3) and (4). The difference between the compounds (2) and (4), both having the CH_3O substituent, may presumably be due to the difference in the length of the carbon chain.

The visible and ultraviolet spectra of the compounds (1), (3) and (4) in choloroform or dichloromethane are similar to the corresponding spectra in the solid state, and show a *d-d* band maximum at about 17.5, 16.6 and $16.7.10^3$ cm^{-1}, respectively. The spectra of these compounds are slightly but definitely different from the spectra of the compound (2) and other complexes[3] of a Cu(sal.*n*-alkyl)$_2$ type with normal magnetic moments, in that the former lack a band (shoulder) at about 22.10^3 cm^{-1}, which is observed in the latter. The significance of this difference, together with the details of the present work, will be reported elsewhere.

(3) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, 36, 755 (1963).