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The Preparation and the Magnetic Property of Bis(*N*-*o*-nitrophenylsalicylideneaminato)copper(II)

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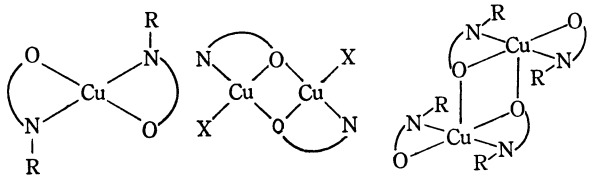
Synopsis. A synthesis of bis(*N*-*o*-nitrophenylsalicylideneaminato)copper(II) is reported. The magnetic properties of the complex and the corresponding *p*-nitro complex are discussed in terms of the steric effect of the nitro group.

In the preparation of bis(*N*-nitrophenylsalicylideneaminato)copper(II) complexes, it is much more difficult to prepare complexes with a nitro group at the *o*-position of the phenyl ring than complexes with the substituent at the *m*- or *p*-position. Thus, the synthesis of bis(*N*-*o*-nitrophenylsalicylideneaminato)copper(II), Cu(sal·*N*-*o*-NO_2·Ph)$_2$, can not be accomplished by any of the following reactions which are used for the preparation of various bis(*N*-R-salicylideneaminato)copper(II) complexes (Fig. 1. I):[1] (1) Cu(sal)$_2$+2 R·NH_2; (2) 2 H·sal·N–R+Cu(Ac)$_2$·H_2O; (3) 2 H·sal+2 R·NH_2+Cu(Ac)$_2$·H_2O (where H·sal=salicylaldehyde, R=alkyl or aryl, H·sal·N–R=*N*-R-salicylideneamine and Ac=CH_3COO).

Verter and Frost[2] successfully prepared the *o*-NO_2 complex by the method of Charles[3]—that is, by the reaction of H·sal, *o*-nitroaniline, and Cu(Ac)$_2$·H_2O in the presence of sodium acetate. We have also succeeded in isolating this complex and the analogous complexes (R=*o*-NO_2-*p*-CH_3·Ph and *o*-NO_2-*p*-CH_3O·Ph) by methods different from that of Charles. Cryomagnetic measurements of the *o*-NO_2 complex and the corresponding *p*-NO_2 complex have been carried out; the results will be discussed in terms of the shielding effect of *o*-substituents.



I II III

Fig. 1. Schematic representations of structures of I: Cu(sal·N–R)$_2$, II: [Cu(sal·N–R)X]$_2$, and III: [Cu(sal·N–R)$_2$]$_2$.

Preparation

A typical synthetic method was as follows: a mixture of Cu(sal)$_2$, Cu(Cl_2CHCOO)$_2$·$4H_2O$, and *o*-nitroaniline in a 1:1:2 mole ratio in ethanol was heated on a water bath under reflux for 1 h. The products were then recrystallized from *N*,*N*-dimethylformamide. They were all brown. The results of elemental analyses are given in Table 1, together with the calculated magnetic moments based on the observed magnetic susceptibilities at room temperature.

The synthesis of Cu(sal·*N*-*o*-NO_2·Ph)$_2$ was also achieved either by a similar procedure using Cu(Ac)$_2$·H_2O or Cu(ClO_4)$_2$·$6H_2O$ instead of Cu(Cl_2CHCOO)$_2$·$4H_2O$ or by the action of water on binuclear complexes of the II type shown in Fig. 1, [Cu(sal·*N*-*o*-NO_2·Ph)X]$_2$, which were prepared by the reaction of Cu(sal)$_2$, *o*-nitroaniline, and CuX_2(where X=Cl[4] or NO_3[5]).

Magnetic Property

The magnetic susceptibilities of Cu(sal·*N*-*p*-NO_2·Ph)$_2$ and Cu(sal·*N*-*o*-NO_2·Ph)$_2$ were measured in the temperature range of 80—300 K by the Gouy method; the results are shown in Fig. 2.

The cryomagnetic data for the *p*-NO_2 complex obeyed the Curie-Weiss law with a positive Weiss constant ($\theta \approx +2$ K), which was evaluated by extrapolating the $(\chi_m - N_\alpha)^{-1}$ *vs.* T curve; this indicated the existence of ferromagnetic interaction in this compound (where χ_m is the magnetic susceptibility per gram-ion of copper (II); N_α, the temperature independent paramagnetism per gram-ion of copper(II), and T, the absolute temperature). The ferromagnetic interaction was also reflected in the X-band ESR spectrum as measured on a powdered sample; *i.e.*, the spectrum showed a weak signal at *ca.* 1500 G due to the $\Delta M_s=2$ transition characteristic of magnetically coupled copper(II) ions,[6] and the intensity increased with a lowering of the temperature, suggesting that the ferromagnetic interaction leads to a triplet ground state. These magnetic properties are quite similar to those of such binuclear complexes as [Cu(sal·N–CH_3)$_2$]$_2$(γ-form),[7] [Cu(sal·N–CH_2CH_2–N·sal)]$_2$,[7,8] [Cu(dmg)$_2$]$_2$,[9] and [Cu(pyo)$_2$-

Table 1. Analytical data and magnetic moments

Complex	Analysis, % Found C	H	N	Cu	Calcd C	H	N	Cu	μ_{eff}[a] (°C) B. M.
Cu(sal·N-*o*-NO_2·Ph)$_2$	56.93	3.46	10.19	11.44	57.20	3.32	10.26	11.64	1.81 (21)
Cu(sal·N-*o*-NO_2-*p*-CH_3·Ph)$_2$	58.48	3.89	9.76	11.17	58.59	3.86	9.76	11.07	1.81 (24)
Cu(sal·N-*o*-NO_2-*p*-CH_3O·Ph)$_2$	55.24	3.75	9.00	10.59	55.49	3.66	9.24	10.48	1.81 (24)

a) Calculated from the expression $\mu_{eff}=2.83\sqrt{(\chi_m - N\alpha)\cdot T}$ assuming $N\alpha=60\times10^{-6}$ emu.

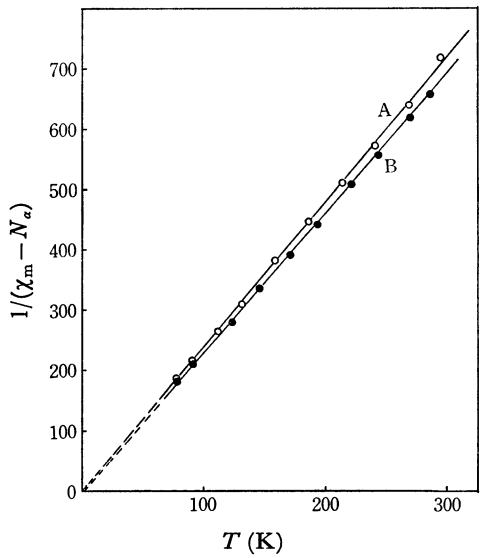


Fig. 2. Variation of reciprocal magnetic susceptibilities with temperature.
A: Cu(sal·N-*o*-NO_2·Ph)$_2$ B: Cu(sal·N-*p*-NO_2·Ph)$_2$
Pascal's constants were used for correction of diamagnetism (-255×10^{-6} emu/mol) and $N\alpha$ was assumed to be 60×10^{-6} emu.

$(NO_3)_2]_2$,[10] in which the coordination around the copper ion is square-based pyramidal, with the fifth position (out-of-plane) occupied by oxygen from an adjacent planar moiety (where dmg=dimethylglyoximato and pyo=pyridine *N*-oxide). The ferromagnetic spin interaction between copper ions in these complexes was interpreted in terms of a σ-type superexchange mechanism *via* the out-of-pane bonds.[7-10] Thus, the *p*-NO_2 complex very probably has a binuclear structure of the III type shown in Fig. 1, [Cu(sal·N–R)$_2$]$_2$, in which the monomeric Cu(sal·N–R)$_2$ units are bridged by the Cu–O out-of-plane bonds.

On the other hand, for the *o*-NO_2 complex, magnetic behavior obeying the Curie law was observed within the range of experimental error. In the powder ESR spectrum, a strong signal at *ca.* 3100 G due to copper(II) ions with $S=1/2$ was observed, and, in contrast to the *p*-NO_2 complex, no absorption was detected near 1500 G over the temperature range of 80—300 K. On the basis of the magnetic data and the previous observation that the *o*-substituents in Cu(sal·N–Ph–Y)$_2$ complexes have a great tendency to shield the fifth coordination site of the copper ions,[4] it seems likely that, in the *o*-NO_2 complex, the shielding effect hinders the formation of a dimer of the III type; consequently, no magnetic interaction occurs between neighboring copper ions (where ph-Y=monosubstituted phenyl).

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