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# Binuclear Copper(II) Propionate Complexes with *N*-Arylsalicylideneamines

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**Synopsis.** Two copper(II) propionate complexes with *N*-arylsalicylideneamines have been prepared. The magnetic and spectral properties of these complexes indicate that they have a carboxylate-bridged binuclear structure.

As a part of a program of magnetochemical studies of polynuclear copper(II) complexes, we have been studying a variety of copper(II) alkanoate complexes with salicylideneamines. In this paper we will report the preparative, magnetic, and spectral properties of newly-prepared copper(II) propionate complexes with the compositions of Cu(Sal·N·ph)$C_2H_5CO_2$ and Cu(Sal·N·*p*-tol)$C_2H_5CO_2$, where Sal·N=·$\overset{2}{\mathrm{O}}$·$C_6H_4$·$\overset{1}{\mathrm{C}}$H=N, ph=phenyl, and *p*-tol=*p*-tolyl. For comparison with the corresponding chloride complexes, cryomagnetic and IR spectral measurements have also been made of the Cu(Sal·N·*p*-tol)Cl complex, the preparation and some characterization of which were previously reported.[1)]

## Results and Discussion

The Cu(Sal·N·*p*-tol)$C_2H_5CO_2$ complex was readily prepared by the reaction of the parent complex, Cu(Sal·N·*p*-tol)$_2$, with copper(II) propionate in hot ethanol. On the other hand, the preparation of Cu(Sal·N·ph)$C_2H_5CO_2$ was found to be much more difficult. We also found that, in the reaction of copper(II) propionate with the salicylideneamine complex, Cu(Sal·N·ph–X)$_2$, where ph–X represents the monosubstituted phenyl group with the X substituent, the preparation of no propionate complexes was accomplished under reaction conditions similar to those above when X=*o*-Cl, *m*-Cl, *p*-Cl, *p*-$NO_2$, *o*-$CH_3$, and *m*-$CH_3$ in Cu(Sal·N·ph–X)$_2$. This fact seems to indicate that both the polar and steric natures of the substituents play an important role in the formation of Cu(Sal·N·ph–X)$C_2H_5CO_2$.

The magnetic susceptibility data in the temperature range of 80—300 K for the propionate complexes are well represented by the Bleaney-Bowers equation:[2)]

$$\chi_A = \frac{g^2N\beta^2}{3kT}\left(1+\frac{1}{3}\exp\frac{-2J}{kT}\right)^{-1} + N\alpha \qquad (1)$$

where $-2J$ is equal to the energy separation between the singlet and triplet states, which gives the degree of the strength of the magnetic interaction, and where the other symbols have their usual meanings. By the best fit of the observed cryomagnetic data to Eq. (1), assuming $N\alpha=60\times10^{-6}$ emu/mol, the values of $-2J=101$ cm$^{-1}$ and $g=2.14$ were evaluated for both the propionates (Fig. 1). The close agreement between the observed and calculated temperature dependences indicates that the propionate complexes have a binuclear structure in crystals. The antiferromagnetic interaction ($J<0$) was also reflected in the X-band ESR spectra of these complexes; *i.e.*, the spectra showed a weak signal at about 1500 G which may be assigned to the $\Delta M_s=2$ transition characteristic of magnetically-coupled copper(II) ions.[2)]

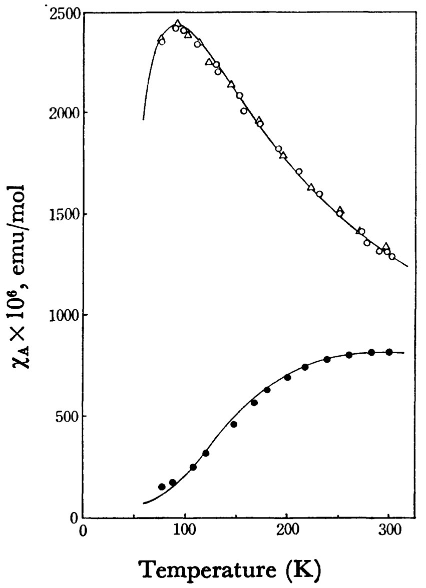

Fig. 1. Variation of magnetic susceptibilities with temperature.
○: Cu(Sal·N·ph)$C_2H_5CO_2$ ($\mu_{eff}$=1.73 B.M. at 26 °C)
△: Cu(Sal·N·*p*-tol)$C_2H_5CO_2$ ($\mu_{eff}$=1.74 B.M. at 23 °C)
●: Cu(Sal·N·*p*-tol)Cl ($\mu_{eff}$=1.35 B.M. at 27 °C)
The solid curves represent the Bleaney-Bowers equation.

The $\chi_A$ *vs.* *T* data of the chloride complex, Cu(Sal·N·*p*-tol)Cl, were also fitted to the theoretical curve calculated from Eq. (1) with the values of $-2J=330$ cm$^{-1}$, $g=2.15$, and $N\alpha=60\times10^{-6}$ emu/mol (Fig. 1). The $-2J$ value is large and practically the same as the value of 360 cm$^{-1}$ determined by Harris *et al.*[3)] for the phenyl complex, Cu(Sal·N·ph)Cl. This indicates the presence of a very much stronger antiferromagnetic interaction in these chloride complexes than in the corresponding propionate complexes.

The reflectance spectral pattern of the propionates, which indicates a square planar configuration around the copper(II) ion, is different from those of the chlorides to which a pseudo-tetrahedral configuration was previously assigned[1,4)] (Fig. 2). Furthermore, these spectral and magnetic properties are contrary to the expectation from the linear relation, "higher energy of

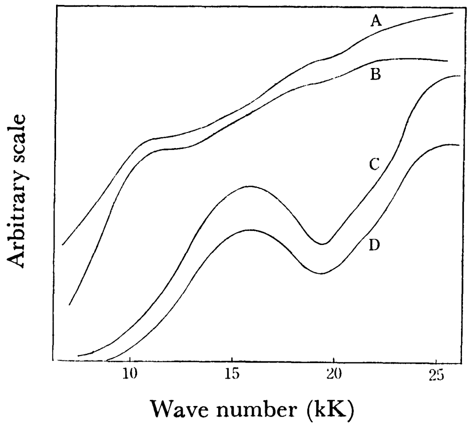

Fig. 2. Reflectance spectra.
A: Cu(Sal·N·ph)Cl B: Cu(Sal·N·*p*-tol)Cl
C: Cu(Sal·N·ph)$C_2H_5CO_2$
D: Cu(Sal·N·*p*-tol)$C_2H_5CO_2$

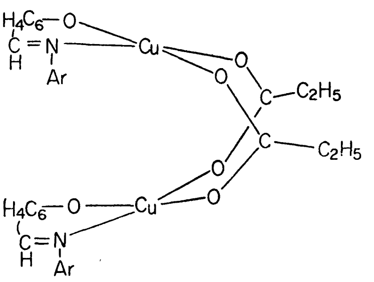

Fig. 3. Proposed binuclear structure of Cu(Sal·N·Ar)-$C_2H_5CO_2$.
(Ar=phenyl or *p*-tolyl group)

d-d bands—lower magnetic moment," established for a series of binuclear copper(II) halide complexes with pyridine *N*-oxides[5] and salicylideneamines.[1,4]

The chloride complexes showed a strong band at *ca.* 1550 $cm^{-1}$, while the band appears at *ca.* 1530 $cm^{-1}$ for the parent bis-salicylideneamine complexes.[3] This band shift to higher energies indicates that, in these chlorides, the binuclear molecule is formed by phenolic oxygen atoms.[6] On the other hand, no significant band shift was observed for the propionate complexes, suggesting that, in these complexes, no phenolic oxygen-bridged structure exists.

These magnetic and spectral data suggest that the propionates possess a carboxylate-bridged binuclear structure analogous to that of copper(II) propionate *p*-toluidine, $[Cu_2(C_2H_5CO_2)_4 \cdot p\text{-toluidine}_2]_n$, the structure of which was recently determined by X-ray analysis.[7] One of the probable binuclear structures is given in Fig. 3.

The difference in magnetic interaction between the propionate and chloride complexes is attributable to change in structure from carboxylate-bridged to phenolic oxygen-bridged entities. In support of this conclusion, it should be noted that the $-2J$ value determined for the propionate complexes in this study is in good agreement with the value of 105 $cm^{-1}$ reported by Yawney *et al.*[7] for copper(II) propionate *p*-toluidine, for which a pair-by-pair spin-spin coupling between copper(II) ions through the carboxylate groups was suggested to account for the demagnetization.[7]

## Experimental

*Preparation of the Propionates.* A mixture of copper(II) propionate monohydrate and bis-(*N*-arylsalicylideneaminato)-copper(II) in ethanol was stirred on a hot plate for an hour. The mole ratio of $Cu(C_2H_5CO_2)_2H_2O$ to $Cu(Sal \cdot N \cdot Ar)_2$ was 3: 1 for the phenyl complex and 1.2: 1 for the tolyl complex. The alcoholic solution was then filtered, and the filtrate was concentrated by warming it gently to produce green crystals. The product was filtered off, washed twice with ethanol and once with ether, and dried at *ca.* 70 °C. Anal. Phenyl complex. Found: C, 57.67; H, 4.56; N, 4.11; Cu, 19.18%; Calcd. for $C_{16}H_{15}NO_3Cu$: C, 57.74; H, 4.54; N, 4.20; Cu, 19.09%. Tolyl complex. Found: C, 58.79; H, 4.91; N, 4.03; Cu, 18.33%; Calcd for $C_{17}H_{17}NO_3Cu$: C, 58.86; H, 4.94; N, 4.04; Cu, 18.32%.

*Physical Measurements.* The magnetic susceptibilities were determined over the temperature range of 80—300 K by the Gouy method using an apparatus which was described previously.[4] The ESR (X-band) spectra were measured on powder samples using a JES–ME–1X spectrometer. The reflectance spectra were obtained on a Hitachi EPR-3T recording spectrophotometer. The IR absorption spectra were recorded on a Hitachi EPI-G2 IR spectrophotometer.

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