Dimeric Copper(II) Nitrato and Chloro Complexes with *N*-(3-Dimethylaminopropyl)salicylideneaminato Ligand Protonated at the Terminal Nitrogen

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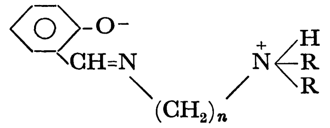
Synopsis. The title complexes have been prepared and characterized. The strong antiferromagnetic interaction observed for the complexes is interpreted in terms of a phenolic-oxygen-bridged dimeric structure with the metal ions in a square-pyramidal geometry.

Previously we reported that chloro[*N*-(3-dimethylaminopropyl)salicylideneaminato]copper(II), Cu(sal·pr·NMe_2)Cl, was obtained in two forms, one monomeric and the other dimeric;1) the corresponding nitrato complex, Cu(sal·pr·NMe_2)NO_3, was obtained only in a monomeric form.2) In order to study the effect of structural change upon the magnetic interaction in such complexes, we have prepared copper(II) nitrato and chloro complexes with the Schiff base ligand protonated at the terminal nitrogen, Cu(sal·pr·$\overset{+}{N}Me_2H)X_2$ (X=NO_3 or Cl), from the reaction of HX and Cu(sal·pr·NMe_2)X in ethanol. The analogous complex, Cu(sal·en·$\overset{+}{N}Et_2H)Cl_2$, has also been synthesized (*cf.* formula I).



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abbreviation

sal·pr·$\overset{+}{N}Me_2H$; n=3, R=CH_3

sal·en·$\overset{+}{N}Et_2H$; n=2, R=C_2H_5

The results of characterization studies on these complexes are presented in this paper.

Experimental

Synthesis. A typical synthetic method is as follows. A solution of one of the acids HX(5 mmol) in ethanol(5 ml) was added to a solution of one of the parent complexes(2 mmol), Cu(sal·pr·NMe_2)NO_3,2) Cu(sal·pr·NMe_2)Cl (monomeric form)1) and Cu(sal·en·NEt_2)Cl,3) in ethanol (50 ml). After the resulting solution had been allowed to stand for several days at *ca.* 5 °C in a freezer, the separated crystals were filtered, washed with ethanol, and dried *in vacuo*. All crystals were orange. Anal. **1.** Cu(sal·pr·$\overset{+}{N}Me_2H)(NO_3)_2$. Found: C, 36.33; H, 4.60; N, 14.01; Cu, 16.02%. Calcd for $C_{12}H_{18}N_4O_7Cu$: C, 36.60; H, 4.61; N, 14.23; Cu, 16.13%. **2.** Cu(sal·pr·$\overset{+}{N}Me_2H)Cl_2$. Found: C, 42.20; H, 5.32; N, 8.22; Cu, 18.65%. Calcd for $C_{12}H_{18}N_2OCl_2Cu$: C, 42.30; H, 5.35; N, 8.22; Cu, 18.65%. **3.** Cu(sal·en·$\overset{+}{N}Et_2H)Cl_2$. Found: C, 43.79; H, 5.69; N, 7.94; Cu, 17.76%. Calcd for $C_{13}H_{20}N_2OCl_2Cu$: C, 44.01; H, 5.68; N, 7.90; Cu, 17.91%.

Physical Measurements. The magnetic susceptibilities in the temperature range 80—300 K were determined by the Gouy method. The IR spectral measurements were made with a Hitachi EPI-G2 IR Spectrophotometer in the 400—4000 cm^{-1} region on Nujol mulls. The reflectance spectra were recorded with a Hitachi Recording Spectrophotometer 323.

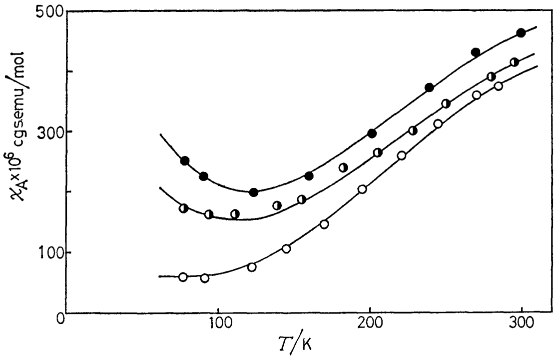

Fig. 1. Variation of magnetic susceptibilities with temperature.
(○): Complex **1**, (◑): Complex **2**, (●): Complex **3**. The solid curves were obtained as described in text.

Results and Discussion

The variable-temperature magnetic susceptibility data observed for complex **1** have been analyzed by the Bleaney-Bowers equation for isotropic exchange in a copper(II) dimer:4)

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

where each symbol has the usual meaning. The data fit the above expression very well: $-2J=554\ cm^{-1}$, $g=2.16$, and $N\alpha=60\times10^{-6}$ cgs emu† (Fig. 1). For complexes **2** and **3**, the cryomagnetic data at low temperatures have been found to be somewhat higher than those predicted by Eq. 1. This type of behavior is most likely due to a small amount of a monomeric Cu(II) impurity.5) Assuming the magnetic moment of 1.8 BM†† for the Cu(II) impurity, the magnetic data have been fitted to a modified equation:5)

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-P) + \frac{0.405P}{T} + N\alpha, \qquad (2)$$

where P is the mole fraction of the Cu(II) impurity. The best fit yields $-2J=554\ cm^{-1}$, $g=2.16$, $N\alpha=60\times10^{-6}$ cgs emu and $P=0.022$ for complex **2** and $-2J=542\ cm^{-1}$, $g=2.20$, $N\alpha=60\times10^{-6}$ cgs emu and $P=0.036$ for complex **3** (Fig. 1).

The IR spectra of the present complexes all show an intence band in the range 1550—1560 cm^{-1} (**1.** 1559; **2.** 1549; **3.** 1550 cm^{-1}), while the corresponding bands in the spectra of the parent monomeric com-

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† 1 cgs emu $mol^{-1}=4\pi\times10^{-6}\ m^3\ mol^{-1}$.

†† 1 BM$=9.274\times10^{-24}\ Am^2$.

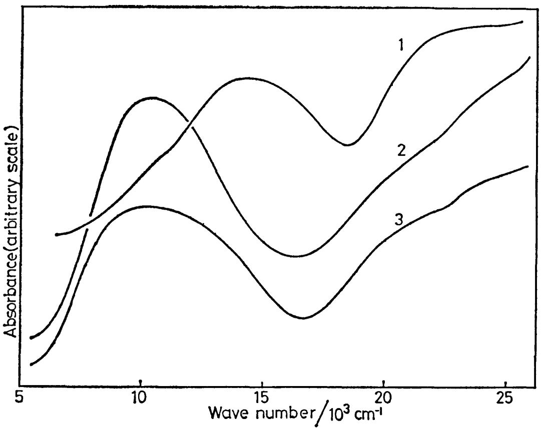
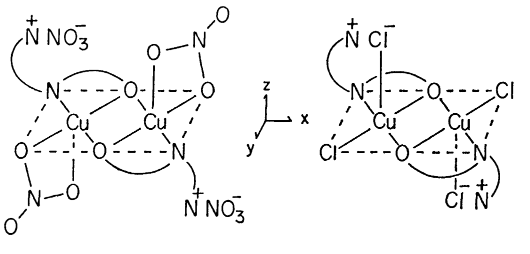


Fig. 2. Reflectance spectra of Complexes **1** (1), **2** (2), and **3** (3).



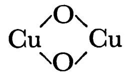
(A) (B)

Fig. 3. Schematic representations of probable structure.
(A) Complex **1** and (B) Complexes **2** and **3**.

plexes, Cu(sal·pr·NMe$_2$)NO$_3$, Cu(sal·pr·NMe$_2$)Cl and Cu(sal·en·NEt$_2$)Cl, appear at 1541, 1529, and 1530 cm^{-1}, respectively. Such band shift toward higher frequencies (15—20 cm^{-1}) is indicative of the presence of bridging phenolic oxygen atoms in the present complexes.[1,2] The band around 2500—2900 cm^{-1} (**1**. 2900; **2**. 2650; **3**. 2600 cm^{-1}) can be assigned to the $\nu(\overset{+}{\mathrm{N}}\text{–H})$ mode, in agreement with the values of 2680 and 2540 cm^{-1} observed for this stretching frequency in *N*-methylpiperidine and triethylamine hydrochlorides.[6] This assignment is further supported by the fact that no band is observed in the same region for the parent monomeric complexes.

The reflectance spectral feature of complex **1** is nearly the same as that of the phenolic oxygen-bridged dimeric copper(II) complex with *N*-ethylsalicylideneaminato ligand, [Cu(sal·Et)NO$_3$]$_2$, in which the metal ions are five-coordinated with four strong bonds and a weak fifth bond with a nitrato oxygen to complete a rough square-pyramid.[7] Complexes **2** and **3** show a broad band at *ca.* 10000 cm^{-1}: a spectral feature indicative of a five-coordination around the metal ion (Fig. 2).

All these results indicate that the complexes in the present study have a phenolic oxygen-bridged dimeric structure with a five-coordinated Cu(II) geometry. The most probable structures are shown in Fig. 3.

The $-2J$ values determined for the present complexes are more than twice those of [Cu(sal·pr·NMe$_2$)X]$_2$ ($-2J_{\mathrm{X=Cl}}=248$ and $-2J_{\mathrm{X=Br}}=260$ cm^{-1}),[1] to which a phenolic oxygen-bridged dimeric structure with the metal ions in a five-coordinated, essentially trigonal bipyramidal, geometry was previously assigned.[1] This result may be taken as evidence in favor of the previous conclusion that the strength of antiferromagnetic interaction in five-coordinated copper(II) dimers containing a  $\mathrm{Cu}\overset{\diagup\mathrm{O}\diagdown}{\underset{\diagdown\mathrm{O}\diagup}{\quad}}\mathrm{Cu}$ bridging system decreases as the distortion of Cu(II) geometry from square-pyramid toward trigonal-bipyramid increases.[1] On the basis of the difference between the assumed structures, the pronounced difference in magnetic interaction can be explained as follows. In the square pyramidal coordination around the Cu(II) ions in the dimeric species shown in Fig. 3, the overlap of singly occupied 3d$_{xy}$ orbitals of the two Cu(II) centers with the oxygen 2p$_x$ orbital may yield an efficient pathway for superexchange (*cf.* the coordinate system given in Fig. 3).[8,9] However, a distortion of the Cu(II) geometry from square-pyramid toward trigonal-bipyramid will give rise to a decrease in successive orbital overlap of Cu(d$_{xy}$)–O(p$_x$)–Cu(d$_{xy}$), leading to a weakening of spin-coupling, *i.e.*, a decrease in $|-2J|$ value.

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