Magnetic and Spectral Properties of Copper(II) Chloride Complexes of Tridentate Salicylideneamines with ONN Set of Donors

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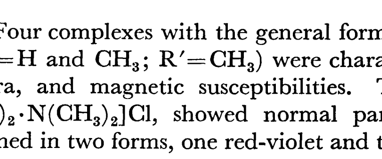
Four complexes with the general formula of Cu[sal·$(CH_2)_n$·N(R)R′]Cl (sal=·$\overset{2}{O}$·C_6H_4·$\overset{1}{C}$H=N·; n=2 and 3; R=H and CH_3; R′=CH_3) were characterized by elemental analyses, IR and visible reflectance spectra, ESR spectra, and magnetic susceptibilities. The complexes where n=2, Cu[sal·$(CH_2)_2$·$NHCH_3$]Cl and Cu[sal·$(CH_2)_2$·$N(CH_3)_2$]Cl, showed normal paramagnetic behavior. The Cu[sal·$(CH_2)_3$·$N(CH_3)_2$]Cl complex was obtained in two forms, one red-violet and the other green. The red-violet form showed the usual magnetic behavior expected for a mononuclear copper(II) complex, whereas the green one exhibited the antiferromagnetic behavior typical of binuclear copper(II) complexes. The magnetic properties of these complexes are discussed in terms of structural considerations. The characterization of the Cu[sal·$(CH_2)_3$·$N(CH_3)_2$]Br complex is also reported.

The results of synthetic and characterization studies on copper(II) chloride complexes of *N*-(hydroxyalkyl)-salicylideneamines with ONO set of donors were reported in previous papers.[1,2] In the course of our studies, we found that the antiferromagnetic interaction in dimeric copper(II) chloride complex with *N*-(2-hydroxyethyl)salicylideneamine, $[Cu(sal·en·OH)Cl]_2$, is much weaker than that in the corresponding *N*-(3-hydroxypropyl) complex, $[Cu(sal·pr·OH)Cl]_2$. This observation prompted us to investigate the analogous complexes with ONN tridentate salicylideneaminato ligands of the general formula



abbreviation

sal·en·N(H)Me; n=2, R=H, R′=CH_3

sal·en·NMe_2; n=2, R=R′=CH_3

sal·pr·NMe_2; n=3, R=R′=CH_3

The complexes Cu[sal·en·N(H)Me]Cl, **1**, and Cu(sal·en·NMe_2)Cl, **2**, were originally synthesized and investigated by Sacconi *et al.*[3] The complex Cu(sal·pr·NMe_2)Cl has been obtained in two forms, one red-violet, **3**, and the other green, **4**; the corresponding bromide complex Cu(sal·pr·NMe_2)Br, **5**, only in a green form. In addition, the interconversion between **3** and **4** has been observed as follows: **3** is converted to **4** by recrystallizing **3** from methanol or chloroform while the reverse conversion is carried out by heating **4** in ethanol. One object of the present work is to elucidate the structure difference between **3** and **4**.

We report here the results of magnetic and spectral studies on these complexes **1**—**5** and discuss their magnetic properties in terms of structural considerations.

Experimental

Syntheses. Compounds **1** and **2** were prepared by methods which were slightly modified from those of Sacconi *et al.*,[3] as follows: *Compound **1**, Cu[sal·en·N(H)Me]Cl*: A solution of copper(II) chloride (10 mmol) in ethanol (50 ml) was added to a mixture of bis(salicylaldehydato)copper(II) (10 mmol) and *N*-methylethylenediamine (20 mmol) in ethanol (30 ml). The solution was stirred at *ca.* 70 °C for 1/2 h and then concentrated to one-fourth of its volume. After the solution had been allowed to stand overnight at *ca.* 5 °C in a freezer, the separated green crystals were collected and recrystallized from chloroform. Found: Cu, 23.02%. Calcd for $C_{10}H_{13}N_2OClCu$: Cu, 23.00%. *Compound **2**, Cu(sal·en·NMe_2)Cl*: A mixture of Cu(sal·en·NMe_2)$_2$ (10 mmol) and copper(II) chloride (10 mmol) in ethanol (30 ml) was stirred on a hot plate for 1/2 h. The green crystals thus precipitated were collected and recrystallized from chloroform. Found: Cu, 21.64%. Calcd for $C_{11}H_{15}N_2OClCu$: Cu, 21.89%.

*Compound **3**, the Red-violet Form of Cu(sal·pr·NMe_2)Cl*: This was prepared by the reaction of Cu(sal·pr·NMe_2)$_2$ and copper(II) chloride according to the procedure described above (Compound **2**). The purification was made by recrystallization from ethanol. This was also obtained by heating Compound **4** in ethanol. Found: C, 47.29; H, 5.67; N, 9.19; Cu, 20.80%. Calcd for $C_{12}H_{17}N_2OClCu$: C, 47.37; H, 5.63; N, 9.21; Cu, 20.88%.

*Compound **4**, the Green Form of Cu(sal·pr·NMe_2)Cl*: A solution of copper(II) chloride (10 mmol) in methanol (30 ml) was added to a solution of Cu(sal·pr·NMe_2)$_2$ (10 mmol) in methanol (20 ml). The mixture was stirred at *ca.* 40 °C for 1/2 h. The green crystals which precipitated were collected and washed with methanol and dried. This was also obtained by recrystallizing Compound **3** from methanol or chloroform. Found: C, 47.14; H, 5.65; N, 9.10; Cu, 21.05%. Calcd for $C_{12}H_{17}N_2OClCu$: C, 47.37; H, 5.63; N, 9.21; Cu, 20.88 %.

*Compound **5**, Cu(sal·pr·NMe_2)Br*: The synthetic procedure is similar to that for Compound **3** except for the use of copper (II) bromide instead of copper(II) chloride. The green crystals collected were recrystallized from ethanol. Found: C, 41.26; H, 4.89; N, 7.99; Cu, 18.10%. Calcd for $C_{12}H_{17}N_2OBrCu$: C, 41.33; H, 4.92; N, 8.03; Cu, 18.22%.

Physical Measurements. The magnetic susceptibilities were determined by the Gouy method in the range from the temperature of liquid nitrogen to room temperature. The effective magnetic moments per copper ion at room temperature were calculated from the equation:

$$\mu_{\text{eff}} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T} \qquad (1)$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituted atoms using Pascal's constant[4] and $N\alpha$ is the temperature-independent paramagnetism per gram-ion of copper(II). The $N\alpha$ was assumed to be 60×10^{-6} cgs emu.[5] The results are given in Table 1. The ESR (X-band) spectra of polycrystalline samples were recorded with a JEOL ESR-apparatus, model JES-ME-1X, at room temperature. 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

Table 1. Magnetic data

Compound	μ_{eff}/B. M. (T/K)	θ/K	$-2J$/cm^{-1}	g[a]
1. Cu[sal·en·N(H)Me]Cl	1.81 (295)	0		
2. Cu(sal·en·NMe$_2$)Cl	1.81 (293)	0		
3. Cu(sal·pr·NMe$_2$)Cl (red-violet form)	1.80 (293)	0		
4. Cu(sal·pr·NMe$_2$)Cl (green form)	1.44 (298)		248	2.10 (2.10)
5. Cu(sal·pr·NMe$_2$)Br	1.42 (295)		260	2.10 (2.09)

a) The data in parentheses were determined by ESR measurements on the polycrystalline samples.

spectra were recorded with a Hitachi EPS-3T recording spectrophotometer.

Results and Discussion

Magnetic Data. The results of the magnetic susceptibility measurements are shown in Fig. 1.

The susceptibility data of Compounds **1** and **2** follow the Curie law down to liquid nitrogen temperature, indicating that they are magnetically diluted in crystals. Hence they are considered to be mononuclear. The red-violet complex **3** also showed the usual magnetic behavior expected for a mononuclear copper(II) complex; a plot of $(\chi_A - N\alpha)^{-1}$ as a function of temperature gives a Weiss constant θ of almost 0 K (Fig. 1). Their X-band ESR spectra provide further evidence for their monomeric nature: the spectra show a strong signal at *ca.* 3100 G due to a copper(II) ion with S=1/2. In contrast to **3**, the green complex **4** and the analogous bromide complex **5** show subnormal magnetic moments at room temperature (*cf.* Table 1), and their magnetic susceptibility data fit the Bleaney-Bowers equation[6)]

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

where each symbol has the general meaning. The J and g values listed in Table 1 were evaluated from the best fit of the cryomagnetic data to Eq. 2, assuming $N\alpha = 60\times10^{-6}$ cgs emu.[5)] The negative values of J indicate the presence of antiferromagnetic interaction in these complexes, and the g values are in good agreement with the average g values obtained from ESR measurements (*cf.* Table 1). The close agreement between the experimental and theoretical $\chi_A - T$ curves is a powerful argument for a binuclear structure in these complexes.

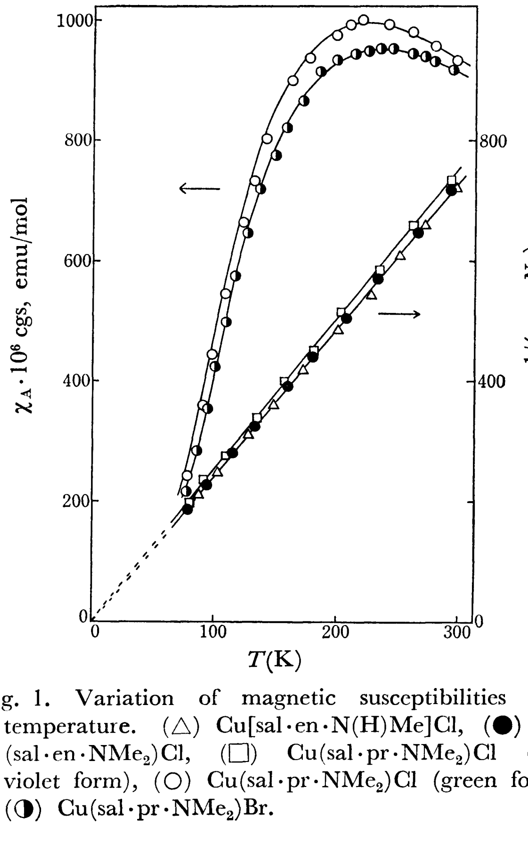


Fig. 1. Variation of magnetic susceptibilities with temperature. (△) Cu[sal·en·N(H)Me]Cl, (●) Cu(sal·en·NMe$_2$)Cl, (□) Cu(sal·pr·NMe$_2$)Cl (red-violet form), (○) Cu(sal·pr·NMe$_2$)Cl (green form), (◑) Cu(sal·pr·NMe$_2$)Br.

These magnetic data clearly indicate that the two forms of Cu(sal·pr·NMe$_2$)Cl, red-violet and green in color, are monomer-dimer type isomers of each other.

IR Spectra. The wave number of the intense band near 1540 cm^{-1} observed for the present complexes **1**—**5** and the parent bis-complexes, Cu(sal·en·NMe$_2$)$_2$ and Cu(sal·pr·NMe$_2$)$_2$, are listed in Table 2. The IR spectra of mononuclear complexes of salicylaldehyde Schiff bases display a sharp band at *ca.* 1530 cm^{-1}, whereas the band in the spectra of polynuclear salicylideneamine complexes with phenolic oxygen-bridges between metal ions appears in the range 1545—1550 cm^{-1}.[7)] This band shift toward higher frequencies is now taken as an umambiguous criterion for the formation of a phenolic oxygen-bridging in polymeric salicylideneamine complexes.[1,2,7—11)]

As is shown in Table 2, the band shift was observed for Compounds **4** and **5**. This indicates the presence

Table 2. IR and reflectance spectral data

Compound	IR absorption band maximum near 1540 cm^{-1} ν/cm^{-1}	Ligand field band maximum[a)] ν/10^3 cm^{-1}
1. Cu[sal·en·N(H)Me]Cl	1531	15.9
2. Cu(sal·en·NMe$_2$)Cl	1534	16.7 sh, 15.1
Cu(sal·en·NMe$_2$)$_2$	1526	16.7 sh, 14.3
3. Cu(sal·pr·NMe$_2$)Cl (red-violet form)	1529	19.0, 14.1, 11.1 sh
4. Cu(sal·pr·NMe$_2$)Cl (green form)	1549	11.2, 9.6 sh
5. Cu(sal·pr·NMe$_2$)Br	1549	12.5, 11.1 sh
Cu(sal·pr·NMe$_2$)$_2$	1534	16.7 sh, 14.1

a) sh=shoulder.

of phenolic oxygen-bridges between copper(II) ions in these complexes. On the other hand, no significant band shift was observed for Compounds **2** and **3**, indicating that, in these complexes, no phenolic oxygen-bridge exists. The strong band at 1531 cm^{-1} for Compound **1** indicates the non-existence of any bridging phenolic oxygen in this complex.

Diffuse Reflectance Spectra. The present complexes give rise to several bands in the 5000—25000 cm^{-1} region in the diffuse reflectance spectra. The wave numbers of the band maxima are collected in Table 2 and their spectral curves are shown in Fig. 2.

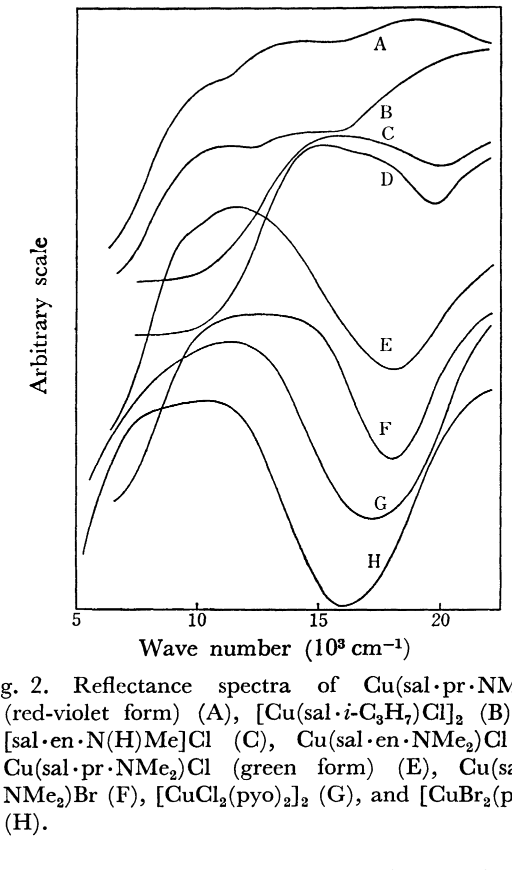


Fig. 2. Reflectance spectra of Cu(sal·pr·NMe_2)Cl (red-violet form) (A), [Cu(sal·*i*-C_3H_7)Cl]$_2$ (B), Cu-[sal·en·N(H)Me]Cl (C), Cu(sal·en·NMe_2)Cl (D), Cu(sal·pr·NMe_2)Cl (green form) (E), Cu(sal·pr·NMe_2)Br (F), [$CuCl_2$(pyo)$_2$]$_2$ (G), and [$CuBr_2$(pyo)$_2$]$_2$ (H).

The spectral feature of Compounds **1** and **2** is apparently of a square planar type (Fig. 2), as pointed out by Sacconi *et al.*[3] Compound **3** gave rise to three ligand-field bands in the 5000—25000 cm^{-1} range. This spectral feature indicates a pseudo-tetrahedral geometry around the metal ion.[8,12] For comparison the reflectance spectral curve of [Cu(sal·*i*-C_3H_7)Cl]$_2$ complex with a pseudo-tetrahedral copper(II) geometry[13] is given in Fig. 2. The spectral features of Compounds **4** and **5** apparently indicate that these have a five-coordinated copper(II) geometry, square-pyramid or trigonal-bipyramid. However, unambiguous structural assignments for these complexes could not be drawn from their spectra, since the differences in spectra among a square-pyramidal, a distorted square-pyramidal, a distorted trigonal-bipyramidal, and a trigonal-bipyramidal structure are not always clear. In Fig. 2, for comparison, are given the reflectance spectral curves of the dimeric 1 : 2 complex of copper(II) chloride with pyridine *N*-oxide, [$CuCl_2$(pyo)$_2$]$_2$, in which the geometry around the copper(II) ion is a tetragonal-pyramid,[14] and the analogous bromide complex, [$CuBr_2$(pyo)$_2$]$_2$, which has a distorted trigonal-bipyramidal copper(II) geometry.[15]

Structure and Magnetic Property. The monomeric four-coordinated planar structure shown schematically in Fig. 3A had been proposed for both Compounds **1** and **2** by Sacconi *et al.*[3] on the basis of their electronic reflectance spectra. Our magnetic and spectral data for these complexes have substantiated their structural assignment.

The structure should be compared with that of Cu(sal·en·OH)Cl, which displays a dimer type of antiferromagnetism.[1,2] In previous papers we assigned a chloride-bridging binuclear structure shown in Fig. 3B for Cu(sal·en·OH)Cl on the basis of its magnetic and spectral properties.[1,2] This assignment is further supported by the fact that the J value of -60 cm^{-1} determined for the complex[1] is practically identical with those of -50——70 cm^{-1} reported for dimeric copper(II) chloride complexes with dithiocarbamates in which a pair of copper(II) ions is bridged by two chloride ions in a similar manner to that shown in Fig. 3B.[16] Since an alcohol group has usually a poorer coordinating ability than does an amine group, it is concluded that the absence of coordination of the OH group in Cu(sal·en·OH)Cl (Fig. 3B) leads to the formation of the chloride-bridged dimer, whereas the coordination of the terminal amine group in Compound **1** or **2** (Fig. 3A) hinders the dimer formation.

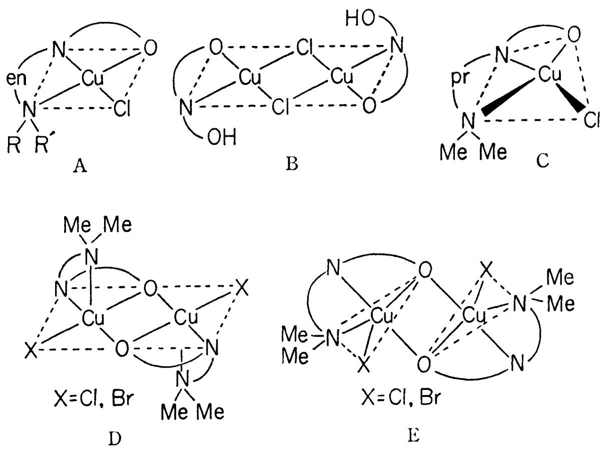


Fig. 3. Schematic representations of possible structure. (A)Cu[sal·en·N(H)Me]Cl and Cu(sal·en·NMe_2)Cl, (B) Cu(sal·en·OH)Cl, (C) Cu(sal·pr·NMe_2)Cl (red-violet form), (D) and (E) Cu(sal·pr·NMe_2)Cl (green form) and Cu(sal·pr·NMe_2)Br.

The monomeric pseudo-tetrahedral structure of the C type shown in Fig. 3 should be assigned to Compound **3** on the basis of its magnetic and spectral data. The magnetic and spectral data for Compounds **4** and **5** showed that these complexes have a phenolic oxygen-bridged binuclear structure with a five-coordinated copper(II) geometry. Molecular models show that two types of five-coordinated metal dimers, one with square-pyramidal and the other trigonal-bipyramidal coordination (Fig. 3D and E), can be produced from sal·pr·NMe_2. This is apparently due to the greater flexibility of the diamine part in sal·pr·NMe$_2$ as compared with that in sal·en·NMe$_2$. Thus, in a similar manner to the case of binuclear four-coordinated copper(II) complexes of the type [Cu(sal·R)X]$_2$, where R=alkyl or aryl and X=Cl,[7,8] Br[9] or NO$_3$,[10,11] the antiferromagnetism observed in these complexes may be interpreted in terms of superexchange interaction through the bridging phenolic oxygen atoms. It has been well established that the strength of antiferromagnetic interaction in [Cu(sal·R)X]$_2$ complexes decreases as the distortion of copper(II) geometry from planar toward tetrahedral increases.[8,13,17,18] With five-coordinated copper(II) complexes, two metal geometries, trigonal-bipyramid and tetragonal-pyramid, are usually encountered, and a continuous structural variation may take place, through structural deformation, between the two regular geometries depending upon the environments of metal coordination. At present, for five-coordinated copper(II) dimers, the correlation of the structure with the detected degree of antiferromagnetic interaction is not apparent.[8] However, comparison of the J values of Compounds **4** and **5** with those of five-coordinated copper(II) dimers found in the literature seems to suggest a conclusion about the metal geometry of these complexes: The $|J|$ values of Compounds **4** and **5** are about one-half of [Cu(sal·pr·OH)Cl]$_2$ ($J=-252$ cm^{-1},[1] distorted trigonal-bipyramidal)[19] and of [Cu(sal·R)X·DMF]$_2$ ($J=-200$ — -250 cm^{-1},[8,20] DMF=N,N-dimethylformamide) to which a square-pyramidal copper(II) geometry was previously assigned.[8,20] The J value of [CuBr$_2$(pyo)$_2$]$_2$ (distorted trigonal-bipyramidal) is -121 cm^{-1} [21] and this is approximately one-fourth of that of the corresponding chloride complex, [CuCl$_2$(pyo)$_2$]$_2$ ($J=-440$ cm^{-1},[21] tetragonal-pyramidal). The J value of [Cu(sal·t-C$_4$H$_9$)(hfa)]$_2$ (hfa=hexafluoroacetylacetonato, slightly distorted trigonal-bipyramidal)[22], -105 cm^{-1},[23] is small and comparable with those of Compounds **4** and **5**. Thus, copper(II) dimers with trigonal-bipyramidal metal coordination happened to give rise to a large $|J|$ value in [Cu(sal·pr·OH)Cl]$_2$, but in the other cases they have shown small values for the exchange integral. On the other hand, the $|J|$ values of copper(II) dimers with tetragonal-pyramidal metal geometry have appeared to be fairly large for the cases so far investigated.[20,21] These facts strongly suggest that the present complexes **4** and **5** take essentially a trigonal-bipyramidal metal coordination. For five-coordinated copper(II) dimers with the same type of ligands, the $|J|$ value is considered to be lowered progressively according as the copper(II) geometry is distorted from regular tetragonal-pyramid toward trigonal-bipyramid; we are now attempting to prepare more copper(II) dimers of the required types in order to clarify this point.

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