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The 2:1 Adduct of Chloro[*N*-(2-dimethylaminoethyl)salicylideneaminato]copper(II) with Chlorides of Copper(II), Manganese(II), and Nickel(II)

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Synopsis. The adducts listed in the title have been prepared, and their trimeric nature confirmed on the basis of elemental analysis and IR and electronic spectra. The magnetic properties of the $MnCl_2$ and $NiCl_2$ adducts have been analyzed in terms of a linear trimer model.

Chloro[*N*-(2-dimethylaminoethyl)salicylideneaminato]copper(II), Cu(sal•en•NMe_2)Cl, was originally synthesized and investigated by Sacconi *et al.*; a monomeric planar structure, I, was proposed for this complex based on the electronic reflectance spectrum.[1] The monomeric nature was confirmed by cryomagnetic and IR spectral studies.[2] Based on the monomeric structure and the knowledge that phenolato and chloro ligands form bridges between pairs of metal ions, it is expected that the complex can be used as a bidental complex-ligand[3] in the synthesis of polynuclear metal complexes. In the reaction of Cu(sal•en•NMe_2)Cl with metal salts MCl_2(M=Cu(II), Mn(II), and Ni(II)) 2: 1 adducts of [Cu(sal•en•NMe_2)Cl]$_2$•MCl_2 were formed. A similar adduct of chloro[*N*-(2-methylaminoethyl)salicylideneaminato]copper(II), Cu(sal•en•NHMe)Cl, with copper(II) chloride has also been prepared.

The spectral and magnetic studies will be reported in this paper.

Experimental

Synthesis. A typical synthetic method is as follows. A solution of one of the metal salts MCl_2 (10 mmol) in ethanol (50 ml) was added to a solution of one of the parent complexes, Cu(sal•en•NMe_2)Cl and Cu(sal•en•NHMe)Cl, and the mixture stirred on a hot plate for 1/2 h. The crystals thus precipitated were collected, washed repeatedly with ethanol and dried. Anal. **1.** [Cu(sal•en•NMe_2)Cl]$_2$•$CuCl_2$. Found: C, 36.84; H, 4.19; N, 7.86; Cu, 26.43%. Calcd for $C_{22}H_{30}N_4O_2Cl_4Cu_3$: C, 36.96; H, 4.23; N, 7.84; Cu, 26.66%. **2.** [Cu(sal•en•NHMe)Cl]$_2$•$CuCl_2$. Found: C, 34.75; H, 3.85; N, 8.17; Cu, 27.55%. Calcd for $C_{20}H_{26}N_4O_2Cl_4Cu_3$: C, 34.97; H, 3.82; N, 8.16; Cu, 27.75%. **3.** [Cu(sal•en•NMe_2)Cl]$_2$•$MnCl_2$. Found: C, 37.54; H, 4.37; N, 7.80; Cu, 17.95; Mn, 7.82%. Calcd for $C_{22}H_{30}N_4O_2Cl_4Cu_2Mn$: C, 37.41; H, 4.28; N, 7.93; Cu, 17.99; Mn, 7.78%. **4.** [Cu(sal•en•NMe_2)Cl]$_2$•$NiCl_2$. Found: C, 37.01; H, 4.20; N, 7.91; Cu, 17.78; Ni, 8.58%. Calcd for $C_{22}H_{30}N_4O_2Cl_4Cu_2Ni$: C, 37.21; H, 4.26; N, 7.89; Cu, 17.90; Ni, 8.27%.

Physical Measurements. The IR spectral measurements were made with a Hitachi EPI-G2 IR Spectrophotometer in the 400—4000 cm^{-1} region in Nujol. The reflectance spectra were recorded with a Hitachi Recording Spectrophotometer 323. The magnetic susceptibilities in the temperature range 80—300 K were determined by the Faraday method using $HgCo(SCN)_4$ as a calibrant.

Results and Discussion

The IR spectra of the adducts prepared in this study all show an intense band in the range 1550—1555 cm^{-1} (**1**, 1555; **2**, 1554; **3**, 1550; **4**, 1551 cm^{-1}), while the band in the spectra of the parent complexes, Cu(sal•en•NMe_2)Cl and Cu(sal•en•NHMe)Cl, appears at 1534 and 1531 cm^{-1} respectively. This band shift towards higher frequencies (15—20 cm^{-1}) indicates the presence of bridging phenolic oxygen atoms in the adducts.[2]

A remarkable feature in the reflectance spectra of the $CuCl_2$ adducts (**1** and **2**) is the appearence of a band in the 9000—10000 cm^{-1} region (Fig. 1) which is absent in the spectra of the parent complexes.[1,2] This feature indicates the presence of Cu(II) in pseudo-tetrahedral coordination.[2,4] The $MnCl_2$ adduct spectrum shows a broad band at *ca.* 15000 cm^{-1} with a shoulder at *ca.* 11000 cm^{-1} (Fig. 1). This band has been attributed to the d-d transition of Cu(II) since Mn(II) complexes have no d-d band below 15000 cm^{-1} regardless of stereochemistry (octahedral or tetrahedral) or spin-states (high- or low-spin). This type of spectra is indicative of five-coordination around Cu(II) and is to be compared with the spectra reported for some distorted square-pyramidal Cu(II) complexes.[2,5] The spectrum of the $NiCl_2$ adduct shows a broad band at *ca.* 15000 cm^{-1} with a shoulder at *ca.* 11000 cm^{-1} and a weak band at *ca.* 6500 cm^{-1} (Fig. 1). Assignment of the former band could not be unambiguously performed since the d-d bands of both Ni(II) and Cu(II) appear

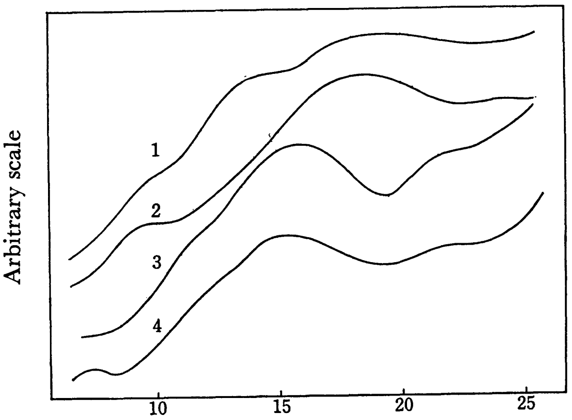
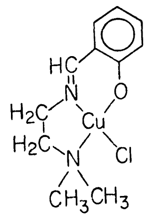


Fig. 1. Reflectance spectra of [Cu(sal•en•NMe_2)Cl]$_2$•$CuCl_2$ (1), [Cu(sal•en•NHMe)Cl]$_2$•$CuCl_2$ (2), [Cu(sal•en•NMe_2)Cl]$_2$•$MnCl_2$ (3) and [Cu(sal•en•NMe_2)Cl]$_2$•$NiCl_2$ (4).



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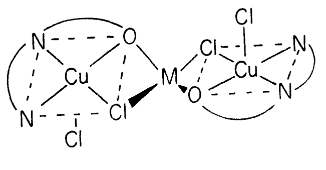

II

in this region. The latter band has been attributed to the transition in the Ni(II) in this adduct and may be assigned to the d-d band in the Ni(II) with a pseudo-tetrahedral geometry. The assignment has been based on the following observations: 1) in the region below 8000 cm^{-1}, no band was observed in the spectra of the other adducts (**1**—**3**) and 2) the position, shape and absorption intensity of the band closely resembles the bands observed at *ca.* 6700 cm^{-1} for pseudo-tetrahedral bis(*N*-alkylsalicylideneaminato)nickel(II) complexes.[6]

On the basis of the analytical and spectral data the adducts have been assigned a trinuclear structure represented schematically by II. Each of the terminal Cu(II) ions(five-coordination) is bridged to the central metal ion(pseudo-tetrahedral four-coordination) with one phenolic oxygen atom and one chloro donor.

The variable-temperature magnetic susceptibility data observed for the $CuCl_2$ adducts (**1** and **2**) followed the Curie-Weiss law ($\chi_M = C/T - \theta$) with $\theta = -7$ and $+6$ K respectively, indicating no appreciable magnetic interaction in the adducts. The pseudo-tetrahedral geometry of the central Cu(II) in the adducts would be expected to be the main structural factor for the magnetism.[7] The cryomagnetic data of the $MnCl_2$ adduct has been analyzed using the theoretical equation 1[3] based on a symmetric linear trimer of Cu–Mn ($S=5/2$)–Cu, assuming no magnetic interaction between the terminal Cu(II) ions. Similarly, the data for the $NiCl_2$ adduct may be expressed by Eq. 2[3] for a Cu–Ni($S=1$)–Cu trimer (Fig. 2);

$$\chi_M = \frac{N\beta^2 g^2}{4k(T-\theta')}[35+84\exp(5J/kT)+35\exp(-2J/kT) \\ +10\exp(-7J/kT)]/[3+4\exp(5J/kT) \\ +3\exp(-2J/kT)+2\exp(-7J/kT)] + N\alpha \tag{1}$$

$$\chi_M = \frac{2N\beta^2 g^2}{k(T-\theta')}[1+5\exp(2J/kT)+\exp(-2J/kT)]/ \\ [3+5\exp(2J/kT)+3\exp(-2J/kT) \\ +\exp(-4J/kT)] + N\alpha \tag{2}$$

where χ_M represents the molar susceptibility corrected for diamagnetism (-384×10^{-6} and -382×10^{-6} cgs emu respectively) using Pascal's constants, J represents the exchange integral between the central and terminal metal ions, g represents the average g value over the three metal ions, θ' represents the Weiss constant term for inter-cluster interaction, and $N\alpha$=T.I.P. per Cu_2Mn or Cu_2Ni. Using Eq. 1, the best fit of the experimental data observed for the $MnCl_2$ adduct gave the following values: $J=+19.4$ cm^{-1}, $g=1.997$ and $\theta'=-25.7$ K with $R=6.63\times10^{-3}$($R=[\sum(\chi_{exp}-\chi_{calcd})^2/\sum\chi_{exp}{}^2]^{1/2}$; discrepancy index), assuming $N\alpha=120\times10^{-6}$ cgs emu.[3] Similarly, the $NiCl_2$ adduct gave the following values: $J=+36.4$ cm^{-1}, $g=2.130$ and $\theta'=-17.8$ K with $R=4.81\times10^{-3}$, assuming $N\alpha=320\times10^{-6}$ cgs emu.[3] The positive J values indicating an intramolecular ferromagnetic interaction may also be related to the geometry of the central metal ion in the adducts. In the case of the $NiCl_2$ adduct, the close agreement between the observed and calculated temperature dependence with very low value of R indicates a negligible orbital contribution to the magnetic susceptibility. This factor may be primarily due to the pseudo-tetrahedral geometry of the central Ni(II) ion.[8]

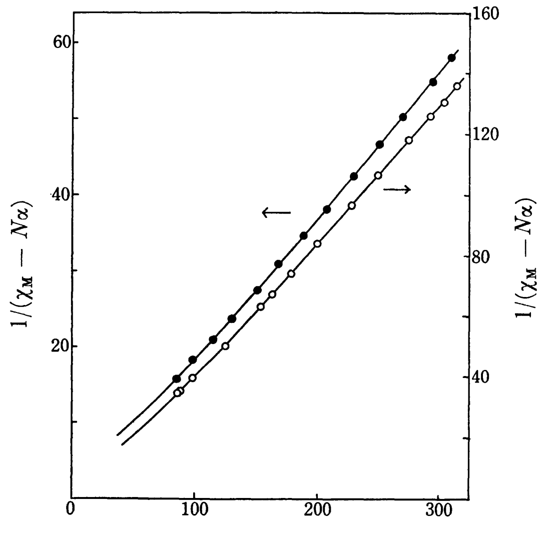

Fig. 2. Variation of reciprocal magnetic susceptibilities with temperature. (●) $[Cu(sal\cdot en\cdot NMe_2)Cl]_2\cdot MnCl_2$, (○) $[Cu(sal\cdot en\cdot NMe_2)Cl]_2\cdot NiCl_2$.
The solid curves were calculated from Eqs. 1 and 2 respectively.

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