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FORMATION OF MAGNETICALLY CONDENSED COMPOUNDS FROM THE REACTIONS OF COPPER(II) WITH ALCOHOLAMINES

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Abstract—Copper(II) reacts with monoethanolamine and with N-2-hydroxyethyl-ethylenediamine in methanol to yield the complexes $Cu(NH_2CH_2CH_2OH)(SCN)_2$ and $Cu(NH_2CH_2CH_2NHCH_2CH_2OH)(SCN)_2$, respectively, while reaction with triethanolamine yields $Cu(N\{CH_2CH_2OH\}_2\{CH_2CH_2O\})SCN$. Magnetic susceptibility data and vibrational spectral data for $Cu(NH_2CH_2CH_2NHCH_2CH_2OH)(SCN)_2$ are consistent with a square planar coordination about the copper with N-bonded thiocyanate ligands in a monomeric unit, while $Cu(NH_2CH_2CH_2OH)(SCN)_2$ is thiocyanate bridged in an exchange-coupled dimeric formulation and $Cu(N\{CH_2CH_2OH\}_2\{CH_2CH_2O\})(SCN)$ is apparently an alkoxo-bridged chain polymer.

INTRODUCTION

There has been considerable interest in the coordination chemistry of alcoholamines, largely because of the remarkable array of structural and magnetic properties found in compounds of these polyfunctional ligands[1]. The diversity of properties is illustrated by the complexes formed with the uninegative ligands 2-dialkylaminoethanolato (alkyl being ethyl, deae, or butyl, dbae) and copper(II) chloride[2]. Both $[Cu(deae)Cl]_4$ and $[Cu(dbae)Cl]_4$ are tetrameric with cubane-type structures[3, 4], yet antiferromagnetic interactions predominate in $[Cu(deae)Cl]_4$ giving a room-temperature magnetic moment of 1.66 B.M. and a Weiss constant of $-102°$ while ferromagnetic interactions predominate in $[Cu(dbae)Cl]_4$ giving $\mu_{eff} = 1.95$ B.M. with a Weiss constant $\theta = +32°$[2]. In view of these unusual properties a study of the compounds formed by alcohol amines and copper(II) thiocyanate has been undertaken.

EXPERIMENTAL

$Cu(NH_2CH_2CH_2OH)(SCN)_2$. Monoethanolamine, mea, (20 ml, a large excess) was added with constant stirring to a solution of hydrated copper(II) perchlorate (22 g) in 50 ml methanol. Sodium thiocyanate (17 g) in 50 ml methanol was added to the resultant blue solution, which was filtered quickly. The blue crystals which separated were collected after two hours, washed with methanol, and dried in a vacuum desiccator. (Found: N, 17.70; Cu, 26.54; SCN^-, 48.18. Calc. for $Cu(mea)(SCN)_2$: N, 17.45; Cu, 26.39; SCN^-, 48.26).

$Cu(NH_2CH_2CH_2NHCH_2CH_2OH)(SCN)_2$. N-2-Hydroxyethyl-ethylenediamine, heen, (5 ml) was added with stirring to a solution of copper(II) perchlorate in 100 ml methanol. Sodium thiocyanate (24 g, a large excess) dissolved in 75 ml methanol was added to the above solution, which was then quickly filtered. The blue product, which began crystallizing out after a short period, was collected twelve hours later, washed with a 1:1 water-methanol mixture, recrystallized from hot methanol, and dried in a vacuum desiccator. (Found: C, 25.02; H, 3.80; N, 19.94; Cu, 22.36; SCN^-, 40.90. Calc. for $Cu(heen)(SCN)_2$, $CuC_5H_{12}N_3OS$: C, 25.39; H, 4.26; N, 19.75, Cu, 22.39; SCN^-, 40.92).

$Cu(N\{CH_2CH_2OH\}_2\{CH_2CH_2O\})SCN$. Triethanolamine, tea, (20 ml) was added with stirring to a solution of hydrated copper(II) perchlorate (22 g) in 100 ml methanol. Sodium thiocyanate (15 g) dissolved in 75 ml methanol was added to the solution, which was filtered and set aside. The yellowish-green product which crystallized out slowly was collected, washed with methanol, and dried in a vacuum dessiccator. (Found: Cu, 23.96. Calc. for $Cu(tea^-)SCN$, $CuC_7H_{14}N_2O_3S$: Cu, 23.55).

Characterization of the complexes. Magnetic susceptibility measurements in the temperature range 1.8° to 300°K on powdered smaples were made with a Foner-type vibrating sample magnetometer[5] at field strengths ranging from 1000 to 10,000 G provided by an electromagnet controlled by a Ventron-Magnion precision power supply. Temperatures were measured with a calibrated gallium arsenide diode[6], and mercury(II) tetrathiocyanatocobaltate(II) was used as the magnetic susceptibility standard[7]. The use and calibration of this equipment has been described in detail elsewhere[8], and the limits of error in the measurement of the magnetic susceptibilities has been determined to be ±1%. The experimental magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants[9], and for the temperature independent paramagnetism of the copper(II) ion (assumed to be 60×10^{-6} c.g.s. units)[10]. Electron paramagnetic resonance spectra were recorded at X-band at 77 K on a Varian model E-3 spectrometer using diphenylpicrylhydrazyl as an internal standard. The resonance fields were read directly from calibrated chart paper after the technique was checked with a Magnion G-502 Precision Gaussmeter and a Hewlett-Packard 5245L frequency counter and found to be accurate to be better than 1% in the region used in this study.[11]. IR spectra were recorded on a Perkin-Elmer model 421 recording spectrometer which was calibrated with an IUPAC-certified polystyrene standard.

RESULTS AND DISCUSSION

Pertinent bands from the IR spectra of the compounds under consideration are tabulated in Table 1.

In these compounds the bands near 3400 cm^{-1}, which may be attributed to the O–H functional group, were extremely broad, thereby indicating substantial hydrogen bonding. Bands arising from the N–H stretching vibrations were found in the region 3140–3320 cm^{-1}. This region of the spectrum is complex, and since no structural information can be obtained from the data, an analysis will not be presented here. There were no absorptions in this region for the compound $Cu(tea^-)SCN$.

The experimental magnetic susceptibility data for a polycrystalline sample of $Cu(tea^-)SCN$ are displayed in Fig. 1. It is apparent from the temperature variation of the magnetic susceptibility that anti-ferromagnetic interactions between copper(II) ions determine the magnetic properties of the material. Several models for interacting

Table 1. IR spectral data for selected functional groups, cm^{-1}

Compound	O–H	N–H	C–N	C–S
$Cu(mea)(SCN)_2$	~3400v.b.	3150–3290	2065s	740w, 800
$Cu(tea^-)SCN$	~3400v.b.	—	2095s	730w, 750
$Cu(heen)(SCN)_2$	3420	3150–3280	2120, 2140s	735w

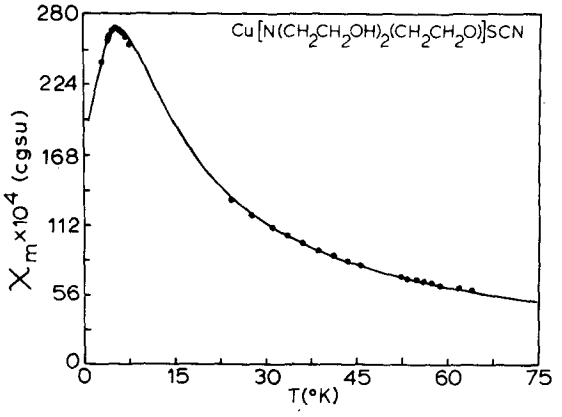

Fig. 1. Magnetic susceptibility data for $Cu(tea^-)SCN$. The experimental data are shown as solid dots, and the best-fit to the Heisenberg linear chain is shown as the solid line.

copper(II) ions were used in attempts to fit the data. All of the models were based on the exchange Hamiltonian

$$H = -2\sum_{i<j} J_{ij}\hat{S}_i\hat{S}_j.$$

The data are only poorly approximated by the following expression for exchange-coupled pairs of copper(II)[12]:

$$\chi_M^{corr} = \frac{g^2N\beta^2}{3k(T-\theta)}\{1 + 1/3\exp(-2J/kT)\}^{-1}. \quad (1)$$

In this expression for the magnetic susceptibility per mole of copper, J is the exchange coupling constant, θ allows for lattice interactions and other deviations from simple theory, and the other symbols have their accepted meanings. The best-fit values of the magnetic parameters, obtained from the minimization of the function

$$\sum_i [(\chi_{Mi}^{obs} - \chi_{Mi}^{calc})/\chi_{Mi}^{obs}]^2$$

using a simplex nonlinear least-squares routine[13], were found to be $J = -3.0\,cm^{-1}$ and $g = 1.79$. The low g value is unrealistic for copper(II) and the model can be confidently rejected[9]. The next magnetic model selected for investigation is represented by the magnetization expression

$$M = \frac{Ng\beta\sinh(g\beta H/kT)}{\exp(-2J/kT) + 2\cosh(g\beta H/kT) + 1} \quad (2)$$

which takes into account the fact that the exchange coupling constant is only slightly larger than the Zeeman energy[14]. A low g value was obtained in this fitting process also. Since improvements are frequently obtained when a molecular field correction is used[15], the field H was set equal to $H_o + \gamma M$ where H_o is the external field and M is the molecular field correction with

$$\gamma = \frac{2zJ'}{Ng^2\beta^2k}$$

Here z is the number of nearest neighboring paramagnetic ions, J' is the lattice interaction constant, and the other symbols have their accepted meanings. The best fit of the magnetization expression with the molecular field correction gave $J = -2.8\,cm^{-1}$, $g = 2.12$, and $\gamma = -13.1°$, from which J' may be calculated to be $-1.4\,cm^{-1}$ for $z = 4$. Such a large value for the lattice interaction parameter suggests that the model is inappropriate and leads to the conclusion that the structure of $Cu(tea^-)SCN$ is composed of higher oligomers or is polymeric.

By careful comparison of the magnetic susceptibility data with other models, it was found that the Heisenberg linear chain approximation of Bonner and Fisher[16] provided a very good fit to the data. The Hamiltonian for spin–spin interactions between neighboring paramagnetic ions along an infinite one-dimensional chain is

$$H = -2J\sum_{i=1}^{N}[\hat{S}_{iz}\hat{S}_{(i+1)z} + \gamma(\hat{S}_{ix}\hat{S}_{(i+1)x} + \hat{S}_{iy}\hat{S}_{(i+1)y})] \quad (3)$$

where J is the exchange coupling constant, and γ can take on values ranging from 0 to 1. In the limit of $\gamma = 1$ the fully isotropic Heisenberg model results. Bonner and Fisher[16] have shown for infinite $S = 1/2$ chains that

$$\frac{kT_{max}}{J} \cong 1.282 \quad (4a)$$

and

$$\frac{|J|\chi_{max}}{g^2\beta^2N} \cong 0.0735. \quad (4b)$$

Since no closed form expressions are available for the magnetic susceptibility of a Heisenberg linear chain, an approximate expression was generated by fitting the numerical data calculated by Bonner[17] to a rational function with g, J and T dependence[13]. The magnetic susceptibility data for $Cu(tea^-)SCN$ was fitted to this model yielding $J = -3.1\,cm^{-1}$ and $g = 2.08$. The best-fit line calculated from these parameters is shown in Fig. 1.

The EPR spectrum of a powdered sample of $Cu(tea^-)SCN$ recorded at X-band and room temperature yielded the g-values $g_1 = 2.042$, $g_2 = 2.146$, $g_3 = 2.237$ and $\langle g\rangle = 2.14$. Since the EPR average g value differed by approx. 3% from the value obtained from the fit of the magnetic data to the Heisenberg linear chain model, a fit of the high-temperature magnetic susceptibility data to the Curie–Weiss law was carried out. This fit yielded $\langle g\rangle = 2.13$, a value in very good agreement with the high-temperature EPR value. Changes in g of this order have been observed in other systems, and do not necessarily indicate structural transformations.

The chain formulation for Cu(tea$^-$)SCN, which is suggested by the magnetic data, is very reasonable when one takes into account the bulky nature and steric requirements of the tea$^-$ ligand. The postulated chain structure for this compound involves one alkoxo-oxygen bridge with the remaining coordination sites on copper being filled by the thiocyanate ligand and oxygen atoms from tea$^-$.

The magnetic susceptibility data in the temperature range 1.4–100°K for Cu(heen)$(SCN)_2$ are given in Fig. 2

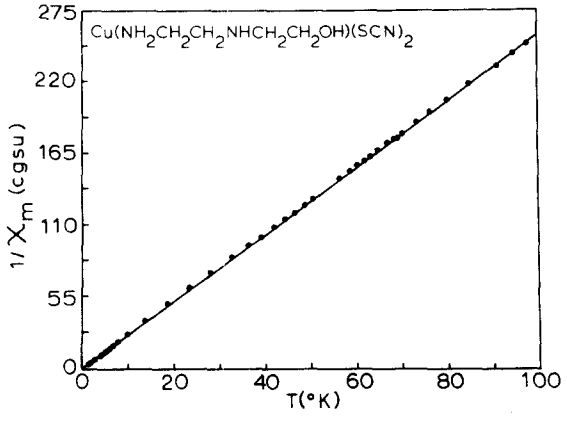

Fig. 2. Magnetic susceptibility data for Cu(heen)$(SCN)_2$. The experimental data are shown as solid dots, and the best fit to the Curie–Weiss law is shown as the solid line.

along with the best-fit line calculated from the Curie–Weiss law $\chi = C/(T-\theta)$ using the parameters $C = 0.3926$ and $\theta = -0.19$°K. From the definition of C, that being $Ng^2\beta^2S(S+1)/3k$, a value of 2.05 may be calculated for $\langle g\rangle$. This value for $\langle g\rangle$ is approx. 3% smaller than the value for $\langle g\rangle$ of 2.11 determined from the X-band EPR spectrum at room temperature. This deviation is comparable to those observed with other members of this series, *vide infra*, and it may be concluded that Cu(heen)$(SCN)_2$ is essentially magnetically dilute.

The magnetic susceptibility data of Cu(heen)$(SCN)_2$ are consistent with a monomeric structure. In this instance the two nitrogen atoms of the aminoalcohol are very likely bonded to copper with N-bonded thiocyanates in cis-positions completing the square-planar coordination. The splitting observed in the C–N stretching band may be accounted for by the allowed symmetric and antisymmetric stretching vibrations in local-site symmetry C_{2v}. An alternate explanation based Cu–N–C–S–Cu bridging for one of the thiocyanates thereby distinguishing the two thiocyanates seems unlikely in view of the very small Weiss constant of -0.19°K which was determined from the magnetic data.

The experimental magnetic susceptibility data for Cu(mea)$(SCN)_2$ are given in Fig. 3. The data are very nicely accounted for by the dimer equation with a molecular field correction to approximate the interdimer interactions. The susceptibility expression for the dimer is

$$\chi_M^{\text{corr}} = \frac{Ng^2\beta^2}{kT\{3+\exp(-2J/kT)\}-4zJ'}. \quad (5)$$

The best fit of the magnetic susceptibility data to this expression yeilds $2J = -10\,\text{cm}^{-1}$, $g = 2.04$ and $zJ' = -4.0\,\text{cm}^{-1}$. The value of zJ' leads to a J' value of $-1.0\,\text{cm}^{-1}$ for $z = 4$ (assumed) and indicates substantial interdimer interactions, however it is clear that the predominant magnetic interaction is pairwise.

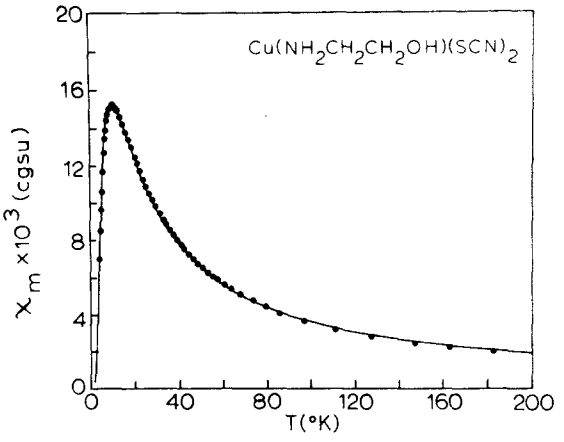

Fig. 3. Magnetic susceptibility data for Cu(mea)$(SCN)_2$. The experimental data are shown as solid dots, and the best fit to the dimer eqn (5) (see text) is shown as the solid line.

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