Ferromagnetic and Antiferromagnetic Interactions in Copper(II) Complexes of Schiff Bases of *S*-Methyl Dithiocarbazate

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Summary The copper complex of the ONS Schiff base of 5-nitrosalicylaldehyde and *S*-methyl dithiocarbazate is ferromagnetic and probably exists as a tetrahedral cluster, while the copper complexes of some other similar Schiff bases are antiferromagnetic.

Co-ordination complexes which exhibit ferromagnetic interaction are currently of interest.[1a–c] The few known examples with copper(II) exhibit a relatively small increase in the magnetic moment on being cooled to low temperatures.[1]

We have studied the magnetic behaviour of the copper(II) complexes of some tridentate ONS Schiff bases of substituted salicylaldehydes with *S*-methyl dithiocarbazate, *viz*. $Cu\{X{\cdot}C_6H_3{\cdot}(O).CH{=}NN{=}C(SMe)S\}$. When $X = 5\text{-}NO_2$, the copper complex shows marked ferromagnetic behaviour and the increase of its magnetic moment when the complex is cooled to liquid nitrogen temperature is the largest yet reported. When X = H, 5-Cl, 5-Br, and 3-MeO, the copper complexes are antiferromagnetic with moments which decrease from *ca.* 1 B.M. at 293 K to *ca.* 0·4 B.M. at 83 K. The i.r. spectra of all the complexes display ν(C–O) within the range 1545—1560 cm^{-1}, indicating the presence of bridging phenolic oxygen atoms.[2]

The moment of the 5-NO_2 complex increases from 2·03 B.M. at 293 K to 2·43 B.M. at 83 K and is field-independent. The maximum spin-only values for the magnetic moment of ferromagnetic clusters of two, three, or four copper atoms are 2·00, 2·24, and 2·45 B.M., respectively.[1a] The magnetic data indicate that the complex contains three or more interacting copper atoms. However, the data do not fit equations for three interacting copper atoms[3] but are quite well described by expressions for tetrahedral or linear polymeric arrangements of copper atoms. By the use of a least-squares procedure, the best fit to the data was found with equation (1) for a tetrahedral arrangement[3] of copper

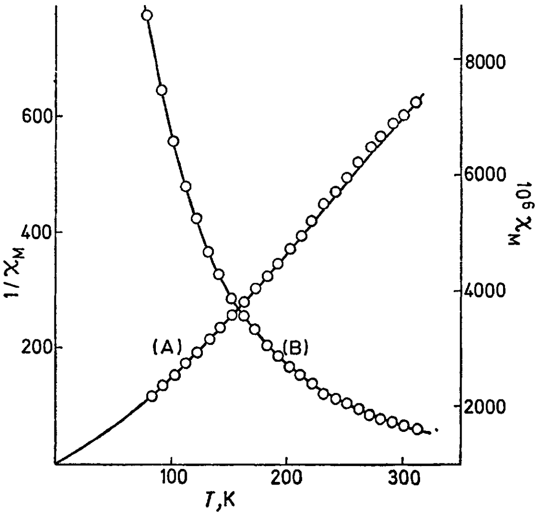

FIGURE. *The temperature dependence of* $1/\chi_M$ (A) *and* $10^6\chi_M$ (B) *for the copper complex of the Schiff base of 5-nitrosalicylaldehyde and* S-*methyl dithiocarbazate. Experimental values are indicated by open circles and the full curves are the calculated values obtained from equation* (1) *for a tetrahedral cluster of copper atoms with the values,* $g = 2{\cdot}00$ *and* $J = 38\ cm^{-1}$.

atoms when $g = 2{\cdot}00$ and $J = 38\ \text{cm}^{-1}$; the sum of the weighted squares of the deviations $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$ was found to be $0{\cdot}31 \times 10^{-2}$ (see Figure). A somewhat poorer fit was obtained with the Ising equation (2) for a linear polymeric arrangement;[4] with $g = 2{\cdot}10$ and $J = 17\ \text{cm}^{-1}$,

$$\chi_M \ (\text{per Cu atom}) = \frac{N\beta^2g^2[30 + 18\exp(-4J/kT)]}{12kT[5+9\exp(-4J/kT)+2\exp(-6J/kT)]} + N\alpha \qquad (1)$$

the value of $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$ was $0{\cdot}39 \times 10^{-2}$. The T.I.P. correction ($N\alpha$) for copper(II) was taken as 60×10^{-6} c.g.s.u.

$$\chi_M = \frac{N\beta^2g^2}{4kT}\exp(2J/kT) + N\alpha \qquad (2)$$

The magnetic interactions reported for complexes with linear polymeric chains of interacting copper atoms are all antiferromagnetic.[5] On the other hand, all the complexes with tetrahedral clusters of copper atoms, which have been investigated, appear to have ferromagnetic interactions.[1a–c, 6] Because of this and the better fit obtained with equation (1), it is considered that the 5-NO_2 complex has a structure involving a tetrahedral cluster. The most likely structure is one with pairs of oxygen-bridged $[Cu(ONS)]_2$ (HONSH = 5-NO_2 Schiff base) units aligned to give a tetrahedral arrangement of metal atoms, as found for the copper complex of the Schiff base derived from 2-aminoethanol and acetylacetone.[7] The electronic spectrum, which shows a broad absorption centred at 21,200 cm^{-1} with a shoulder at *ca.* 14,000 cm^{-1}, is not markedly different from the spectra of the antiferromagnetic copper complexes of the other ONS Schiff bases. All the spectra show strong absorption in the u.v.

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