Inorganica Chimica Acta, 44 (1980) L291–L294
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Spin Spin Interactions in Polymeric Copper(II) Complexes: Cu(II)(Piperidylcarbamate)$_2$(Cu(I)X)$_4$ (X = Cl, Br)

PETER D. W. BOYD*, JANET HOPE and RAYMOND L. MARTIN**

Research School of Chemistry, Australian National University, P. O. Box 4, Canberra, A.C.T., Australia 2600

Received January 12, 1980

The reaction of copper(II) bis(N,N-dialkyldithiocarbamates) with copper(II) halides can lead to a variety of complexes containing copper(II) or copper(II) and copper(I) ions [1, 2]. Bis(piperidyldithiocarbamate)copper(II), [Cu(pipdtc)$_2$] reacts with copper(II) halides leading to a series of compounds containing both copper(II) and copper(I) ions of the form Cu(II) (pipdtc)$_2$(Cu(I)X)$_n$ (X = Cl, Br, n = 4, 6) [1, 2]. X-ray crystal structures of the bromide complexes for n = 4, 6 show them to consist of polymeric sheets of the copper(II) bisdithiocarbamate complex linked through Cu(I)Br chains, each copper(II) ion being bridged to four copper(I) ions by the dithiocarbamate sulphur atoms [1], Fig. 1. The analogous chloride complex Cu(II)(pipdtc)$_2$(CuCl)$_4$ is isostructural with the corresponding bromide compound.

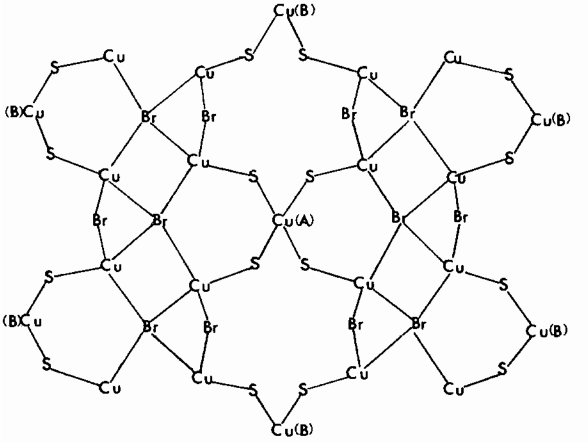

Fig. 1. Partial structure of Cu(pipdtc)$_2$(CuBr)$_4$ showing linkages from central copper(II) ion(A) to all other copper(II) ions (B) joined by five atom bridges-S–Cu(I)–Cl–Cu(I)–S-linkages showing only copper, bromide and sulphur atoms.

These complexes provide an opportunity to compare interactions between copper(II) ions in a two dimensional sheet structure with varying numbers of bridging links and varying bridging halides. Magnetic susceptibilities in the temperature range 4.2 K to 300 K have been measured to investigate the exchange interactions within these two dimensional sheet complexes.

Experimental

Magnetic susceptibilities of the compounds were measured using a modified Oxford Instruments Faraday balance described elsewhere [3]. Corrections for the diamagnetism of the ligands and metal ions were made using Pascal's constants [4]. Samples of the complexes Cu(pipdtc)$_2$(CuBr)$_4$ and Cu(pipdtc)$_2$(CuBr)$_6$ were those previously reported [1]. The complex Cu(pipdtc)$_2$(CuCl)$_4$ was obtained by a modification† of the published method [1] in which the ratio of Cu(pipdtc)$_2$ to copper(II) halide ratio was reduced from 20:1 down to 2:1. *Anal:* Calc. for $C_{12}H_{20}N_2S_4Cu_5Cl_4$: C, 18.47%; H, 2.58%; N, 3.59%; S, 16.44%; Cu, 40.77%; Cl, 18.60%; Found for Cu(pipdtc)$_2$(CuCl)$_4$: C, 18.55%; H, 2.67%; N, 3.29%; S, 16.16%; Cu, 40.71%; Cl, 18.74%. The C–N and C–S stretching frequencies were found at 1520 cm^{-1} and 955 cm^{-1} as reported previously [1].

Results and Discussion

The magnetic susceptibility of Cu(pipdtc)$_2$(CuCl)$_4$ in the temperature range 4.2 K to 300 K passes through a broad maximum at *ca.* 115 K then increases rapidly at lower temperatures, Fig. 2. In contrast the susceptibility of Cu(pipdtc)$_2$(CuBr)$_4$ passes through a maximum at a 60 K and then increases rapidly at lower temperatures whilst Cu(pipdtc)$_2$(CuBr)$_6$ has a broad maximum at *ca.* 250 K. The increase in susceptibility at low temperatures is due to a small amount of paramagnetic impurity [5]. It was not possible to recrystallise these complexes once prepared and it is likely that small amounts of sparingly soluble Cu(pipdtc)$_2$ crystallise in the initial preparation of these complexes.

---

*To whom correspondence should be addressed at: Chemistry Department, University of Auckland, Auckland, New Zealand.

**Present address: Monash University, Clayton, Vic., Australia.

†The preparation of Cu(pipdtc)$_2$(CuCl)$_4$ attempted as described in reference 2 to a complex which on analysis had a formulation Cu(pipdtc)$_2$(CuCl)$_2$. Calculated for $C_{12}H_{20}N_2S_4Cu_3Cl_2$: C, 12.18%; H, 3.46%; N, 4.81%; S, 22.03%; Cu, 32.75%; Cl, 12.18%. Found for Cu(pipdtc)$_2$(CuCl)$_2$: C, 12.40%; H, 3.54%; N, 5.22%; S, 22.07%; Cu, 32.68%; Cl, 12.40%. The structure of this complex is at present unknown.

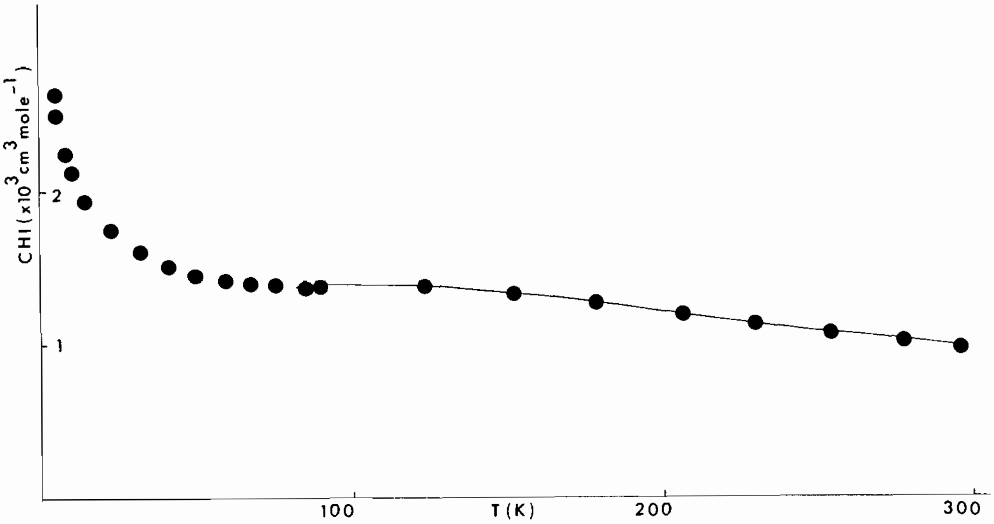

Fig. 2(a). Magnetic susceptibility ($\chi \times 10^3$ cm^3/mole) of Cu(pipdtc)$_2$(CuBr)$_4$ against temperature (▲). Calculated curve for g = 2.05 J = 51 cm^{-1} N_α = 40 × 10^{-6} cm^3/mole is shown by the full line to be compared with the experimental data (●) corrected for paramagnetic impurity, x = 0.03.

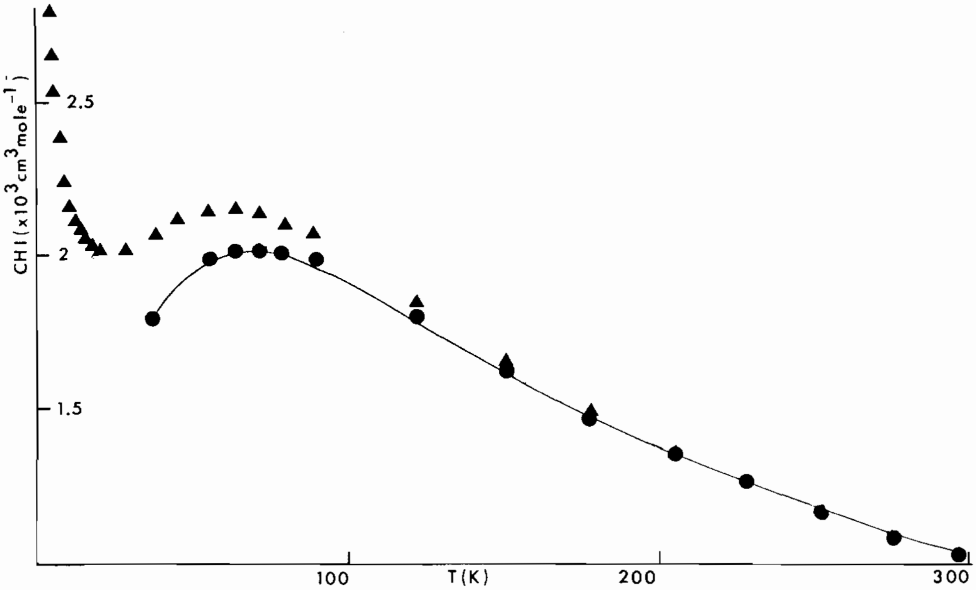

Fig. 2(b). Magnetic suceptibility ($\chi \times 10^3$ cm^3/mole) of Cu(pipdtc)$_2$(CuCl)$_4$ against temperature (●). Calculated curve for g = 2.1, J = 83 cm^{-1} N_α = 40 × 10^{-6} cm^3/mole, x = 0.014 is shown by the full line.

The sheet structure of these complexes suggests that their magnetic behaviour may be explained by the properties of a Heisenberg quadratic layer antiferromagnet [6, 7]. In the case of Cu(pipdtc)$_2$-(CuBr)$_4$ the magnetic susceptibility was fitted, using a nonlinear least squares method, to an expression given by Lines [8] for the susceptibility of a quadratic layer antiferromagnet where g is

$$\chi = Ng^2\beta^2/FxJ \qquad (1)$$

$$F = 3\theta + \sum_{i=1}^{6} C_n/{}^{n-1}, \theta = kT/JS(S+1), S = \tfrac{1}{2}$$

the Zeeman splitting factor and J the isotropic exchange parameter for the Heisenberg isotropic exchange interaction $JS_1 \cdot S_2$. The amount of paramagnetic impurity was estimated to be 3.0% (assuming g = 2.05) [5]. The fitting procedure was used only in the region where the above expansion is valid namely at temperatures greater than kT $\simeq$ 0.9 JS(S + 1) $\simeq$ 50 K [8]. Good agreement was achieved (g =

2.05, J = +51 cm^{-1}) Fig. 2(a), for fits to the experimental data corrected for a Curie Law impurity with g = 2.05.

In contrast it was found more difficult to estimate the amount of paramagnetic impurity in $Cu(pipdtc)_2(CuCl)_4$ as in the region where reasonable estimates could be made the theoretical expression for the Heisenberg sheet was not accurate. From the position of the maximum in the susceptibility curve an estimate of J was made using the formula of Lines $kT_{max}/J = 1.12\ S(S + 1) + 0.1$ and found to be 85 cm^{-1}. Figure 2(b) shows a calculated curve obtained by a least square fit of the experimental data above 80 K to expression (1) including a Curie Law paramagnetic impurity $\chi = x\chi_{impurity} + (1 - x)\chi_{Heis.Sheet}$ using g and J as variable parameters. An initial estimate of the Curie Law impurity was made from the difference between the calculated and observed values of χ at the lowest temperature where the expression (1) was valid and the previously estimated value of J. The amount of impurity was estimated by systematically varying X and performing least squares fits to the data in the region of validity of expression (1) and found to be 1.4 % ± 0.1 whilst the final values of g and J were 2.1 and 83 cm^{-1} respectively. The value of g was found to be higher than that found for the analogous bromide complex and other copper(II) bisdiakyldithiocarbamate complexes [11], where g = 2.05 ± 0.01.

It was not possible to use either of the above procedures to account for the observed susceptibility of $Cu(pipdtc)_2(CuBr)_6$ and only an estimate of J could be made *ca.* 184 cm^{-1}, significantly larger than the $Cu(pipdtc)_2(CuX)_4$ complexes.

The magnitude of the antiferromagnetic exchange interactions (75 cm^{-1}, 51 cm^{-1} and 185 cm^{-1} for $Cu(pipdtc)_2(CuCl)_4$, $Cu(pipdtc)_2(CuBr)_4$ and $Cu(pipdtc)_2(CuBr)_6$ respectively) is unexpected in view of the large distance and multiple atom bridges of the type Cu(II)–S–Cu(I)–X–Cu(I)–S–Cu(II). The magnitudes should be compared with interactions of other typical binuclear and polynuclear copper(II) complexes with sulphur or halide bridges such as the bis(diethyldithiocarbamate)copper(II) dimer (J = 0) [10], the bis(di-n-butyldithiocarbamate) copper(II) dimer (J = 24 cm^{-1}) [13] the sulphur bridged dimer dichloro(1H^+thiocarbonohydrazidium NS) copper(II) chloride (J = 25 cm^{-1}) [12] and the large number of halide bridged copper(II) complexes where antiferromagnetic interactions range from 4 to 20 cm^{-1} for chloride and 20 to 40 cm^{-1} for chloride complexes [13, 14]. Further many multiatom bridged copper(II) complexes show diminished magnitudes of interaction compared with monatomic bridges [15].

The size of the interaction appears to be a combination of the large number of bridges between any two copper(II) ions (four for $Cu(pipdtc)_2(CuX)_4$), leading to a multiplicity of exchange pathways, and the presence of mixed valence copper ions bridged by dithiocarbamate sulphur atoms. Although formally these complexes are type I mixed valence compounds [16] as judged by the differing geometry around the copper(II) and copper(I) ions [1] and the similarity of the Cu(II) $(pipdtc)_2$ geometry to that of other copper(II) dithiocarbamates [17], it is possible that they are of type II with some delocalisation of the unpaired electron from the copper(II) to the copper(I) sites. In the case of copper(II) bisdithiocarbamates there is extensive delocalisation of the unpaired electron onto the dithiocarbamate sulphur ligands [18], the principle components of the HOMO being $0.72\ d_{x^2-y^2} + 0.38\ p_x - 0.37\ p_y$ [18], to facilitate this process.

The extent of type II mixed valence behaviour will depend on the relative energies of the metal 'd orbitals' of each copper(II) site which is determined by the metal ligand interactions [16]. The greater interaction found in the chloride complex $Cu(pipdtc)_2(CuCl)_4$ compared to the analogous bromide may reflect a large mixed valence interaction particularly as the efficiency of superexchange mechanisms involving bromide ligands is in general greater than that of chloride. The increase in interaction in $Cu(pipdtc)_2(CuBr)_6$ may be related to the larger number of links between copper(II) ions.

In conclusion these complexes show that the occurrence of mixed valence metals in extended superexchange pathways of the form Cu(II)–S–Cu(I)–X–Cu(I)–S–Cu(II) can lead enhanced exchange interactions between the paramagnetic ions.

Acknowledgements

We thank The Queen Elizabeth II Fellowships Committee for the award of a Fellowship (to P.D.W.B.) and Mr Peter Barlow for technical assistance.

References

1 R. M. Golding, A. D. Rae, B. J. Ralph and L. Sulligoi, *Inorg. Chem., 13,* 2499 (1974).

2 A. R. Hendrickson, R. L. Martin and D. Taylor, *J. Chem. Soc. Chem. Comm.,* 843 (1975).

3 S. V. Evans, D. J. Mackey and R. L. Martin, *J. Chem. Soc. Dalton Trans.,* 1515 (1976).

4 Landolt-Börstein, Numerical Data and Functional Relationships in Science and Technology, Vol. 2, 'Magnetic Properties of Coordination and Organometallic Transition Metal Compounds', Springer Verlag (1966).

5 A. P. Ginsberg, *Inorg. Chimica Acta, 5,* 45 (1971).

6 L. J. DeJongh and A. R. Miedema, *Adv. Phys., 23,* 1 (1974).

7 R. L. Carlin and A. J. Duyneveldt, 'Magnetic Properties of Transition Metal Complexes', p. 156, Springer Verlag (1977).

8 M. E. Lines, *J. Phys. and Chem. Solids, 31,* 101 (1970).

9 M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, *7*, 2548 (1968).

10 A. J. Duyneveldt, J. A. Van Santen and R. L. Carlin, *Chem. Phys. Letts.*, *13*, 585 (1976).

11 P. D. W. Boyd, S. Mitra, C. L. Raston, G. L. Rowbottom and A. H. White, submitted to *J. Chem. Soc. Dalton Trans.*

12 W. E. Hatfield, H. W. Richardson and J. R. Wasson, *Inorg. Nucl. Chem. Lett.*, *13*, 137 (1977).

13 W. E. Estes, D. P. Gavel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, *17*, 1415 (1978).

14 V. H. Crawford and W. E. Hatfield, *Inorg. Chem.*, *16*, 1336 (1977).

15 'Extended Interactions between Metal Ions in Transition Metal Complexes', ed. L. V. Interrante, *Amer. Chem. Soc. Symp. Ser.*, *no. 5* (1975).

16 M. B. Robin and P. Day, *Adv. Inorg. Nucl. Chem.*, *10*, 247 (1967).

17 For example: $Cu(S_2CNEt_2)_2$; M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Cryst.*, *19*, 886 (1965).

18 C. P. Keijzers and E. de Boer, *Mol. Phys.*, *6*, 1743 (1975).