Spin–Spin Interactions in the Paired Binuclear Cluster Tetrakis[μ-chloro-diethyldithiocarbamatocopper(II)]

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The magnetic susceptibility as a function of temperature between 4.2 and 300 K has been determined for the new tetrameric complex $[\{CuCl(S_2CNEt_2)\}_4]$. On the basis of the known *X*-ray crystal structure, it is shown that the susceptibility can be interpreted in terms of three isotropic-exchange interactions acting between each of the four copper(II) ions. It is established that the principal effect of the interdimer exchange interaction is to lift the degeneracy of the two triplet-spin levels which characterise a pair of non-interacting dimers.

RECENTLY it has been found that the reaction between $[Cu(S_2CNEt_2)_2]$ and $CuCl_2{\cdot}2H_2O$ in refluxing ethanol yields the μ-chloro-bridged dimer $[\{CuCl(S_2CNEt_2)\}_2]$ (Cu–Cu 3.348 Å) together with a very small quantity of a mixed-valence copper(II)–copper(I) reduction product $[Cu_3Cl_3(S_2CNEt_2)_2]$.[1] A single-crystal *X*-ray study of the main reaction product has established that the symmetrical chloro-bridged dimers are weakly associated through intermolecular Cu–Cl (2.874 Å) and Cu–S (2.882 Å) interactions to yield discrete centrosymmetric tetrameric units (Figure 1). Each copper atom is essentially five-co-ordinate (approximately square-based pyramid) as is found in the structure of the parent $[Cu(S_2CNEt_2)_2]$. This form of association is known for several planar binuclear copper(II) complexes [2] and leads to an increase in the co-ordination number about the metal atom from four to five.

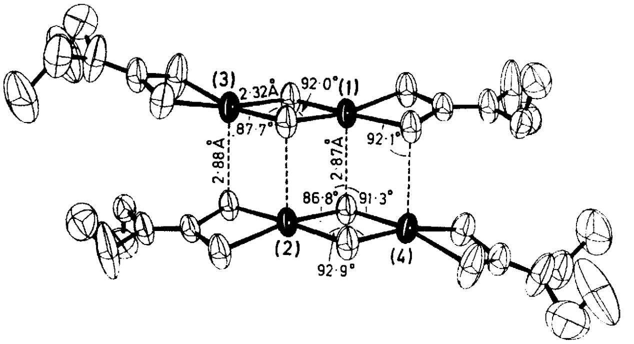

FIGURE 1 The structure of $[\{CuCl(S_2CNEt_2)\}_2]$

This class of tetrameric cluster, with four metal atoms lying at the apices of a parallelogram, provides an opportunity to compare both the signs and magnitudes of the intramolecular-exchange coupling constants which characterise spin–spin interactions in the molecule. Accordingly, the magnetic properties of $[\{CuCl(S_2CNEt_2)\}_2]$ have been measured in the temperature range 4.2—300 K and the susceptibilities analysed in terms of an isotropic-exchange interaction between each of the four copper(II) atoms.

EXPERIMENTAL

The complex was prepared as described previously.[1] Susceptibilities were measured on a Faraday balance described elsewhere.[3] Corrections for diamagnetism of the ligands and metal ion were made using Pascal's constants.[4]

RESULTS

The measured inverse susceptibility (χ^{-1}) and average magnetic moment ($\mu_{eff.}$) per Cu atom are shown as a function of temperature in Figure 2. The magnetic moment decreases from a value of 1.63 B.M. at 300 K to the value of 0.35 B.M.† at 10 K and then remains independent of temperature from 10 to 4.2 K. The linear low-temperature part of the plot of inverse susceptibility against temperature establishes quite clearly the presence of a paramagnetic impurity. Attempts to remove the impurity by recrystallisation were unsuccessful because some decomposition of the tetramer always occurs in solution.

The *X*-band e.s.r. spectrum of the same sample at room temperature consisted of a broad signal centred on *g ca.* 2 with evidence of another superimposed signal which disappeared on cooling to 77 K leaving the broad line (width *ca.* 3 000 G). On further cooling to 4.2 K the broad signal disappeared and a weak signal appeared. This new signal is not due to the tetramer for on cooling below 4.2 K its intensity increased. The method for preparing the tetramer suggests that the most likely paramagnetic impurity is the parent $[Cu(S_2CNEt_2)_2]$. Indeed, the signal observed at 4.2 K is very similar to the perpendicular part of the doublet spectrum of Cu^{2+} in the parent $[Cu(S_2CNEt_2)_2]$.[5]

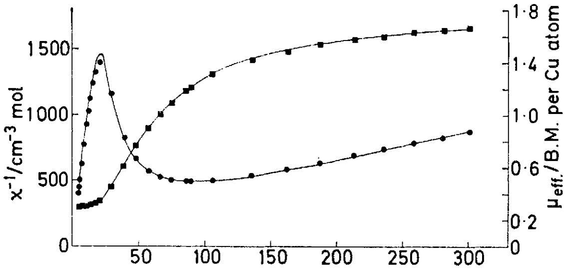

FIGURE 2 Temperature dependence of magnetic susceptibility (●, χ^{-1}) and magnetic moment (■, $\mu_{eff.}$) of $[\{CuCl(S_2CNEt_2)\}_4]$. Experimental points are compared with values (full lines) calculated from equation (2) with $g = 2.02$, $2J_{12} = -55$, $2J_{14} = 22$, $2J_{13} = -104$ cm^{-1}, and $x = 0.028$

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† Throughout this paper: 1 G = 10^{-4} T; 1 B.M. ≈ 9.27×10^{-24} A m^2.

[1] A. R. Hendrickson, R. L. Martin, and D. Taylor, *J.C.S. Chem. Comm.*, 1975, 843.

[2] See, for example, J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 203.

[3] D. J. Mackey, S. V. Evans, and R. L. Martin, *J.C.S. Dalton*, 1976, 1515.

[4] F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metal Complexes,' Chapman and Hall, London, 1973.

[5] W. E. Hatfield and J. F. Villa, *Inorg. Chim. Acta*, 1971, **5**, 145.

THEORY AND CALCULATIONS

For a tetramer of this type, the isotropic HDVV exchange Hamiltonian may be written as in (1). The four $s = \frac{1}{2}$ ions

$$\mathscr{H} = -2J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2 - 2J_{13}(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) - 2J_{14}(\mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_2 \cdot \mathbf{S}_3) - 2J_{34}\mathbf{S}_3 \cdot \mathbf{S}_4 \quad (1)$$

couple to give states of total spins $S = 0,0,1,1,1,$ and 2. Hatfield and Inman [6] and Sinn [7] calculated the eigenvalues for the case $s_1 = s_2 = s_3 = s_4 = \frac{1}{2}$, and Griffith [8] reported a general formulation for a tetramer of interacting ions of any spin within the Heisenberg–Dirac–Van Vleck Hamiltonian. We evaluated the eigenvalues of (1) using the method suggested by Hatfield and Inman.[6] The susceptibility can be calculated using the Van Vleck formula [9] where E^i are numerically obtained eigenvalues from the matrix given by

$$\chi = \frac{N\beta^2 g^2}{4kt} \cdot \frac{F}{G} + \text{t.i.p.} \quad (2)$$

$$F = 10\exp\{[(K/2) + N]/kT\} + 2\exp\{[(K/2) - N]/kT\} + 2\exp\{[(-K/2) + (L^2 + M^2)^{\frac{1}{2}}]/kT\} + 2\exp\{[(-K/2) - (L^2 + M^2)^{\frac{1}{2}}]kT\}$$

$$G = 4\exp\{[(K/2) + N]/kT\} + 2\exp\{[(K/2) - N]/kT\} + 3\exp\{[(-K/2) + (L^2 + M^2)^{\frac{1}{2}}]/kT\} + 3\exp\{[(-K/2) - (L^2 + M^2)^{\frac{1}{2}}]/kT\} + \sum_{i=1}^{4}\exp(-E^i/kT)$$

Hatfield and Inman [6] and $K = J_{12} + J_{34}$, $L = J_{14} - J_{13}$, $M = J_{12} - J_{34}$, and $N = J_{14} + J_{13}$.* The temperature-independent paramagnetism (t.i.p.) was taken as 60×10^{-6} cm^3 mol^{-1} per Cu atom. The Cu–Cu separation between atoms 3 and 4 is very large (6.128 Å) and, since there is no superexchange path which does not involve a third copper atom, we assumed in all the calculations that J_{34} is zero.

The experimentally observed susceptibility of $[\{CuCl(S_2CNEt_2)\}_4]$ is described by equation (3) where χ_{tet} is the

$$\chi_{obs.} = (1 - x)\chi_{tet} + x\chi_{mon} \quad (3)$$

tetramer susceptibility given by equation (2) and χ_{mon} is the susceptibility of a monomeric copper(II) complex [9] assumed to have a molecular weight of one quarter of that of the tetramer. We assumed that χ_{mon} is described by the Curie Law with g values the same as for the dimeric parent. This leaves as a parameter the mol fraction x of paramagnetic impurity which can be well determined from the low-temperature behaviour of $\chi_{obs.}$; χ_{mon} is also corrected for the t.i.p. of the copper atom of 60×10^{-6} cm^3 mol^{-1}.

The experimental susceptibilities were fitted to both the dimer and tetramer models by a least-squares procedure as a function of g, J, and mol fraction of paramagnetic impurity x. When a dimer model was assumed with the 'interdimer' interactions J_{12}, $J_{14} = J_{23}$ set to zero, the parameters $g = 1.98$, $2J_{13} = 2J_{24} = -102.0$ cm^{-1}, and $x = 0.030$ were obtained. However, when the 'interdimer' interactions were introduced the sum of squares $\Sigma(\chi_{calc.} - \chi_{obs.})^2$ decreased by a factor of six to give best fit values of $g = 2.02$, $2J_{12} = -55$ cm^{-1}, $2J_{14} = 22$ cm^{-1}, $2J_{13} = -104$ cm^{-1}, and $x = 0.028$. Although the magnitude of the principal exchange interaction J_{13} is not altered significantly, the inclusion of the two 'interdimer' parameters clearly improved the fit and gave a physically reasonable g value (Table 1).

TABLE 1

Calculated and observed susceptibilities ($\times 10^{-6}$ cm^3 mol^{-1}) for $[\{CuCl(S_2CNEt_2)\}_4]$ [a]

T/K	4.20	4.80	5.63	7.04	8.80	10.48	11.96	13.68	15.53	17.39
$\chi_{obs.}$	2 557	2 268	1 966	1 612	1 289	1 084	978	885	810	758
$\chi_{calc.}$ [b]	2 613	2 295	1 963	1 582	1 279	1 084	959	852	772	721
T/K	20.8	29.5	38.6	47.8	57.1	66.0	74.6	85.3	89.5	105.9
$\chi_{obs.}$	718	856	1 188	1 514	1 763	1 916	1 998	2 037	2 042	2 006
$\chi_{calc.}$ [b]	690	864	1 200	1 515	1 754	1 906	1 992	2 037	2 042	2 011
T/K	135.4	162	187	212.9	235.3	258.1	280.2	300.5		
$\chi_{obs.}$	1 857	1 701	1 567	1 443	1 350	1 272	1 204	1 148		
$\chi_{calc.}$ [b]	1 864	1 708	1 572	1 446	1 349	1 262	1 187	1 125		

[a] To convert into S.I. units χ should be multiplied by $4\pi \times 10^{-6}$ and the magnetic moment is then given by the expression $\mu = 797.74\,(\chi T)^{\frac{1}{2}}$. [b] Calculated for g 2.02, $J_{12} = -27.5$ cm^{-1}, $J_{14} = 11.2$ cm^{-1}, $J_{13} = -52.4$ cm^{-1}, and $x = 0.028$.

Since there have been previous criticisms of the validity of the tetramer model,[10] it was decided to investigate in detail the goodness of fit in multiparameter space. The g value of 2.02 obtained from the least-squares minimisation procedure was lower than anticipated even though at the highest temperatures this corresponded to the gradient of the plot of χ^{-1} against T in the uncoupled limit. In order to further investigate the effect of g on the quality of fit, minimisations were made for various fixed values of g. It was found that as g was increased in value the sum of squares increased significantly; for example, the sum increased by a factor of 3 if $g = 2.06$. No significant correlation was found between the exchange parameters after computation of contour maps of $(\chi_{calc.} - \chi_{obs.})^{-2}$ for a large range of exchange-parameter values, the maps showing a unique fit of the model to the experimental data. Accordingly we have some confidence in the values of the exchange parameters for this model.

DISCUSSION

An interesting and unexplained feature of the magnetic properties exhibited by tetranuclear copper(II) complexes of this type is the relative insensitivity of the magnitude of the principal exchange interaction J_{13} to the model (*i.e.* dimer against tetramer) on which the calculations are based. The origin of this behaviour emerges from a consideration of the energy-level scheme for two non-

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* The denominator G given in ref. 6 is in error and requires a factor of 2 in the second exponential term.

[6] W. E. Hatfield and G. W. Inman, *Inorg. Chem.*, 1969, **8**, 1376.

[7] E. Sinn, *Co-ordination Chem. Rev.*, 1970, **5**, 313.

[8] J. S. Griffith, *Mol. Phys.*, 1973, **24**, 833.

[9] K. E. Hyde, G. Gordon, and G. F. Kokoska, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2155.

[10] E. Sinn, *Inorg. Chem.*, 1970, **9**, 2376.

interacting copper(II) dimers compared with that for a single dimer (*cf.* Figure 3). The 16-fold degeneracy is lifted partly to yield three sets of levels at energies $3J_{13}$, J_{13}, and $-J_{13}$ corresponding to $S = 0$; 1,1; and 2,1,0 respectively. In this situation the susceptibility expression (2) reduces to that for two copper dimers as expected. The predominant effect of introducing interdimer interactions is to split the two triplet states lying at J_{13} leaving the remaining two sets of levels virtually unaffected. When this splitting is large the susceptibility of the tetramer should conform reasonably well to singlet–triplet behaviour especially at lower temperatures. Since the degenerate pair of levels at J_{13} are both triplets, the magnetic susceptibility should be sensitive to the magnitudes of interdimer-exchange interactions J_{12} and J_{23} but not to their sign.

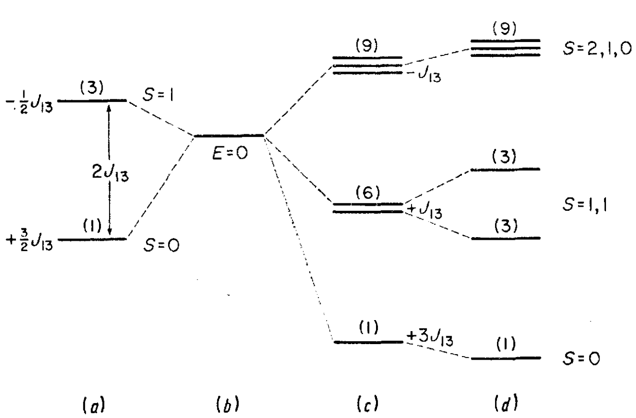

FIGURE 3 Energy-level scheme for the copper(II) tetramer: (*a*) singlet–triplet levels for a single Cu_2 dimer; (*b*) arbitrary zero energy; (*c*) energy levels for two non-interacting Cu_2 dimers; (*d*) effect of interdimer Cu_2–Cu_2 interaction

The magnitudes of isotropic-exchange integrals for the various paths in $[\{CuCl(S_2CNEt_2)\}_4]$ reveal that there is a principal intradimer antiferromagnetic interaction ($2J_{13}$ -104 cm^{-1}) between copper atoms (1) and (3) and (2) and (4) in the dichloro-bridged dimers, a smaller interdimer antiferromagnetic interaction ($2J_{12}$ -55 cm^{-1}) between copper atoms (1) and (2) which are bridged by two chlorine atoms, and an interdimer ferromagnetic interaction ($2J_{14}$ 22 cm^{-1}) between copper atoms (1) and (4) and (2) and (3) bridged by one chlorine and one sulphur atom. The major interaction $J_{13} = J_{24}$ is large compared with exchange constants found in other di-μ-chloro-copper(II) dimers (Table 2). The lack of correlation between the magnitude and sign of the interaction with the Cu–Cl–Cu bond angles is contrary to the results of recent calculations.[11,12] However, the variations in co-ordination numbers and geometries about the individual copper(II) atoms in the tabulated complexes impose differences in electronic structures on the ground and excited states. In these circumstances exchange interactions of varying signs and magnitudes, for even the same Cu–Cl–Cu angles, are not unexpected.

The difference between the dichloro-bridged interaction J_{12} and the mixed chlorine–sulphur-bridged interaction J_{14} is, at first sight, unusual, for the symmetry properties of the orbitals involved in the two exchange paths appear to be reasonably similar. Closer examination of the structure of $[\{CuCl(S_2CNEt_2)\}_4]$ shows that the dichloro-bridged interaction J_{12} occurs between copper atoms with the same co-ordination environment, namely a dithiocarbamate chelate and three chlorine atoms. On the other hand, the ferromagnetic interaction J_{14} occurs between copper atoms with different co-ordination environments. In this case, the second copper atom is chelated by a dithiocarbamate ligand, two chlorine atoms, and a sulphur atom from another chelate. Clearly the electronic structure of the ground and excited states of the two types of copper atoms will be different. Furthermore, Villa and Hatfield[13] reported a ferromagnetic interaction of 24 cm^{-1} in dimeric $[\{Cu(S_2CNEt_2)_2\}_2]$ where two planar $Cu(S_2CNEt_2)_2$ chelates are weakly associated through the dithiocarbamate sulphur atoms in a manner similar to that found in $[\{CuCl(S_2CNEt_2)\}_4]$. However, recent measurements by Van Duyneveldt *et al.*[14] suggest that this exchange interaction in $[\{Cu(S_2CNEt_2)_2\}_2]$ is less than 1 cm^{-1}. Thus it appears that these two factors, *i.e.* the difference in co-ordination geometry about the individual copper atoms and the observed small and possibly ferromagnetic interaction *via* sulphur in $[\{Cu(S_2CNEt_2)_2\}_2]$, lead to the opposite signs for J_{12} and J_{14}.

TABLE 2

Exchange constants of some dichloro-bridged copper(II) complexes

Complex	$2J$/cm^{-1}	Cu–Cl–Cu	Ref.
$[Cu_2Cl_6]^{2-}$	36	93.7	*a*
$[\{CuCl_2(dmg)\}_2]$ [b]	6.3	88	*c*
$[\{CuCl_2(2Me\text{-}py)\}_2]$ [d]	7.4	101.4	*e*
$[Cu_2Cl_8]^{4-}$	−14.6	95.2	*f*
$[\{CuCl_3(gnd)\}_2]$ [g]	−82.6	98	*h*
$[\{CuCl(S_2CNEt_2)\}_4]$	−55	86.8	*i*
	−104	92.9	*i*

[a] C. Chow and R. D. Willett, *J. Chem. Phys.*, 1973, **59**, 5903. [b] dmg = Dimethylglyoximato(2−). [c] N. T. Watkins, E. D. Dixon, V. H. Crawford, K. T. McGregor, and W. E. Hatfield, *J.C.S. Chem. Comm.*, 1973, 133. [d] 2Me-py = 2-Methylpyridine. [e] D. Y. Yeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chim. Acta*, 1971, **5**, 257. [f] K. T. McGregor, D. B. Losee, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1974, **13**, 756. [g] gnd = Guanidinium. [h] R. F. Drake, V. H. Crawford, N. W. Lang, and W. H. Hatfield, *Inorg. Chem.*, 1974, **13**, 1246. [i] This work.

The superexchange paths involving the chlorine atoms must involve both *s* and *p* orbitals of the ligand. An important difference from the binuclear complexes (Table 2) is that the chlorine atoms here are bonded simultaneously to three metal atoms instead of two, a factor which must change the hybridisation of the orbitals on the chlorine atom from that found in binuclear complexes. From

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[11] K. Arundel and C. G. Barraclough, R.A.C.I. Symp. Magnetism and Transition-metal Compounds, 1975, Monash University.

[12] P. J. Hay, J. C. Thibeauld, and R. Hoffman, *J. Amer. Chem. Soc.*, 1975, **97**, 4884.

[13] J. F. Villa and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 2038.

[14] A. J. Van Duyneveldt, J. A. Van Santen, and R. L. Carlin, *Chem. Phys. Letters*, 1976, **38**, 585.

orbital-symmetry considerations, ferromagnetic-exchange paths[15] between atoms (1) and (3) [(2) and (4)] can be found, *viz.* $(x^2 - y^2)_1 \| p_x \perp p_y \| (x^2 - y^2)_3$. The principal antiferromagnetic paths are $(x^2 - y^2)_1 \| s \| (x^2 - y^2)_3$ and $(z^2)_1 \| s \| (z^2)_3$. In this case, the antiferromagnetic paths are predominant as they are in the interaction between atoms (1) and (2) where the paths such as $(x^2 - y^2)_1 \| s \| (z^2)_2$ led to spin pairing. Paths such as $(x^2 - y^2)_1 \| p_x \perp p_z \| (z^2)_2$ are ferromagnetic. In the mixed chlorine–sulphur-bridged copper atoms it appears that the ferromagnetic path involving sulphur such as $(x^2 - y^2)_1 \| p_y \perp p_z \| (z^2)_4$ is particularly important. In this case, however, the orbital energies at each copper centre are different due to the dissimilar co-ordination environments. This could lead to a varying importance of the paths due to the change in U in superexchange terms of the form b^2/U, where U is the excitation energy of a metal or ligand electron from a metal or ligand orbital to a ligand or metal orbital.[16]

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[15] A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.

[16] J. P. Goodenough, 'Magnetism and the Chemical Bond,' Interscience, New York, 1963.