Magnetic Properties and Superexchange in Single Chloride-bridged Copper(II) Chain Compounds

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Magnetic susceptibility data have been measured in the temperature range 1.75 to 60 K for the following structurally characterized, single chloride-bridged copper(II) chain compounds: dichlorobis(dimethyl sulphoxide)copper(II), dichlorobis(imidazole)copper(II), aquo(caffeine)dichlorocopper(II), and dichloro[2-(2′-methylaminoethyl)-pyridine]copper(II). The first two compounds exhibit antiferromagnetic intrachain interactions with exchange coupling constants of −6.1 and −2.1 cm^{-1}, respectively, while the second two compounds exhibit ferromagnetic interactions with J values of 0.48 and 1.58 cm^{-1} respectively. Except for dichlorobis(imidazole)copper(II), which undergoes long-range magnetic ordering below 7.7 K, the exchange coupling constants become more negative as the angle at the chloride bridge increases from 113.6° in dichloro[2-(2′-methylaminoethyl)pyridine]-copper(II) to 144.6° in dichlorobis(dimethyl sulphoxide)copper(II).

CURRENT research activity on the structural and magnetic properties of low-dimensional transition-metal compounds is aimed toward an understanding of the structural and chemical features which govern magnetic dimensionalities and the signs and magnitudes of exchange coupling constants. Hatfield and co-workers [1] have shown that the angle at the bridging oxygen atom determines the value of the exchange coupling constant, J, in a series of di-μ-hydroxo-bridged copper(II) compounds. In this series of compounds all spectator ligands are co-ordinated through nitrogen-donor atoms, the copper–nitrogen bond distances are all nearly equal, the copper–oxygen bond distances are essentially equal (±0.03 Å), and the $N_2CuO_2CuN_2$ structural units are approximately planar. The only structural feature that varies is the angle at the bridge and it is reasonable to conclude that this angle determines the sign and magnitude of the exchange coupling constant in this series of compounds. The results of recent studies [2-5] on di-μ-halogeno-bridged chain compounds have shown that both the geometry of the bridge as well as the geometry of the spectator ligands influence the exchange coupling constants. However, studies [6] on a series of di-μ-chloro-bridged nickel(II) dimeric compounds revealed that neither the bridge angle nor the Ni–Cl bridge bond distances dominate the superexchange interactions. For this series of compounds the co-ordination geometry about the nickel(II) ion, and thus the relative orientation of the d orbitals on the nickel ion, appears to determine the nature of the superexchange interactions.

As a part of our research programme, which is devoted to the determination of the relationship between the value of the exchange coupling constant and the geometry (bond angles, bond distances, and bridging ligands) of the superexchange pathway, we have measured the magnetic susceptibility of $Cu(dmso)_2Cl_2$ (dmso = dimethyl sulphoxide),[7,8] $Cu(imH)_2Cl_2$ (imH = imidazole),[9] $Cu(caf)(OH_2)Cl_2$ (caf = caffeine),[10] and $Cu(maep)Cl_2$ [maep = 2-(2′-methylaminoethyl)pyridine],[11] and have determined the exchange coupling constants. The results of our studies on these single chloride-bridged copper(II) chain compounds are described in this paper.

EXPERIMENTAL

Samples of $Cu(dmso)_2Cl_2$ and $Cu(imH)_2Cl_2$ [9] were prepared as described in the literature. Single crystals of $Cu(caf)(OH_2)Cl_2$ were provided by Professor M. Cingi and a powdered sample of $Cu(maep)Cl_2$ was generously donated by Dr. R. B. Wilson.

Magnetic susceptibilities were measured on powdered samples in the temperature range 1.75 to 60 K using Princeton Applied Research vibrating sample magnetometers. The details of magnetic data collection, temperature measurement, and data analysis have been described fully elsewhere.[1,3]

RESULTS

Magnetic susceptibility data were reported [8] in 1971 for $Cu(dmso)_2Cl_2$. For the purposes of this work, a new data set was collected. The new data, which are in good agreement with the 1971 data, are given in Figure 1, where a broad maximum in magnetic susceptibility near 14 K may be seen. The broad maximum is indicative of antiferromagnetically coupled copper(II) ions, and the temperature variation of the magnetic susceptibility may be described by the Heisenberg model of isotropic antiferromagnetic exchange coupling. Within this model the Hamiltonian is $\mathscr{H} = -2J\Sigma\hat{S}_i \cdot \hat{S}_j$. Bonner and Fisher [12] have carried out machine calculations on short chains and rings and extrapolated their results to the limit of an infinite chain. Their results, which were presented in graphical form, have been used widely for the analysis of the magnetic properties of chains of $S = \frac{1}{2}$ ions. Since an exact expression for the magnetic susceptibility of an infinite chain has not been derived, Jotham [13] and Hall [14] have developed polynomial expressions which describe the results of Bonner and Fisher [12] very well. The advantage of these polynomials lies in the fact that they permit data analysis using computer programs. The polynomial derived by Jotham [13] is given in (1) where $P = kT/|2J|$, while that developed by Hall [14] is given in (2) where $x = kT/|J|$. The solid line in Figure 1 is the best fit of equation

(2) to the data with the magnetic parameters $J = -6.1$ cm^{-1} and $g = 2.11$, where the criterion for the best fit is

$$\chi_m = \frac{Ng^2\beta^2}{|2J|}(0.092\,281 + 0.186\,1P - 0.205\,56P^2 + 0.074\,679P^3 - 0.009\,180\,8P^4) \qquad (1)$$

$$\chi = \frac{Ng^2\beta^2}{kT} \cdot \frac{0.250 + 0.149\,95x^{-1} + 0.300\,94x^{-2}}{1 + 1.986\,2x^{-1} + 0.688\,54x^{-2} + 6.062\,6x^{-3}} \qquad (2)$$

that set of parameters which gives the minimum value of the function $\sum(\chi_i^{obs.} - \chi_i^{calc.})/(\chi_i^{obs.})$ using a non-linear Simplex fitting routine. A like fit is obtained using equation (1).

Magnetic susceptibility data for $Cu(imH)_2Cl_2$ were reported[4] in 1978. Since it was not possible to analyze the data using either Heisenberg or Ising theory, a new, more extensive data set was collected for the purposes of this study. The data for $Cu(imH)_2Cl_2$, which are given in Figure 2, have features which reflect antiferromagnetic intrachain interactions, and which suggest three dimensional ordering below 7.7 K. The data above 12 K may be described very accurately by equation (2) with $J = -2.1$ cm^{-1} and $g = 2.07$. As may be seen in Figure 2, below 12 K the experimental data deviate from the calculated line, being less than the calculated values. The magnetic susceptibility reaches a maximum at 7.7 K and appears to approach a non-zero value as the temperature approaches zero. This zero temperature limiting value of the magnetic susceptibility is about two-thirds of the maximum value, a magnitude expected for a typical antiferromagnetically ordered substance. In addition, the magnetization of the material is field dependent at 4.2 K, a property expected of an ordered material. Unfortunately, it has not been possible to obtain large enough single crystals of this compound, and therefore we are unable to characterize the ordered state.

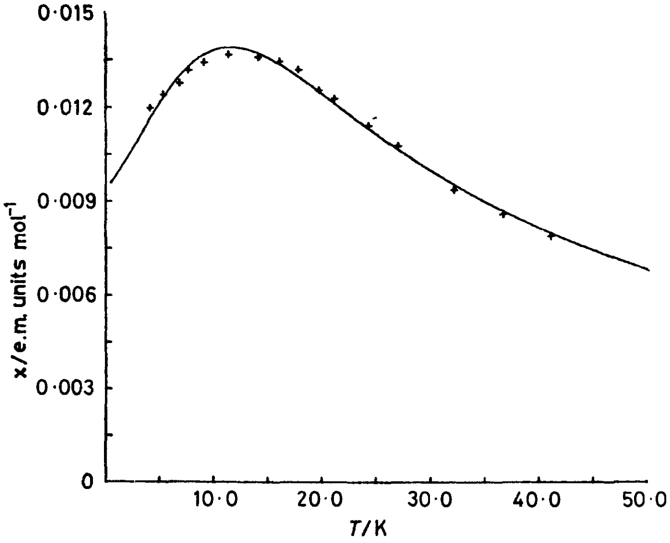

FIGURE 1 Magnetic susceptibility data for $Cu(dmso)_2Cl_2$. The solid line is the best fit of the Heisenberg chain model to the experimental data with $J = -6.1$ cm^{-1} and $g = 2.11$

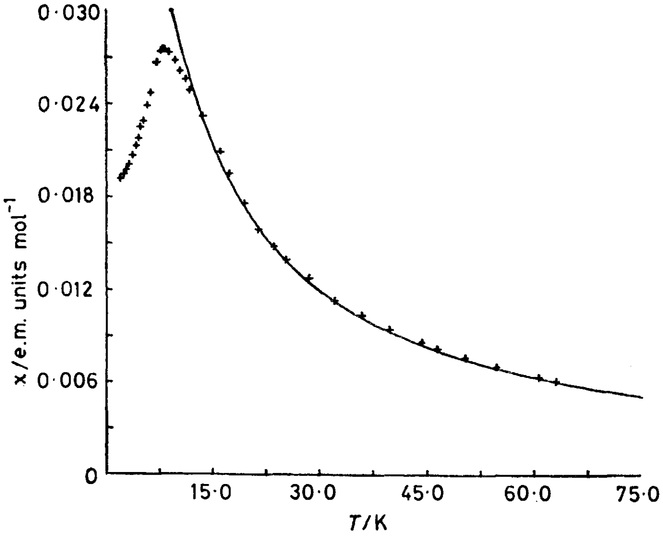

FIGURE 2 Magnetic susceptibility data for $Cu(imH)_2Cl_2$. The solid line is the best fit of the Heisenberg chain model to the experimental data with $J = -2.1$ cm^{-1} and $g = 2.07$. Note the typical three-dimensional antiferromagnetic behaviour below 7.7 K

Magnetic susceptibility data for $Cu(caf)(OH_2)Cl_2$ and $Cu(maep)Cl_2$ are given in Figures 3 and 4, respectively. These data may be described by the series expansion for the Heisenberg model for ferromagnetically coupled $S = \frac{1}{2}$ ions which was derived by Baker *et al.*[15] The expansion is given here as equation (3) where $K = J/2kT$. The best fit

$$\chi_m = \frac{Ng^2\mu_B{}^2}{4kT}[(1 + 5.797\,991\,6K + 16.902\,653K^2 + 29.376\,885K^3 + 29.832\,959K^4 + 14.036\,918K^5)/(1 + 2.797\,991\,6K + 7.008\,678\,0K^2 + 8.653\,864\,4K^3 + 4.574\,311\,4K^4]^{\frac{2}{3}} \qquad (3)$$

of equation (3) to the data for $Cu(caf)(OH_2)Cl_2$ yields $J = 0.48$ cm^{-1} and $g = 2.13$, while the best fit of the equation to the data for $Cu(maep)Cl_2$ yields $J = +1.58$ cm^{-1} and $g = 2.14$.

DISCUSSION

The four compounds under consideration in the present work all have the single chloride-bridged structure shown

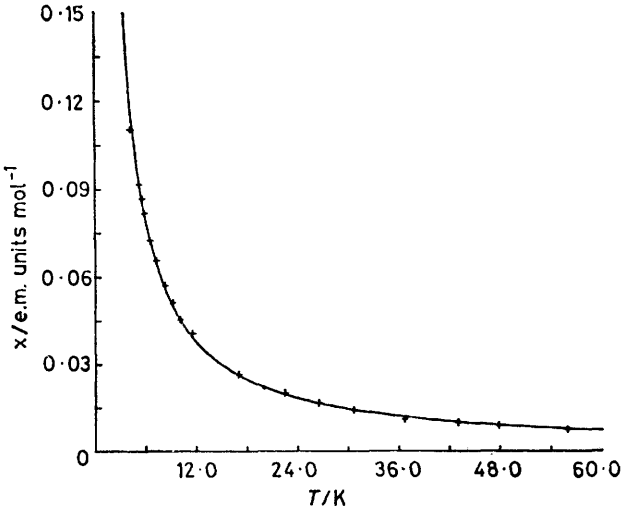

FIGURE 3 Magnetic susceptibility data for $Cu(caf)(OH_2)Cl_2$. The solid line is the best fit of the ferromagnetic Heisenberg chain model to the experimental data with $J = 0.48$ cm^{-1} and $g = 2.13$

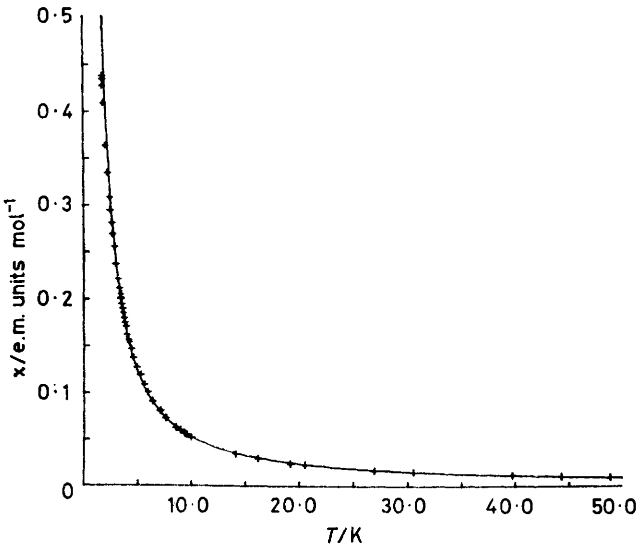

FIGURE 4 Magnetic susceptibility data for Cu(maep)Cl_2. The solid line is the best fit of the ferromagnetic Heisenberg chain model to the experimental data with $J = 1.58$ cm^{-1} and $g = 2.14$

in Figure 5. In all of the compounds the co-ordination around the copper(II) ions is approximately tetragonal pyramidal, with the base of the pyramids being formed by two donor atoms from the non-chloride spectator ligands and two chlorides, while the axial site is occupied by a chloride from an adjacent unit. The chain is propagated through the sharing of this single chloride ion. The pyramidal bases are not exactly planar, and the distortion from planarity increases in the order Cu(imH)$_2$Cl$_2$ $\sim$ Cu(maep)Cl$_2$ $<$ Cu(caf)(OH$_2$)Cl$_2$ $<$ Cu(dmso)$_2$Cl$_2$. The deviations from planarity are clearly reflected in the *trans* L–Cu–L′ angles. These angles would be 180° for planar bases of the tetragonal pyramids. The *trans* L–Cu–L′ angles are given in Table 1. The deviation from planarity is so great in Cu(dmso)$_2$Cl$_2$ that a description of the structure in terms of a trigonal bipyramid must also be considered. Willett and Chang [7] however have argued convincingly against the trigonal-bipyramidal description and have cited structural, spectral, and e.s.r. evidence which are consistent with a tetragonal-pyramidal description.

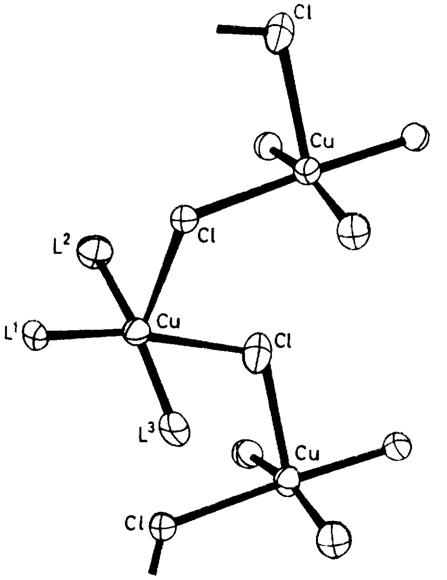

FIGURE 5 Schematic illustration of the single chloride-bridged copper(II) chain compounds under investigation. L¹, L², L³ represent the non-bridging ligands and chloride ions

The co-ordination geometry of the copper(II) ions in Cu(dmso)$_2$Cl$_2$ is similar to that seen in the $Cu_2Cl_8^{4-}$ dimeric unit in [Co(en)$_3$]$_2$[Cu$_2$Cl$_8$]Cl$_2$·2H$_2$O (en = ethylenediamine),[16] where there is a comparable problem concerning the description of the structure. However, single-crystal e.s.r. results [17] for $Cu_2Cl_8^{4-}$ show that the ground state is predominantly $d_{x^2-y^2}$, and confirm the tetragonal-pyramidal description. The discussion of structural effects on exchange coupling in this series of single chloride-bridged chains will be presented in terms of the tetragonal-pyramidal geometry, but it must be recognized that the symmetry of the co-ordination environment is very low in all of the compounds, and that extensive mixing of the *d* orbitals occurs.

TABLE 1

trans L–Cu–L′ angles in the single chloride-bridged copper chain compounds

Compound	Angle	Value/°	Ref.
Cu(dmso)$_2$Cl$_2$	O(5)–Cu–O(5)	173.01(26)	7
	Cl(2)–Cu–Cl(3)	146.13(9)	
Cu(imH)$_2$Cl$_2$	N(1)–Cu–N(3)	174.3(10)	9
	Cl(1)–Cu–Cl(2)	166.9(3)	
Cu(caf)(OH$_2$)Cl$_2$	N(9)–Cu–O(10)	161.0(4)	10
	Cl(1)–Cu–Cl(2)	178.8(1)	
Cu(maep)Cl$_2$	N(1)–Cu–Cl(2)	165.7(1)	11
	N(2)–Cu–Cl(1)	176.0(2)	

The interatomic bond distances, bond angles, and exchange coupling constants which are important for this discussion are collected in Table 2. Since there is no correlation of J with the copper–copper separation, a through-space mechanism for exchange coupling can be eliminated, and more reasonable superexchange mechanisms may be considered. Except for Cu(imH)$_2$Cl$_2$, the exchange coupling constant becomes more negative as the angle at the chloride bridge increases. This is the expected behaviour in the angular dependence if the chloride-ion *s*-orbital contribution to the covalent bridge bonding is considered as the dominating influence for large angles about the bridging atom. In this context it is important to note that Ritter and Jansen [18] have shown that model calculations using spherically symmetric Gaussian wave functions for the unperturbed atomic orbitals predict a reversal of the sign of the coupling constant over a range of bridge angles between $80 < \phi < 120°$. Although these calculations using non-directional magnetic ion and intervening bridge-ion orbitals are difficult to apply directly to our low-symmetry experimental results, the results are generally consistent with our observations. Additionally, Hay *et al.*[19] have used a molecular-orbital argument to show that the exchange coupling constant in the hypothetical dimer, Cl$_4$Cu–Cl–CuCl$_4$, will show a larger negative value as the distortion proceeds from tetragonal-pyramidal geometry toward trigonal-bipyramidal geometry. During this process the metal-ion d_{z^2} orbitals become oriented in such a manner as to permit more efficient overlap with the bridging chloride s_z and p_z orbitals.

TABLE 2

Structural and magnetic parameters for single chloride-bridged copper(II) chain compounds

Compound	J/cm^{-1}	Cu–Cl$_{b,l}$/Å [a]	Cu–Cl$_{b,s}$/Å [b]	Cu–Cu/Å	Cu–Cl$_b$–Cu/°	Ref.
Cu(dmso)$_2$Cl$_2$	−6.1	2.702(2)	2.290(2)	4.757(2)	144.6(1)	7, 8
Cu(imH)$_2$Cl$_2$	−2.1	2.751(6)	2.365(4)	4.37(?)	117(?)	4, 9
Cu(caf)(OH$_2$)Cl$_2$	0.48	2.788(2)	2.319(2)	4.597(2)	128.1(?)	10
Cu(maep)Cl$_2$	1.58	2.785(2)	2.300(2)	4.263(2)	113.58(5)	11

[a] Cu–Cl$_{b,l}$ is the long copper–chloride bridge distance. [b] Cu–Cl$_{b,s}$ is the short copper–chloride bridge distance.

This mechanism provides a basis for the understanding of the largest J value, which is found in the Cu(dmso)$_2$Cl$_2$ complex. The basal plane in Cu(dmso)$_2$Cl$_2$ is severely distorted toward trigonal-bipyramidal geometry.

It is of interest to compare the angles between the best least-squares planes of the tetragonal pyramids with the Cu–Cl$_b$–Cu angles. These least-squares planes are probably a good approximation of the planes in which the unpaired σ^* electrons reside. In Cu(dmso)$_2$Cl$_2$ the angle between the planes is 137.14° while the Cu–Cl$_b$–Cu angle is 144.6°. The somewhat greater bond angle results from the severe distortion of the basal plane in Cu(dmso)$_2$Cl$_2$, as described in detail above. The angle between the planes in Cu(imH)$_2$Cl$_2$ is 21.97°. This 22° deviation from parallel planarity of adjacent basal planes, plus the distortion of the basal planes, leads to a Cu–Cl$_b$–Cu angle of 117°. The angle between the best least-squares planes in Cu(caf)(OH$_2$)Cl$_2$ is 87.04° while the bridge angle is 128°, and the angle between the planes in Cu(maep)Cl$_2$ is 142.91° with a bridge angle of 114°. It seems probable that overall crystal and molecular packing forces determine the relative orientations of the CuL$_2$Cl$_2$ units relative to the bridging chloride, and that the exchange-coupling interactions are determined by the relative orientation of these units. Fortunately, three of these compounds have reasonably well isolated chains and the trend in their properties becomes apparent. That is, $2J$ becomes more negative as the bridge angle increases, but before this conclusion can be accepted as being general, more structural and magnetic data on new compounds must be collected. The magnetic data for Cu(imH)$_2$Cl$_2$ reflect both antiferromagnetic intrachain interactions and interchain interactions. These latter interactions, which lead to long-range ordering below 7.7 K, are presumably transmitted by the hydrogen-bonding network between the imidazole ligand on one chain and a chloride on a neighbouring chain. The two independent hydrogen-bonding distances N–H ··· Cl are 3.16 and 3.39 Å. It has been proposed [20] that hydrogen-bonding superexchange pathways lead to long-range ordering in [NH(CH$_3$)$_3$][CuCl$_3$]·2H$_2$O, although the ordering occurs at much lower temperatures in this latter compound.

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