Positive Exchange Coupling Constant in the Dimer Bis-(*NN*-diethyldithiocarbamato)copper(II)

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Summary Based on magnetic susceptibility data from 4·2 to 56K it is shown that the sulphur-bridged dimer $[Cu(edtc)_2]_2$ has a triplet ground state and a weak lattice antiferromagnetism noticeable below 15K.

ONLY recently have positive exchange coupling constants for copper dimers been recognized.[1,2] In bis-(*NN*-diethyldithiocarbamato)copper(II), $[Cu(edtc)_2]_2$, the copper ions are arranged in pairs with two sulphur atoms bridging[3] as shown in the Figure, and we have recently shown[4] by e.s.r. the existence of spin–spin interactions. We now report our findings on the magnetic susceptibility of $[Cu(edtc)_2]_2$ from 4·2 to 56K which demonstrate that the ground state in this biologically related[5,6] compound is of triplet multiplicity.

The compound was prepared as previously reported.[4] The data were obtained with a Foner-type vibrating-sample magnetometer,[7] and the calculations were carried out with a Raytheon 706 computer. Appropriate diamagnetic[8] and TIP corrections were applied. The field strength was $1 \times 10^{+4}$ G in all measurements and a calibrated precision germanium resistance thermometer was used.

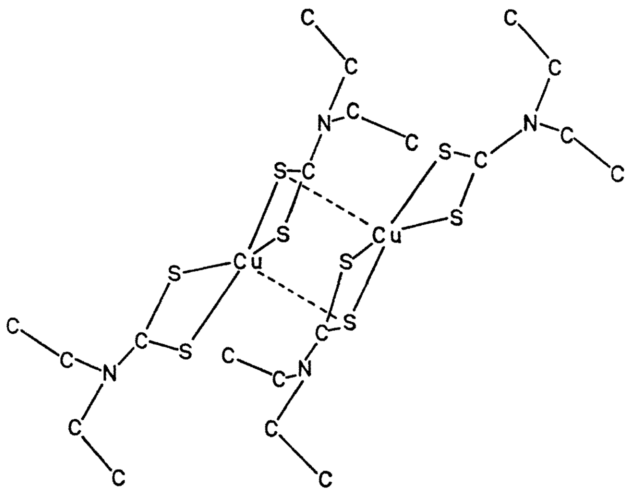

FIGURE. *Schematic of the structure of* $[Cu(edtc)_2]_2$. *Hydrogens are omitted for clarity.*

The Table contains the experimental data as well as the calculated susceptibilities and effective moments. Equations (1) and (2) were used in the calculations in conjunction

Experimental magnetic susceptibilities ($\times 10^4$), *effective moments, and calculated best fit for* $[Cu(edtc)_2]_2$

Temperature	χ_M(exp.)	χ_M(calc.)	μ_{eff}(exp.)	μ_{eff}(calc.)
56·1	77·1	77·8	1·86	1·87
43·2	103	103	1·88	1·88
27·3	167	167	1·91	1·91
19·5	239	237	1·93	1·92
14·8	314	313	1·93	1·93
12·2	376	376	1·92	1·92
10·0	456	454	1·91	1·91
8·63	521	519	1·89	1·89
7·32	593	598	1·86	1·87
6·62	647	652	1·85	1·86
5·98	710	709	1·84	1·84
5·38	778	772	1·83	1·82
5·06	818	811	1·82	1·81
4·82	850	842	1·81	1·80
4·21	914	934	1·75	1·77

with a fitting program. Values of $2J = + 24{\cdot}0\ \text{cm}^{-1}$, $g = 2{\cdot}04$, and $\theta = - 1{\cdot}37$K resulted from the best fit (sum of squares of deviations equal to 6×10^{-6}).

$$\chi = \frac{Ng^2\beta^2}{3k(T-\theta)}\left[1 + (1/3)e^{-2J/kT}\right]^{-1} \quad (1)$$

$$\mu_{eff} = 2{\cdot}83(\chi T)^{1/2} \quad (2)$$

The g value compares quite favourably with [9] the e.s.r. value of 2·049. The positive values of $2J$ indicates that the triplet state is the ground state with the singlet state lying 24·0 cm^{-1} above it. This is the first system where a copper cluster bridged by sulphur atoms has been shown to possess a triplet ground state. The spin coupling is between copper ions in the distinct dimers, where the p-orbitals in the sulphur atom and the unpaired electrons on the $d_{(x^2-y^2)}$ orbitals of the copper atoms interact *via* a σ-orbital mechanism with intra-atomic direct exchange as described by Goodenough[10] and Anderson.[11]

It is illuminating to compare the value of $2J$ obtained here with the value of $2J$ obtained in ref. 9. Gregson and Mitra obtained $2J = 7{\cdot}0\ \text{cm}^{-1}$ by magnetic susceptibility measurements from 80 to 300K and $2J = 1\ \text{cm}^{-1}$ from e.s.r. measurements. These values are quite different from the value calculated by us and are indicative of the lack of large variation of the magnetic parameters at high temperatures which makes the fitting procedure very inacurate.

Finally, the θ value obtained by us of $-1{\cdot}37$K signifies that there is an additional magnetic interaction occurring. The magnitude of the energy of this interaction is only about 1 cm^{-1}, but nevertheless contributes substantially to the susceptibility, especially at low values of kT. The negative sign of the interaction indicates that it is produced by a lattice antiferromagnetic interaction. This fact is also reflected by the decrease in μ_{eff} below 15K. This type of interaction has also been observed in the other[12] "ferromagnetic" metal cluster reported for which appropriate data are available. It should be pointed out that the θ values obtained from the Curie–Weiss law such as those from ref. 9 may not be comparable with the θ values obtained from the modified Langevin equation [equation (1)].

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