

ESR study of exchange coupled pairs in copper diethyl-dithiocarbamate

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Abstract. ESR investigations on exchange coupled pairs of Cu ions in single crystals of $\text{Cu}(\text{dte})_2$, isomorphously diluted with the corresponding diamagnetic zinc salt, are reported. The spin Hamiltonian parameters for the coupled species ($S=1$) are: $g_{\parallel}=2.1025$, $g_{\perp}=2.031$, $A=75.1 \times 10^{-4} \text{ cm}^{-1}$, $B=14.8 \times 10^{-4} \text{ cm}^{-1}$, $D=276.0 \times 10^{-4} \text{ cm}^{-1}$ and $E=46.7 \times 10^{-4} \text{ cm}^{-1}$. While the g and A tensors show tetragonal symmetry, the zero-field splitting tensor is rhombic and has principal axes different from those of the g and A tensors. Intensity measurements made down to 4.2 K indicate that the exchange is ferromagnetic with $|J| \sim 10 \text{ cm}^{-1}$. Direct dipole-dipole interaction appears to be the major contribution to the zero-field splitting. A calculation on the distributed point dipole model shows that dipolar interaction is considerably modified by the high covalency of the Cu-S bond and accounts for the rhombic nature of the tensor. The possible exchange mechanisms in $\text{Cu}(\text{dte})_2$ —direct exchange and superexchange through the bridging sulphurs—are discussed.

Keywords. Exchange interaction; ESR; copper diethyldithiocarbamate.

1. Introduction

Among the known stable complexes of copper with sulphur coordination, copper diethyldithiocarbamate (dte) is the most widely studied. ESR investigations in single crystals (Reddy and Srinivasan 1965; Weeks and Fackler 1968; Gregson and Mitra 1968), in solutions and in the glassy state and in polycrystalline specimens (Vanngard and Patterson 1961, Gersman and Swalen 1962, Anufrienko *et al* 1967, Yordanov and Shopov 1971, Prabhananda *et al* 1972) have been carried out and the spin Hamiltonian parameters for the isolated $\text{Cu}(\text{dte})_2$ molecule determined. The present ESR investigation was originally taken up with a view to studying the ^{33}S hyperfine (h.f.) structure in $\text{Cu}(\text{dte})_2$ diluted in a suitable diamagnetic host like $\text{Zn}(\text{dte})_2$. However, at the high gain necessary for observing ^{33}S lines, additional weak lines were observed, which are found to arise from pairs of copper ions coupled by exchange interaction and have formed the subject of the detailed study reported in this paper. Since these lines overlapped the ^{33}S h.f. lines and were stronger, they prevented an investigation of the ^{33}S h.f. structure. We report in this paper the results of the ESR study of exchange coupled pairs in $\text{Cu}(\text{dte})_2$ diluted in single crystals of $\text{Zn}(\text{dte})_2$, in the temperature range 4.2—300 K. Preliminary results were reported by Cowsik *et al* (1970, 1971).

2. Crystal structure

$\text{Cu}(\text{dte})_2$ and $\text{Zn}(\text{dte})_2$ were prepared and mixed crystals grown as described by Reddy and Srinivasan (1965).

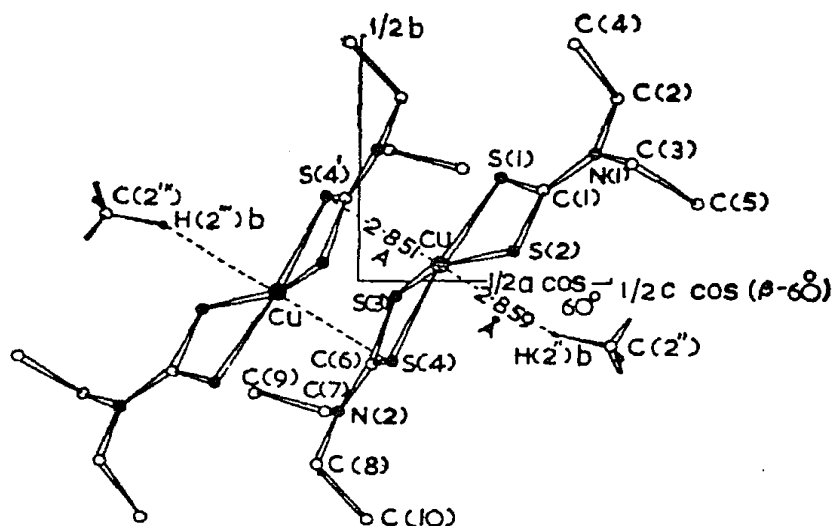


Figure 1. Orthographic projection of the structure down the line which makes an angle of 90° with the b -axis and $60^\circ - (\beta - 90^\circ) = 36^\circ 8'$ with the c -axis.

The crystal structures of the complexes have been solved by Bonamico *et al* (1965a, 1965b). $\text{Cu}(\text{dtc})_2$ crystallizes in the monoclinic space group $P2_1/c$, $z=4$. The unit cell parameters are: $a=9.907$, $b=10.627$, $c=16.591$ Å and $\beta=113^\circ 52'$. The Cu atom has a distorted tetragonal pyramidal coordination with four sulphur atoms in a plane, at an average distance of 2.31 Å and a sulphur atom from the centrosymmetrically related molecule at the apex, at a distance of 2.85 Å (figure 1). Each pair of centrosymmetrically related Cu atoms (3.59 Å apart) share sulphur atoms, thus creating a bimolecular unit. The zinc complex also belongs to the same space group. The structure is identical to that of $\text{Cu}(\text{dtc})_2$ except for small changes in the position of the metal atoms. Also, the fact that mixed crystals could be grown in all proportions suggests the compounds are almost isostructural.

3. Room temperature ESR results

The ESR measurements were made on an X-band spectrometer using 100 kHz modulation in the temperature range $4.2-300$ K. A proton resonance probe was used for magnetic field measurements with DPPH as the g -marker.

Single crystals containing a very low percentage of Cu show the expected spectrum from isolated Cu ions ($S=1/2$, $I=3/2$). At high gain, weak lines were observed outside the $S=1/2$ spectrum on both the low and high field sides. In single crystals with higher concentration of Cu, the intensity of these lines increased relative to that of the $S=1/2$ spectrum. A careful examination showed that the lines fell into two groups each consisting of seven lines. The lines within each group were unequal in intensity. These observations suggested that the additional lines originate from an exchange coupled species with $S=1$ with approximately equivalent coupling to two nuclei each with $I=3/2$ (the triplet spectrum).

Exchange coupling between two ions with spin $S=1/2$ gives rise to a diamagnetic singlet state and a paramagnetic triplet state. ESR transitions are observed between the states of the triplet. The zero-field splitting (z.f.s.) of the triplet levels gives rise to two fine structure transitions. In the present case, each fine structure line is further split into seven h.f. components due to equivalent coupling to the two copper nuclei of the exchange coupled pair. The relative intensities of the seven lines corresponding to the values $3, 2, 1, 0, -1, -2$ and -3 of the total magnetic quantum number M_I , are in the ratio $1:2:3:4:3:2:1$. In general, all the h.f. lines could not be seen

because of overlap with the lines of the doublet spectrum. The lines of the triplet spectrum are much broader than the doublet lines.

The observed triplet spectrum is ascribed to inversion related pairs of Cu atoms with a separation of 3.59 Å. Since there are four molecules in the unit cell, in general, two sets of pair lines are observed. The two pairs become equivalent for magnetic field orientations in the *ac*-plane.

The pair spectrum was first studied in the *ac*-plane (figure 2a). In certain orientations, the central h.f. component ($M_I=0$ line) was seen just outside the extreme h.f. line of the doublet spectrum. The principal axes of the *g* and *A* tensors for the doublet and triplet spectra coincide. While the *g* values for the two are approximately the same in all orientations, the h.f. separation for the coupled species is roughly half that for the isolated ion. This implies that exchange is sufficiently fast to average the h.f. interaction to half that for a single ion. However, for orientations near the maximum z.f.s. direction, the h.f. separation is larger in the low field fine structure transition than in the high field transition. This implies that *A* and *D* are of the same sign i.e., negative, since *A* is known to be negative for cupric complexes. However, the observed differences are larger than could be attributed completely to second order effects. The *g* and h.f. tensors have approximately tetragonal symmetry while the z.f.s. tensor is considerably rhombic.

The angular variation of the spectrum was then studied in the plane defined by the *b*-axis and the maximum z.f.s. direction in the *ac*-plane (D_{\max}). D_z , the maximum z.f.s. direction in the D_{\max} *b* plane, corresponds to the *z* principal direction of the fine structure tensor. The angle between the *b*-axis and the D_z direction was found to be 68°. This would agree with the metal-metal direction being the *z* direction of the z.f.s. tensor.

Since the z.f.s. tensor was found to be rhombic, it was also necessary to fix its *x* and *y* directions. Angular variation study was difficult because the intensity of the pair spectrum decreased with increasing ψ , the angle between *H* and D_z . Therefore, the

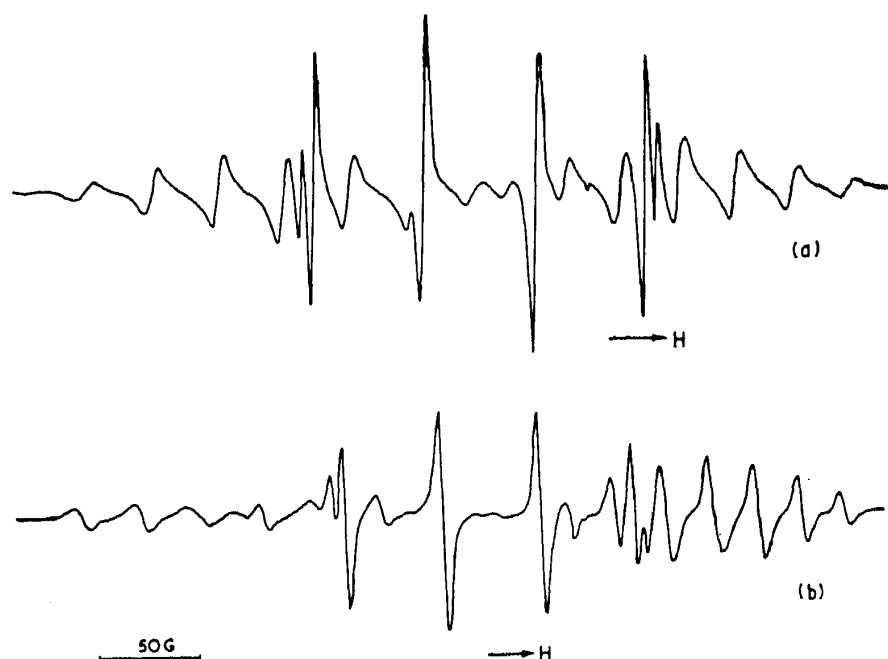


Figure 2. (a) ESR spectrum of Cu, Zn(dtc)₂ with *H* along the D_{\max} direction in the *ac*-plane ($T=300$ K).

(b) ESR spectrum with *H* along the D_{\max} direction in the *ac* plane ($T=20$ K).

axes were first inferred from symmetry considerations and then checked by experiment.

Experimentally it was found that the g_{\parallel} direction is along the Cu-S(4') direction and the D_z direction is along the Cu-Cu' direction (see figure 1). The major contribution to the rhombic term arises from a distribution of the unpaired spin. From an examination of the ligand geometry, the normal to the Cu-S(4)-Cu'-S(4') plane ($g_{\parallel}D_z$ plane) is inferred to be a principal axis of the z.f.s. tensor. Anisotropy in the g -factor also introduces a rhombic term. The normal to the Cu-S(4)-Cu'-S(4') plane being the line of intersection of the tetragonal plane of the g -tensor and the plane normal to D_z , it would be a principal axis of the z.f.s. tensor from this consideration too. The third principal direction should lie in the $g_{\parallel}D_z$ plane, normal to D_z .

From the crystal structure one finds that in $\text{Cu}(\text{dte})_2$, the b -axis lies almost in the Cu-S(4)-Cu'-S(4') plane. Experimentally too, the g_{\parallel} direction was found to be within a few degrees of the $D_z b$ plane. The x and y directions were, therefore, determined from measurements in the ac and $D_z b$ planes. The error involved in this assumption is about 5° . A check on the results was made by remounting the crystal with the D_z direction vertical and studying the spectrum in the xy plane.

4. The spin Hamiltonian

The ESR spectrum of a pair of identical ions with effective spins $S_1 = S_2 = 1/2$, with g -tensors whose principal axes and values coincide and the axes of spin-spin interaction coincide with those of the g -tensor, has been studied in considerable detail. The Hamiltonian for the system (omitting h.f. interaction) is (Abraham and Bleaney 1970):

$$\begin{aligned} \mathcal{H} = & \beta [g_x H_x (S_{1x} + S_{2x}) + g_y H_y (S_{1y} + S_{2y}) + g_z H_z (S_{1z} + S_{2z})] \\ & + \mathcal{J} S_1 \cdot S_2 + \mathcal{J}_x S_{1x} S_{2x} + \mathcal{J}_y S_{1y} S_{2y} + \mathcal{J}_z S_{1z} S_{2z} \end{aligned} \quad (1)$$

The allowed values of the total spin operator $S = S_1 + S_2$ are a singlet $S = 0$ at $-3\mathcal{J}/4$ and a triplet $S = 1$ at $\mathcal{J}/4$ in zero field. ESR transitions are observed only between the states of the triplet. The triplet levels which are degenerate in zero field when exchange is purely isotropic, are split by anisotropic exchange. This initial splitting gives rise to two fine structure transitions. The isotropic exchange term does not have a direct effect on the nature of the ESR spectrum and only determines the temperature variation of the ESR intensity. Therefore, in the spin Hamiltonian describing the angular variation of the spectrum from $S = 1$ species, the isotropic exchange term can be omitted and the Hamiltonian rewritten as

$$\mathcal{H} = \beta [g_x H_x S_x + g_y H_y S_y + g_z H_z S_z] + D [S_z^2 - \frac{1}{3} S(S+1)] + E (S_x^2 - S_y^2) \quad (2)$$

where $D = \frac{3}{4} \mathcal{J}_z$ (3)

$$E = (\mathcal{J}_x - \mathcal{J}_y)/4 \quad (4)$$

The solution of the spin Hamiltonian is simple for H parallel to x , y or z . The solutions are not simple analytical functions for general orientations of the magnetic field and the energy values and transitions are calculated using perturbation theory when the Zeeman interaction is much greater than D .

If the nuclear spin is non-zero, the h.f. interaction term to be added is

$$S_1 \cdot A_1 \cdot I_1 + S_2 \cdot A_2 \cdot I_2$$

For $J \gg g\beta H \gg A$, each fine structure transition is split into $4I+1$ components corresponding to the different allowed values for M_I , the total nuclear magnetic quantum number corresponding to the total nuclear spin $I_1 + I_2 = 2I$ (Slichter 1955). To first order the spacing between successive h.f. lines is half that for the isolated ion spectrum. The intensity of the components is proportional to the statistical weight of the corresponding nuclear state defined by M_I .

In the case of $\text{Cu}(\text{dte})_2$, the axes of the g -tensor and the h.f. interaction coincide and are different from those of the spin-spin interaction.

The g and A tensors have tetragonal symmetry and the z.f.s. tensor is rhombic. Therefore, the Hamiltonian is written as

$$\begin{aligned} \mathcal{H} = & \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + D[S_z^2 - \frac{1}{3}S(S+1)] \\ & + E(S_x'^2 - S_y'^2) + AS_zI_z + B(S_xI_x + S_yI_y) \end{aligned} \quad (5)$$

with $S=1$, $I=3$. x, y, z are the principal axes of the g and A tensors and x', y', z' those of the fine structure tensor.

The solution of the Hamiltonian is complicated by the non-coincidence of principal axes. For $g\beta H \gg D$, perturbation solutions can, however, be obtained. The fine structure tensor is first expressed in the g -tensor frame in which the tensor becomes non-diagonal. Eigenvalues have to be evaluated by perturbation methods even along the x, y, z axes.

It was explained earlier that the normal to the $g_{\parallel}D_z$ plane is a coincident principal axis of the g and fine structure tensors. This is taken as the $y=y'$ direction. The x, z, x' and z' directions are located in the $g_{\parallel}D_z$ plane. Neglecting h.f. interaction and expressing the fine structure tensor in the x, y, z frame, we have

$$\begin{aligned} \mathcal{H} = & \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] - \frac{1}{3}DS(S+1) \\ & + (D \cos^2 \alpha + E \sin^2 \alpha)S_z^2 + (D \sin^2 \alpha + E \cos^2 \alpha)S_x^2 - ES_y^2 \\ & - (D-E) \sin \alpha \cos \alpha (S_xS_z + S_zS_x) \end{aligned} \quad (6)$$

where α is the angle between g_{\parallel} and D_z .

To carry out the perturbation, the Hamiltonian is transformed to a reference system (x'', y'', z'') in which the Zeeman interaction is diagonal. The solutions are comparatively simple if the magnetic field is in one of the principal planes. For example, let us consider the magnetic field applied in the zx plane ($\sim g_{\parallel}D_z$ plane) at an angle θ with the g_{\parallel} direction (the sense being defined). Then, the Hamiltonian transformed to the x'', y'', z'' system is

$$\begin{aligned} \mathcal{H} = & g\beta HS_z'' - \frac{1}{3}DS(S+1) \\ & + (D_{\alpha} \cos^2 \omega + E_{\alpha} \sin^2 \omega + F_{\alpha} \sin \omega \cos \omega) S_z''^2 \\ & + (D_{\alpha} \sin^2 \omega + E_{\alpha} \cos^2 \omega - F_{\alpha} \sin \omega \cos \omega) S_x''^2 - ES_y''^2 \\ & + (-D_{\alpha} \sin \omega \cos \omega + E_{\alpha} \sin \omega \cos \omega - F_{\alpha} \sin^2 \omega) S_x'' S_z'' \\ & + (-D_{\alpha} \sin \omega \cos \omega + E_{\alpha} \sin \omega \cos \omega + F_{\alpha} \cos^2 \omega) S_z'' S_x'' \end{aligned} \quad (7)$$

$$\begin{aligned}
D_\alpha &= D \cos^2 \alpha + E \sin^2 \alpha \\
E_\alpha &= D \sin^2 \alpha + E \cos^2 \alpha \\
F_\alpha &= -(D - E) \sin \alpha \cos \alpha \\
\cos \omega &= g_{\parallel} / g \cos \theta \\
\sin \omega &= g_{\perp} / g \sin \theta \\
g^2 &= g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta
\end{aligned} \tag{8}$$

This Hamiltonian contains similar terms as an axial Hamiltonian with coinciding g and fine structure axes, expressed in a coordinate system rotated from the z direction in the zx plane. The solution for such a case has been given by Bleaney (1951). The solution of equation (7) can be worked out similarly using basic states M_s with z'' as the quantizing axis. The energy values and transitions contain similar terms with the coefficients being dependent on D , E , α and ω . The long expression is not reproduced here. A similar analysis is possible in the yz and xy planes.

By fitting the experimental results in the ac and bD_z planes to the Hamiltonian of eq. (5) the following values are obtained for the spin Hamiltonian parameters.

$$\begin{aligned}
g_{\parallel} &= 2.1025 \\
g_{\perp} &= 2.031 \\
A &= 75.1 \times 10^{-4} \text{ cm}^{-1} \\
B &= 14.8 \times 10^{-4} \text{ cm}^{-1} \\
D &= 276.0 \times 10^{-4} \text{ cm}^{-1} \\
E &= 46.7 \times 10^{-4} \text{ cm}^{-1}
\end{aligned}$$

5. Low temperature studies

The ESR spectrum at room temperature provided unmistakable evidence for exchange coupling, and the exchange integral appeared to be sufficiently greater than the h.f. interaction. Since the value of \mathcal{J} , in such cases, can be estimated only from the temperature variation of the intensity of the triplet spectrum, ESR studies at low temperature were taken up.

At 77 K the pair spectrum lines were considerably narrowed with respect to the isolated ion lines, thereby causing an apparent enhancement of the intensity of the pair lines. The $S=1$ spectrum was sufficiently strong at 77 K implying that either the exchange interaction is ferromagnetic, or if antiferromagnetic, very small. However, the evidence was not conclusive. Spectra with H along the D_{\max} and D_z directions at various temperatures down to 4.2 K were recorded.* One of these recordings is reproduced in figure 2b.

A striking feature of the recording is the inequivalence of the two fine structure transitions. Although the binomial distribution in h.f. intensities is preserved in the high field transition, the low field transition is weaker and is split into a number of components. The extreme lines at the high and low field ends have similar intensities. The $M_I = 0$ line of the low field transition appears to be affected most. A satisfactory explanation of this experimental feature could not be given with the few recordings that were available to us. This is attributed to the presence of isolated paramagnetic ions in the neighbourhood of the pairs. These cause local fields at the site of the pairs.

*Thanks are due to the Department of Chemistry, University of British Columbia, for providing facilities to one of us (R.S.) to record the low temperature spectra in the range 77–4.2 K.

These fields have a static as well as a fluctuating component. The static component may cause a g -shift and a change in D for the pairs, thus displacing the lines from their nominal positions. There are several possible positions near a pair for the third paramagnetic ion, and at the large concentrations used, the number of such groups would be considerable. The intensity of the expected seven lines decreases and the displaced lines acquire a certain intensity. The g and D changes appear to fortuitously cancel in the high field transition. It is not clear how the different h.f. transitions are affected differently in the low field transition. The effect is less pronounced at high temperatures as the polarization field of the isolated spins is low. Relaxation effects may also be partly responsible.

Other possible explanations which could account for this unusual effect were also considered. A decrease in \mathcal{J} at low temperatures could permit admixtures of singlet and triplet levels through h.f. interaction. This, however, does not explain the difference in behaviour of the two fine structure transitions. Second order effects in h.f. coupling, cross terms between D and A , difference in the h.f. constants of ^{63}Cu and ^{65}Cu , etc., are not sufficiently large to explain the observed difference. Motional effects would also affect the two transitions symmetrically.

Definite conclusions can be drawn only after more detailed experiments are performed. It appears reasonable to estimate \mathcal{J} from the intensity variation of the high field transition. From intensity measurements below 20 K the coupling was found to be ferromagnetic with $|\mathcal{J}|=10\text{ cm}^{-1}$. We had made a preliminary estimate of the exchange integral in $\text{Cu}(\text{dtc})_2$ as $|\mathcal{J}|=30\text{ cm}^{-1}$. In this determination the line widths had been assumed to be constant. On cooling, the triplet lines narrow down faster than the lines of the doublet spectrum. Since this has been taken into account now, the present estimate is likely to be more reliable. Several different estimates of \mathcal{J} in $\text{Cu}(\text{dtc})_2$ are available. Villa and Hatfield (1971a) have studied the pair spectrum in a polycrystalline sample of $\text{Cu}(\text{dtc})_2$ diluted with $\text{Zn}(\text{dtc})_2$, and from susceptibility measurements (Villa and Hatfield 1971b) they conclude that the exchange is ferromagnetic with $|\mathcal{J}|=24\text{ cm}^{-1}$. Based on susceptibility data Gregson and Mitra (1968) report $\mathcal{J}=+8\text{ cm}^{-1}$ and Hara *et al* (1969) conclude there is very little exchange in $\text{Cu}(\text{dtc})_2$. From ESR line width measurements Pal *et al* (1968) estimate $\mathcal{J}=0.08\text{ cm}^{-1}$. Obviously, the disagreement is due to the measurements not being sensitive to \mathcal{J} at temperatures $T \gg |\mathcal{J}|/k$. Also, the intensity effects are not as pronounced and striking as in the case of antiferromagnetic coupling.

Ferromagnetic coupling is rather unusual in copper complexes. In the investigations reported, except in a few cases (Hatfield *et al* 1970, Barnes *et al* 1970, Villa and Hatfield 1971c), the coupling has been found to be antiferromagnetic (Konig 1966, Kokoszka and Gordon 1969). Van Rens *et al* (1972) have studied the ESR spectrum of Ag-Ag pairs in $\text{Ag}_2\text{Zn}(\text{dtc})_2$ and have found evidence for a triplet ground state.

The spin Hamiltonian parameters show considerable change at low temperatures (table 1). The observations indicate that some structural changes take place on cooling. The $\text{Cu-S}(4)\text{-Cu}'\text{-S}(4')$ unit undergoes a change which increases the value of D . D_{max} is not increased by the same factor suggesting a possible rotation of the principal directions with respect to the crystallographic axes. This is supported by changes in g and A values also.

The observed spectra show several interesting features which demand further investigation

Table 1. Temperature variation of spin Hamiltonian parameters

Temperature K	D_{\max} direction				D_z direction				D_{\max}/D
	g_{isol}	g_{pair}	h.f.	z.f.s.	g_{isol}	g_{pair}	h.f.	z.f.s.	
			Separation K_{isol} $\times 10^4 \text{ cm}^{-1}$	D_{\max} $\times 10^4 \text{ cm}^{-1}$			Separation K_{isol} $\times 10^4 \text{ cm}^{-1}$	D $\times 10^4 \text{ cm}^{-1}$	
300	2.078	2.077	111.1	198.1	2.098	2.091	130.9	276.0	0.717
20	2.064	2.065	91.0	210.4	2.066	2.061	102.2	352.2	0.597
12	2.057	2.058	82.5	214.0	2.053	2.048	86.7	355.4	0.602

6. The zero-field splitting tensor

Since the magnetic ions involved in the exchange interaction do not have orbital momentum, the important contributions to the z.f.s. arise from (i) pseudo-dipolar interaction and (ii) magnetic dipole-dipole interaction. The antisymmetric exchange term is not applicable in $\text{Cu}(\text{dte})_2$ as the exchange coupled molecules are related by a centre of inversion.

The axis of pseudo-dipolar interaction is expected to coincide with the g_{\parallel} direction. From the Bleaney-Bowers formula (Bleaney and Bowers 1952) the pseudo-dipolar interaction corresponding to $|\mathcal{J}| = 10 \text{ cm}^{-1}$ is calculated to be $D_{\text{ex}} = 0.003 \text{ cm}^{-1}$ which is much smaller than the experimental value of 0.028 cm^{-1} . This mechanism is relatively unimportant in cases where the exchange integral is small. The magnetic dipole-dipole interaction for the Cu-Cu separation of 3.59 \AA , assuming point dipoles at the Cu sites, is $D_{\text{dip}} = 0.061 \text{ cm}^{-1}$ with the metal-metal direction as the axis of the interaction. The sign of D_{dip} is negative. D_{ex} is also negative for ferromagnetic coupling. The net z.f.s. observed is a tensor sum of the two

$$D = D_{\text{ex}} + D_{\text{dip}}$$

In copper acetate and related compounds, the line joining the metal atoms lies along the g direction. Also, the exchange integral being high, D_{ex} is the important contribution to the z.f.s. In $\text{Cu}(\text{dte})_2$, the calculated angle between the g_{\parallel} and the Cu-Cu' direction is 36° . D_{ex} being much smaller than D_{dip} , the z.f.s. is decided mainly by the dipole-dipole interaction, and the z -direction of the z.f.s. tensor lies close to the Cu-Cu' direction. Other cases have been reported where the principal axes of the g and D tensors do not coincide (Van Rens *et al* 1972, Kokoszka *et al* 1967, Buluggiu *et al* 1971).

The calculated z.f.s. is much larger than the experimental value. Also, the rhombic component comes out to be zero in the point dipolar approximation except for a small contribution from the anisotropy in the g -factor. From the ESR study of the isolated Cu ion in $\text{Cu}, \text{Zn}(\text{dte})_2$, the Cu-S bond is known to be highly covalent. The magnetic interaction between the two ions is considerably modified by spin delocalization. Smith and Owen (1971) have suggested a modified point dipole approach to take into account the effects of spin delocalization on spin-spin interaction. The spin densities transferred to the different atoms are considered as point dipoles at the respective atomic sites and the magnetic dipolar interaction is worked out for this distribution on the point dipole model. It is assumed that each Cu atom transfers a fraction of its spin to each

of the four in plane S ligands. Thus there are two Cu atoms each with a charge $(1-4f)$ and eight S atoms with a charge f on each of them (figure 3). The contributions to the spin Hamiltonian parameters D and E of the z.f.s. are:

$$D_{\text{calc}} = \frac{3}{2} g^2 \beta^2 / r^3 (1 - 9.4037f + 26.5562 f^2)$$

$$E_{\text{calc}} = g^2 \beta^2 / r^3 (2.3764 f - 8.8497 f^2).$$

A molecular orbital calculation for $\text{Cu}(\text{dte})_2$ using the spin Hamiltonian parameters determined by Reddy and Srinivasan (1965) gives $f=0.1$. This gives

$$D_{\text{calc}} = 197.5 \times 10^{-4} \text{ cm}^{-1}$$

$$E_{\text{calc}} = 60.4 \times 10^{-4} \text{ cm}^{-1}$$

Covalent binding is seen to alter the z.f.s. parameters considerably. D_{dip} is reduced to a third of the point dipole value. This is low compared with the experimental D value and the calculated E value has come out larger than that observed. The trends, however, are qualitatively right.

It is evident that the disagreement is due to the over simplified model used. Spin densities have been localized at the atomic sites and overlap has been neglected. When the delocalization is large, the dipole approximation is not sufficiently accurate. A rigorous calculation would involve the expansion of the charge distribution in a series of multipoles and calculation of the interaction between the multipole expansions of the two charge distributions.

Since D_{dip} is the major contribution to z.f.s. and D_{ex} is very small, one would expect the D_z direction to be along the axis of D_{dip} , i.e., the Cu-Cu' direction. The angle between the b -axis and the Cu-Cu' line is calculated to be 79° in pure $\text{Cu}(\text{dte})_2$. In the isomorphous zinc compound the corresponding angle is 65° . The angle between the b -axis and D_z determined from experiment is 68° . This is closer to the metal-metal direction in the zinc(dte)₂ lattice probably because the relative orientations of the two $\text{Cu}(\text{dte})_2$ molecules are influenced mainly by packing considerations and hence determined by the host lattice. The anisotropy in g -factor may also influence the z -direction slightly.

7. Mechanism of exchange

$\text{Cu}(\text{dte})_2$ is one of the few copper compounds in which the exchange interaction is ferromagnetic. The possible exchange mechanisms are (i) direct exchange, and (ii) superexchange through the bridging sulphur atoms.

(i) Since Cu, S(4), Cu' and S(4') lie in the xz -plane (figure 4) direct exchange can arise from the overlap of the d_{xz} orbitals of the Cu atoms. Unpaired spin density is introduced into the Cu d_{xz} orbital through spin-orbit admixture with the Cu $d_{x^2-y^2}$ orbital. However, the Cu-Cu' distance is rather large (3.59 Å).

(ii) Two superexchange paths involving electron correlation through the ligand sulphur atoms S(4) and S(4') appear to be important in $\text{Cu}(\text{dte})_2$. They are:

(a) ^{33}S h.f. interaction study has demonstrated the Cu-S binding to be highly covalent in $\text{Cu}(\text{dte})_2$. The spin density from the $d_{x^2-y^2}$ orbital of Cu is covalently transferred to the p_x orbital of S(4) (figure 4 (ii)a). This polarizes its doubly occupied p_z orbital through intra-atomic exchange. The p_z orbital of S(4) overlaps with the $d_{3z^2-r^2}$

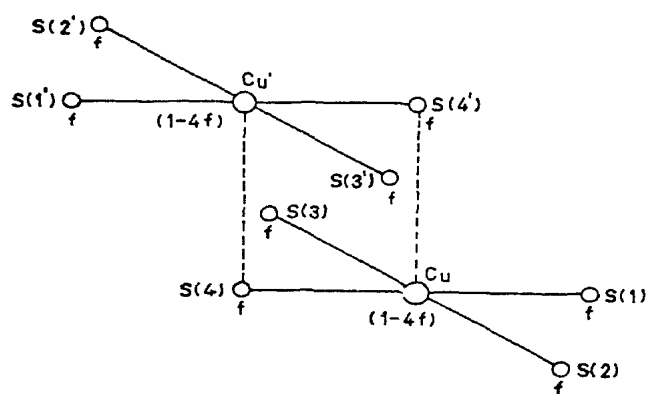


Figure 3. Geometry of exchange coupled Cu atoms and the associated ligands. The fraction of the magnetic moment considered localized at each site is indicated.

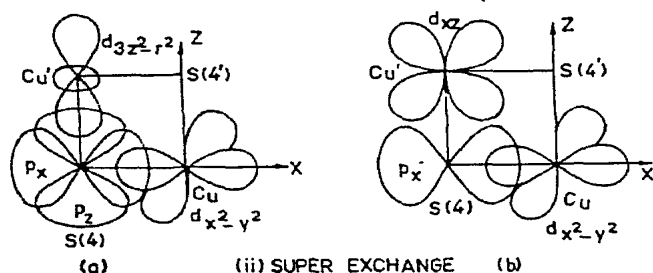
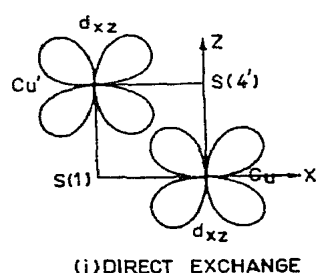


Figure 4. Exchange paths in $\text{Cu}(\text{dte})_2$.

orbital of Cu' , which is orthogonal to the $d_{x^2-y^2}$ orbital on the same atom; this could lead to ferromagnetic exchange. A similar path exists via $\text{S}(4')$.

(b) The p_x orbital on $\text{S}(4)$ is involved in out of plane π -bonding with the d_{xz} orbital on Cu' and in σ -bonding with the $d_{x^2-y^2}$ orbital on Cu , thus establishing another path for spin correlation (figure 4(ii) b).

The relative importance of these mechanisms could probably be decided by a numerical calculation.

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