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Spin-Spin Coupling in Magnetically Condensed Complexes. X. EPR of Bis(N,N-diethyldithiocarbamato)Copper(II) [1]

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Solid solutions of bis(N,N-diethyldithiocarbamato)copper(II) in a zinc matrix were studied by means of EPR. The spectra may be interpreted with a $S=1$ Hamiltonian giving proof of spin-spin interactions between pairs of copper ions within isolated dimers. The magnetic parameters obtained were used to calculate the MO coefficients α, β, k and k_0 which indicated high in-plane covalency. The observed spin interactions were then interpreted in terms of electron delocalization via the bridging sulfur atoms.

Introduction

The dithiocarbamates are biologically important compounds[2,3] and the system composed of copper(II) and N,N-diethyldithiocarbamate (edtc) has been studied extensively in the last decade.[4-9] Vangard and Peterson[4] were the first to report the EPR properties of the system, followed by Gersmann and Swalen.[5] The system has been studied in a variety of conditions: solution,[6] single crystal,[7] zinc and/or nickel doped single crystals,[8,9] and powders.[5] These studies have yielded the anisotropic magnetic parameters g and A, and the MO parameters α, β, γ, k and k_0[10] all deduced from the doublet state spectra of copper(II). Furthermore, some investigators have also carried out magnetic susceptibility measurements on this system,[7,11,12] but there is no general agreement as to the existence of interactions between copper(II) ions in the dimeric molecule. Very recently, Smith, *et al.*,[13] reported the observation of a dimeric species in chloroform solutions. Their complex was reported as being possibly square anti-prismatic with a Cu—Cu distance of approximately 4.5 A. During our systematic investigation of spin-spin coupling in magnetically condensed compounds, we have studied the EPR of $Cu(edtc)_2$ in a zinc matrix and have observed distinct interactions between pairs of copper(II) ions. The interactions can be interpreted in terms of a dimer with $S=1$. The structures of the copper and zinc compounds are depicted in Figure 1.

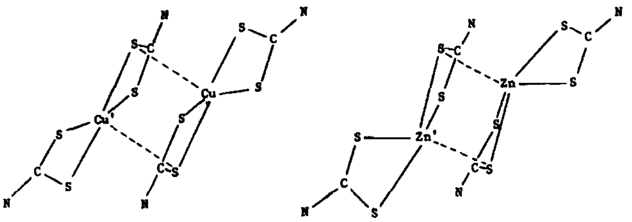

Figure 1. Schematic drawings of the structures of $Cu(edtc)_2$ and $Zn(edtc)_2$. The ethyl groups were left out for clarity.

Experimental Section

Solid solutions of $Cu(edtc)_2$ in $Zn(edtc)_2$ were prepared by mixing water solutions of copper and zinc chlorides in the appropriate proportions with an excess of the ligand in aqueous solution. The precipitate was filtered, washed with water three times, and dried over P_4O_{10}. Care was exercised to use carbonate-free water in all the preparations. *Anal*: Calcd. for $Zn_2(C_5H_{10}NS_2)_4$: C, 33.16; H, 5.53; N, 7.74; S, 35.43. Found: C, 32.91; H, 5.64; N, 7.45; S, 35.14.

The Cu:Zn proportions ranged from approximately 1:500 to 1:1000. The EPR spectra were obtained at 298°K and 77°K with a Varian E-3 spectrometer at 9.18 GHz. The best resolved spectra are shown here. Diphenylpicrylhydrazyl (DPPH) was used as an internal standard.

Results

Spectra were recorded in the region 0 to 5000 G. The results can best be interpreted in terms of intense doublet spectra (coming from Cu—Zn pairs) overlapping distinct triplet spectra (from Cu—Cu pairs). To clarify the situation further, specific areas of the spectra will be presented separately. Our assignments were made from the shape and arrangement of the bands.

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a. *The 2500 G region.* This region contains a sequence of six bands which are shown in Figure 2. This sequence of lines can be interpreted as the low field parallel transition of the triplet state which is centered at 2855 G, with the seventh component hidden under a strong doublet band. The band at about 2880 G belongs to doublet species, with the ^{65}Cu splitting clearly resolved.

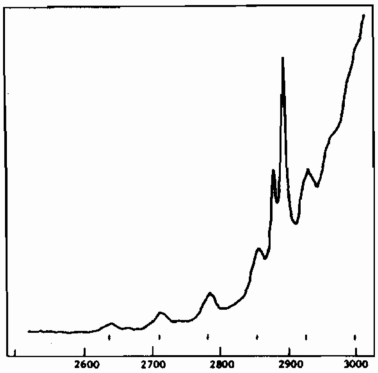

Figure 2. The EPR of Zn: Cu(edtc)$_2$ in the 2500 G region (298°K).

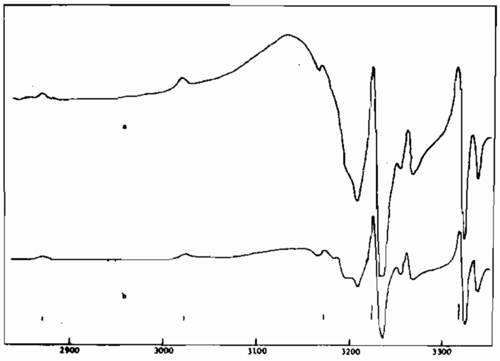

Figure 3. The EPR of Zn: Cu(edtc)$_2$ in the 3100 G region (77°K). a) Normal concentration of copper; b) smaller concentration of copper.

b. *The 3100 G region.* This region is shown in Figure 3, from about 2850 to 3350 G. It has the complexity expected from the powder spectrum of a copper doublet species with non-equivalent ions[9] in the unit cell. However, various features are identifiable. The sequence of bands at about 2872, 3022, and 3172 G, together with another band expected at 3318 G (covered) can be ascribed to the parallel sequence from the doublet species. Using the information from the single crystal study[9] the very strong bands at 3225 and 3318 G can be assigned as the outer limits of the perpendicular band from the doublet. The other bands and shoulders can be attributed to the remainder of the perpendicular spectrum complicated by the ^{65}Cu doublets.

Figure 3b, where the copper concentration was much smaller, shows a proportionally much smaller peak at about 3130 G. This effect is produced by the statistically expected larger decrease in dimer concentration than in overall copper concentration. That field position is, therefore, assigned to the low field perpendicular band from the triplet species. There are, in addition, some other unassignable absorptions[5] in this particular area.

c. *The 3400 G region.* The sequence of four lines shown in Figure 4a can be assigned to the high field parallel transition from the triplet, centered at 3412 G. The band apparent at 3360 G (Figure 4b) which is partially obscured by a doublet band from the 3100 G region, can be assigned (see discussion) to the high field perpendicular band from the triplet species.

d. *The 1500 G region.* Four of the seven lines expected for H_{MIN} are centered at 1590 G, with other half field bands being located in the 1600-1700 G region (Figure 5).

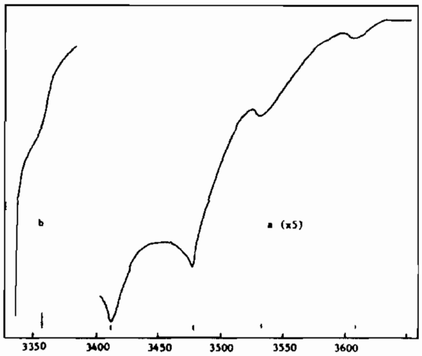

Figure 4. The EPR of Zn: Cu(edtc)$_2$ in the 3400 G region (298°K).

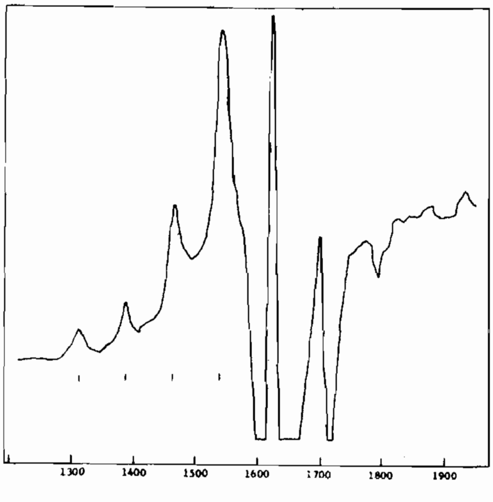

Figure 5. The half field bands of Zn: Cu(edtc)$_2$; 1500 G region (77°K).

Discussion

The crystal structure[14] of the Zn(edtc)$_2$ shown in Figure 1 indicates that the zinc atoms are linked in discrete dimers by an in-plane Zn–S bond and a longer out-of-plane Zn–S bond. The environment around the zinc ions can be described best[14] as a trigonal bi-

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Table I. EPR and Molecular Orbital Data of Cu(edtc)$_2$[a].

Reference	$g_\parallel$	$g_\perp$	$<g>$	A(10^4)	B(10^4)	α^2	β^2	γ^2	k	k$_0$	D(10^4)
This work [b]	2.09	2.03	2.05	68 [c]	5 [c]	.51	.96	.88	.20	.40	270
7				75 [c, d]							290 [d]
Single Crystal	2.09	2.03	2.05	—	—	—	—	—	—	—	—
8	2.08	2.02	2.04	160	40	.58	.79	.89	—	—	—
9	2.11	2.02	2.05	152	22	.50	$\simeq$1.	.70	.23	.45	—

[a] Units in cm^{-1}. [b] Other parameters are: S = 0.005; P = 0.036; T = 0.44; λ = 825; Δ_1 = 21980; Δ_2 = 24000. [c] A/N and B/N are given. [d] From half field lines.

Table II. EPR Data for Doublet Cu(edtc)$_2$[a].

Reference	$g_\parallel$	$g_\perp$	$<g>$	A	B	λ	k
This work	2.11	2.02	2.06	.0147	.0028	835 (350)	0.31 (0.50)
7	2.12	2.02	2.06	.0146	.0039	350	0.72
9	2.11	2.02	2.06	.0142	.0022	—	—

[a] All units in cm^{-1}.

pyramid while the environment around copper in the analogous copper compound can be best described[15] as a square pyramid (Figure 1). In the concentration range of copper that was used in this investigation, it would be expected that the majority of copper ions would have zinc partners in the dimers, but that a significant concentration of dimers with Cu—Cu pairs would be formed.

Triplet Spectra. The triplet state spectra observed in Figures 2-5 can be interpreted with the spin=1 Hamiltonian (1),

$$H = \beta[g_\parallel H_zS_z + g_\perp(H_xS_x+H_yS_y)] + DS_z^2 + (A/N)S_zI_z + (B/N)(S_xI_x+S_yI_y) - 2/3D \tag{1}$$

where all the symbols have their usual meaning and N is the number of nuclei with which the electronic spins are simultaneously interacting[16] (N=2 for dimers). It is assumed that the Z magnetic axis is the pseudo C_{4v} axis in the metal ions. This assumption is supported by the single crystal work of Reddy and Srinivasan[9] and Kokoszka, *et al.*[17,18]

The nuclear hyperfine position of the parallel bands can then be fit[19] by equation (2), where I=3; M_s=1, 0; M_I= +3, +2, ... −3

$$\omega_0 = g_\parallel \beta H + 2D(M_s-1/2) + (A/N)M_I + [(B/N)^2/\omega_0][I(I+1)-M_I^2+(2M_s-1)M_I] \tag{2}$$

and ω_0 is the radiofrequency energy. B/N was taken to be 5 G as a maximum approximation from the spectra. The value of A/N was obtained directly from Figures 2 and 4. The $g_\parallel$ and D values calculated are shown in Table II. Considering the D value calculated from the parallel lines, noting that $H_{\parallel 2}-H_{\perp 1} \simeq D$, and using the assigned low field perpendicular band at 3130 G, one expects the high field perpendicular transition to be in the 3450 G region. The band at 3460 G was assigned, therefore, to this transition. With these bands, a value of $g_\perp$ of 2.03 obtained.

The average $<g>$ shown in Table I was then calculated from equation (3).

$$<g> = (1/3)(g_\parallel + 2g_\perp) \tag{3}$$

As a final check of internal consistency D was also calculated from the half field line,[20] using equation (4). A D value of

$$D = \{(3/4)[\omega_0^2 - (2<g>\beta H_{MIN})^2]\}^{1/2} \tag{4}$$

0.029 cm^{-1} was obtained which compares favorably with the D value of 0.027 cm^{-1} calculated from the experimental data obtained at full field. The difference observed is quite reasonable since small changes in the choice of H_{MIN} would produce large changes in the calculated D value. Also, non-coincidence of the D and g tensors could produce differences of the order of magnitude observed here.

At this time the type of triplet species under investigation can be described. The equation for dipole-dipole interaction[19,21] (5)

$$D_{dd} = (3/4)g^2\beta^2 < (1-3\cos^2\theta)/\vec{r}_{1,2}^{\,3} >_{max} \tag{5}$$

can be approximated by equation (6) using the point charge model,

$$R_{calc} = [0.325 g_\parallel^2 (1-3\cos^2\theta)/D_{dd}]^{1/3} \tag{6}$$

assuming that each electron is at a copper nucleus and that the molecular symmetry axes and magnetic axes are coaxial. Here $\vec{r}_{1,2}$ is the intermetallic (interelectronic) vector and θ is the angle between $\vec{r}_{1,2}$ and the external magnetic field. In this case θ=40° (see Figure 1 and reference 11) which gives a value of R_{calc} of 3.4 A in good agreement with the intermetallic distan-

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ce in the zinc matrix of 3.54 A. However, the intermetallic distance in the pure copper compound is 3.58 A, also very close to the value of R_{calc}, and further criteria are needed in order to establish the nature of the dimers. These criteria are afforded by a comparison of the g values obtained in this work and the g values obtained in the pure compound,[7] shown in Table I. They are the same within experimental error and this leads us to postulate that the Cu–Cu dimers doped into the zinc matrix have the same geometry as they have in the pure copper compound.

The copper atoms in the pure compound have square pyramidal C_{4v} symmetry and it will be appropriate, therefore, to use the g values and hyperfine coupling constants obtained in this work in conjunction with the molecular orbitals derived by Maki and McGarvey[22] and by Neiman and Kivelson,[23] equation (7), for square planar D_{4h} complexes

$$
\begin{aligned}
{}^{*}B_{1g} &= \alpha d_{x^2-y^2} - (1/2)\alpha'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}) \\
{}^{*}B_{2g} &= \beta d_{xy} - (1/2)(1-\beta^2)^{1/2}(p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)}) \\
{}^{*}A_{1g} &= \alpha_1 d_{z^2} - (1/2)(1-\alpha_{1^2})^{1/2}(\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}) \\
{}^{*}E_g &= \begin{cases} \gamma d_{xz} - [(1-\beta^2)^{1/2}/\sqrt{2}](p_z^{(1)} - p_z^{(3)}) \\ \gamma d_{yz} - [(1-\beta^2)^{1/2}/\sqrt{2}](p_z^{(2)} - p_z^{(3)}) \end{cases} \\
\sigma^{(i)} &= (1/\sqrt{3})(\sqrt{2}p^{(i)} \pm s^{(i)})
\end{aligned}
\tag{7}
$$

(same electronic arrangement as C_{4v}) in order to obtain the MO coefficients. Furthermore, only those parameters obtained from the triplet state spectra will be used, because as will be seen later, there are changes in these parameters if the second ion in the dimer is not copper. This indicates the importance of observing the triplet state spectra, since it is only from them that some of the appropriate hyperfine splitting parameters can be obtained.

The molecular orbitals[23] used in this description are shown in equations (7) and using equations (8) the fraction of the unpaired

$$
\begin{gathered}
\alpha^2 = (7/4)[(A_s/P - (A_{\parallel}/P) + (g_{\parallel} - g_s) + (3/7)(g_{\perp} - 2.0023)] \\
\alpha^2 + \alpha'^2 + 2\alpha\alpha' S = 1
\end{gathered}
\tag{8}
$$

electron remaining on the copper ion can be assessed.[8]

Here A_s, the isotropic hyperfine coupling constant, is calculated from the anisotropic hyperfine splittings. P has a calculated value of 0.036 cm^{-1} and $S = 0.005$ for diethyldithiocarbamate.[5,9]

The rest of the coefficients can be calculated with the usual equations.[9] The values obtained for α^2, β^2, γ^2, k and k_0 are given in Table I. Mixing of higher ligands levels has been neglected.

The values obtained are within expectancy, and they indicate strong covalency in the in-plane σ bonding, almost complete ionic character in the in-plane π bonding and moderate covalency in the out of-plane π bonding. The observed in-plane covalency is attributed to the ability of the soft[24] sulfur atoms to form covalent bonds and to delocalize the d electrons. Furthermore, the mechanism of spin-spin coupling observed in the EPR spectra ($S = 1$) can now be ascribed to an exchange mechanism, in which the copper electrons within a dimer are interacting by covalency and delocalization through the in-plane sulfur atoms, one of which bonds axially to the other (out-of-plane) copper ion of the dimer. This is, therefore, a *bona fide* case where the axial or out-of-plane interactions[25-27] play an important role in the observed magnetic properties. It would be interesting to extend this theory to consider the axial σ bonding, since it may also display strong covalency.

Finally, the assumption of coincidence of the axis of the different magnetic tensors can be reviewed. As seen from Table I, the A and D values obtained from the full field lines are 7×10^{-4} cm^{-1} and 2×10^{-3} cm^{-1} smaller, respectively, than the values obtained from the half-field lines. These phenomena can be produced by non-coincidence of the g, A and D tensors and differences of the same order of magnitude as the ones observed in this work have been reported before.[28,29] The magnetic parameter values obtained from full fields were used in the calculations in this work. The use of the low field values would produce a maximum change of 2% in the calculated parameters. It is believed from the self-consistency observed and from the well defined g tensors[7] that the errors introduced by assuming that the magnetic tensors are coaxial are not large. The use of dilute single crystals and of higher degrees of sophistication in the theoretical treatment will probably provide the ultimate answer to this aspect of the problem.

Doublet Spectra. The magnetic parameters for the doublet species in the Cu–Zn dimers are distinctly different from those in the pure state, in solutions, or in the triplet state. This indicates that the copper ions are going into the C_{3v} zinc lattice occupying the zinc positions. Copper(II) in a trigonal bipyramidal arrangement is expected to show a reverse spectrum,[30,32] that is, $g_{\perp} > g_{\parallel}$. Also, equations (10) should be used[30,31] to interpret the

$$
\begin{gathered}
g_{\parallel} = 2.00 \\
g_{\perp} = 2[1 - (3k^2\lambda)/\Delta_2]
\end{gathered}
\tag{10}
$$

experimental results, where all the symbols their usual meaning and Δ_2 is the energy difference between the d_{z^2} and the d_{xz}, d_{yz} orbitals. However, since the EPR spectrum experimentally observed in a normal one, and the values of k and λ calculated from equations (10) are indicative of strong covalency, but somewhat below reasonable values (see Table II), we are led to

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believe, then, that the distortions about the copper in the Cu–Zn pairs are comparable or larger than previously observed distortions[31,3,34] in compounds such as [Cu(tren)NCS](SCN). Exchange interactions could also produce the effects observed in the g values.[6,29,35]

Conclusions

The following conclusions can be drawn from this work:

1) The Cu(edtc)$_2$ system has been shown by EPR to exhibit interactions between adjacent copper ions within the distinct dimers.

2) It is necessary to observe the triplet state spectra in order to obtain the correct parameters for MO calculations.

3) As expected, high covalency is observed in both systems: the Cu–Cu dimers (triplet) and the Cu–Zn dimers (doublet).

4) Covalency and out-of-plane intramolecular interactions between the copper ions in the dimers explain the magnetic properties of Cu(edtc)$_2$.

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