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An Electron Spin Resonance Study of the Copper(II) Chelates of Certain Monothio-β-diketones and Diethyldithiocarbamate

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The esr spectra of copper(II) chelates of the monothio-β-diketones of the type $R_1C(SH){=}CHCOR_2$, where $R_1 \equiv$ phenyl and $R_2 \equiv$ phenyl and where $R_1 \equiv \alpha$-thienyl and $R_2 \equiv$ perfluoromethyl, have been studied in a range of frozen solvents. The magnetic parameters associated with the spectra due to monomeric species observed in the $g = \sim 2$ region have been determined by consideration of axial and orthorhombic spin Hamiltonians and compared with those obtained from the spectra of copper(II) diethyldithiocarbamate under similar circumstances. For each copper(II) monothio-β-diketone chelate, low-field lines were observed at 77°K which have been attributed to $\Delta M = 2$ transitions arising from the presence of dimeric species in the frozen solvent. Solution of a spin Hamiltonian which includes the magnetic dipole–dipole interaction for the coupled copper(II) ions and the application of computer simulation of the line shapes has enabled the distance of *ca.* 4 Å between the copper(II) ions in the dimeric species to be determined. A possible structure is considered for the dimeric species which would be compatible with this calculated distance.

The preparation and characterization of a number of metal chelates of the monothio-β-diketones 3-mercapto-1,3-diphenylprop-2-en-1-one (dpmb) and 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-but-3-en-2-one (ttmb) have been studied by Ho, *et al.*,[1] and Chaston, *et al.*[2] The copper(II) chelates $Cu(dpmb)_2$ or $Cu(ttmb)_2$ can be prepared by reaction of copper(II) salts with the corresponding ligand. Chaston and Livingstone describe the chemical stability of these compounds in terms of the delocalization of charge within the chelate ring, resulting in a greater charge density on the oxygen atom, thus stabilizing the copper(II) state. Other monothio-β-diketones which have electron-attracting groups bound to the carbon atom of the carbonyl group (*e.g.*, OC_2H_5 or CF_3) reduce copper(II) to copper(I) giving polymeric chelates.[1] Here the ligands involve bonding by the sulfur atoms alone. On the other hand monothio-β-diketones possessing strongly electron-attracting groups bound to the same carbon atom as the sulfur atom do not reduce copper(II) to copper(I). The copper(II) chelate of ttmb has the thienyl ring system at the sulfur end of the molecule which stabilizes the copper(II) state.

Enough information is available to indicate that stabilization of the copper(II) in these chelates is strongly influenced by the nature of the substituent attached to the carbon atoms bonded to the oxygen and sulfur atoms. The present study was undertaken to provide more precise information about the electronic environment of the copper(II) in the monothio-β-diketonate chelates and the information derived from these systems is compared with that obtained from the copper(II) chelate of diethyldithiocarbamic acid. The previous investigations have indicated that the magnetic susceptibilities of these copper(II) chelates correspond to the spin-free values and there is no evidence for the occurrence of exchange coupling.

Experimental Section

Esr spectra were recorded at both room temperature and 77°K as the first derivative of the absorption signal. A Varian V-4531, 100-kHz multipurpose cavity was used in conjunction with a 3-cm spectrometer of conventional design operative in the absorption mode with the klystron locked to the resonant cavity by an automatic frequency controller operating at 455 kHz.

The microwave frequency was measured using a 12.4-GHz Hewlett-Packard 540B transfer oscillator and a Hewlett-Packard Model 5245L frequency counter.

The magnetic field position was calibrated by proton resonance using a marginal oscillator. The resonance absorption lines of protons in rubber or naphthalene were used since they fulfill the necessary condition of small line width and strong signal.

The monothio-β-diketones and their copper(II) chelates were prepared by methods previously described.[1,2]

Results and Discussion

Previous investigations of the esr spectra of transition metal ion compounds have shown that the solvent composition which provides the best host lattice is of paramount importance in obtaining well-resolved spectra. In particular Gersmann and Swalen[3] showed that, with a judicious choice of solvent composition, glasses could be obtained at low temperatures which allow the observation of well-resolved signals due to copper(II) diethyldithiocarbamate, the best results being obtained using a solvent composition consisting of chloroform containing 60% by volume of toluene.[3] In the present investigation the resolution of the spectra of the copper(II) chelates of the monothio-β-diketones observed in frozen solution was found to be critically dependent on the solvent composition. The spectra, observed at room temperature, of the Cu^{II}–dpmb and –ttmb chelates were well resolved in solvents such as chloroform and the intensities of the signals were those expected from solutions containing monomeric species.

At sample temperatures of 77°K the spectra obtained for $Cu(dpmb)_2$ and $Cu(ttmb)_2$ in various solvents are shown by Figures 1 and 2, respectively. The spectra due to $Cu(dpmb)_2$ in dimethyl sulfoxide and petroleum ether are almost isotropic, the resolution increasing in chloroform and petroleum ether containing 20% pyridine. The best resolution was obtained using dimethyl sulfoxide containing 20% chloroform, and similar results were observed for $Cu(ttmb)_2$. Figure 3 depicts the spectra obtained from copper(II) diethyldithiocarbamate in chloroform–toluene and chloroform–pyridine solutions at 77°K where well-resolved spectra are observed.[4]

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[1] R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1179 (1966).

[2] S. H. H. Chaston and S. E. Livingstone, *ibid.*, **20**, 1065 (1967).

[3] H. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

[4] A. D. Toy, J. R. Pilbrow, and T. D. Smith, *J. Chem. Soc. A*, 1029 (1969).

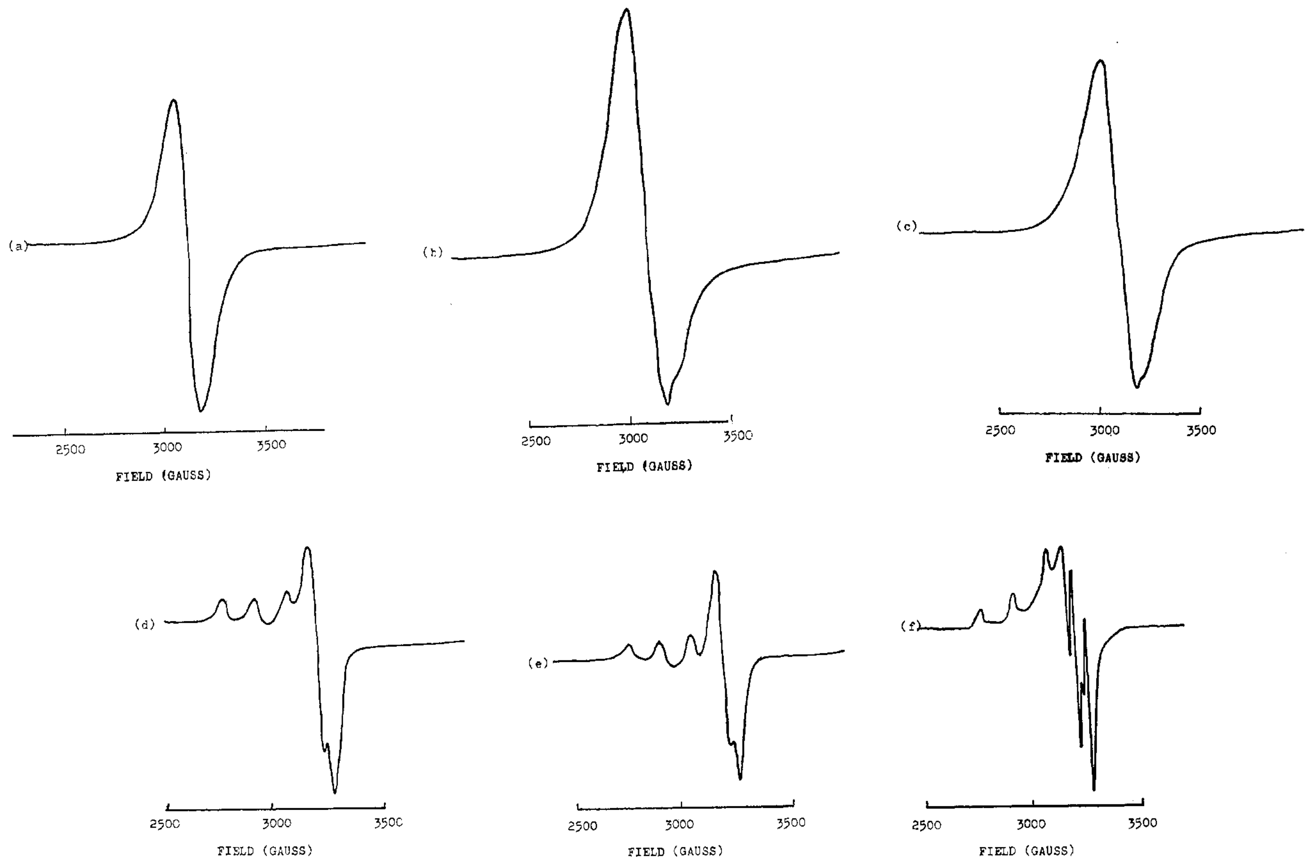

Figure 1.—Esr spectra of 0.01 *M* Cu(dpmb)$_2$ at 77°K and 9.230 GHz in various solvents: (a) dimethyl sulfoxide, (b) petroleum ether (bp 100–120°), (c) chloroform, (d) pyridine, (e) petroleum ether (bp 100–120°) containing 20% by volume of pyridine, and (f) dimethyl sulfoxide containing 20% by volume of chloroform.

At 77°K in addition to the well-resolved spectra observed in the $g = \sim 2$ region for copper(II) monothio-β-diketonate solutions, a further component of each spectrum was observed at *ca.* 1500 G under the conditions of best resolution as shown in Figure 4. The low-field lines are attributed to $\Delta M = 2$ transitions arising from magnetic dipolar coupling of the copper(II) ions in a dimeric species which is present to a limited extent in frozen solution.

Theoretical Considerations of the Esr of Copper(II) in Monomeric and Dimeric Complexes.—Copper(II) has a free-ion ground state ^{2}D which is split by an octahedral crystal field to give a doubly degenerate E$_g$ ground state and a triply degenerate T$_{2g}$ excited state. Axial distortions, as well as the Jahn–Teller effect in many cases, remove the degeneracy of the E$_g$ orbital doublet and partially remove the degeneracy of the T$_{2g}$ triplet. Generally the ground state is $|x^2 - y^2\rangle$ with an effective spin of $^1/_2$ where $g_{\|} \approx 2.3$ and $g_{\perp} \approx 2.07$. In addition the hyperfine interaction is always found to be anisotropic.

In some cases rhombic distortions are observed and for these the ground state involves some mixing in of the T$_{2g}$ orbitals. The spin Hamiltonian then has three principal components of both the g and hyperfine tensors.

(a) **Monomeric Copper(II) Complexes with Axial Symmetry.**—The esr spectra due to these complexes may be described by the spin Hamiltonian

$$\mathcal{H} = \beta[g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + AS_zI_z + B(S_xI_x + S_yI_y) \quad (1)$$

where β is the Bohr magneton and $g_{\|}$, $g_{\perp}$, A, and B have their usual meaning. For copper $S = {}^1/_2$ and $I = {}^3/_2$.

(b) **Monomeric Copper(II) Complexes with Orthorhombic Symmetry.**—The esr spectra due to complexes where the central copper(II) ion has an orthorhombic distribution of ligand atoms may be represented by the spin Hamiltonian

$$\mathcal{H} = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z \quad (2)$$

(c) **The Esr of Dipolar Coupled Copper(II)–Copper(II) Pairs.**—In addition to complexes which contain one copper(II) ion (monomers), there are many systems known in which dimerization occurs and in which the copper(II) ions become sufficiently close that the dipole–dipole interaction between them manifests itself in the esr spectrum. The theory of the magnetic interactions in copper(II) pairs is basically the familiar singlet–triplet problem. A feature which aids the interpretation of such dimer spectra is the appearance in many cases of $\Delta M = 2$ transitions. An exchange interaction may also occur but it is not thought to be important in the examples given in this paper. A weak exchange interaction simply separates the singlet states from the triplet and this has very little influence on the transitions within the triplet states.

In turns out that for X-band frequencies ($\sim$9.2 GHz) we may use nondegenerate perturbation theory, taking the Zeeman term as the zero-order interaction. The hyperfine interaction is the perturbation in the

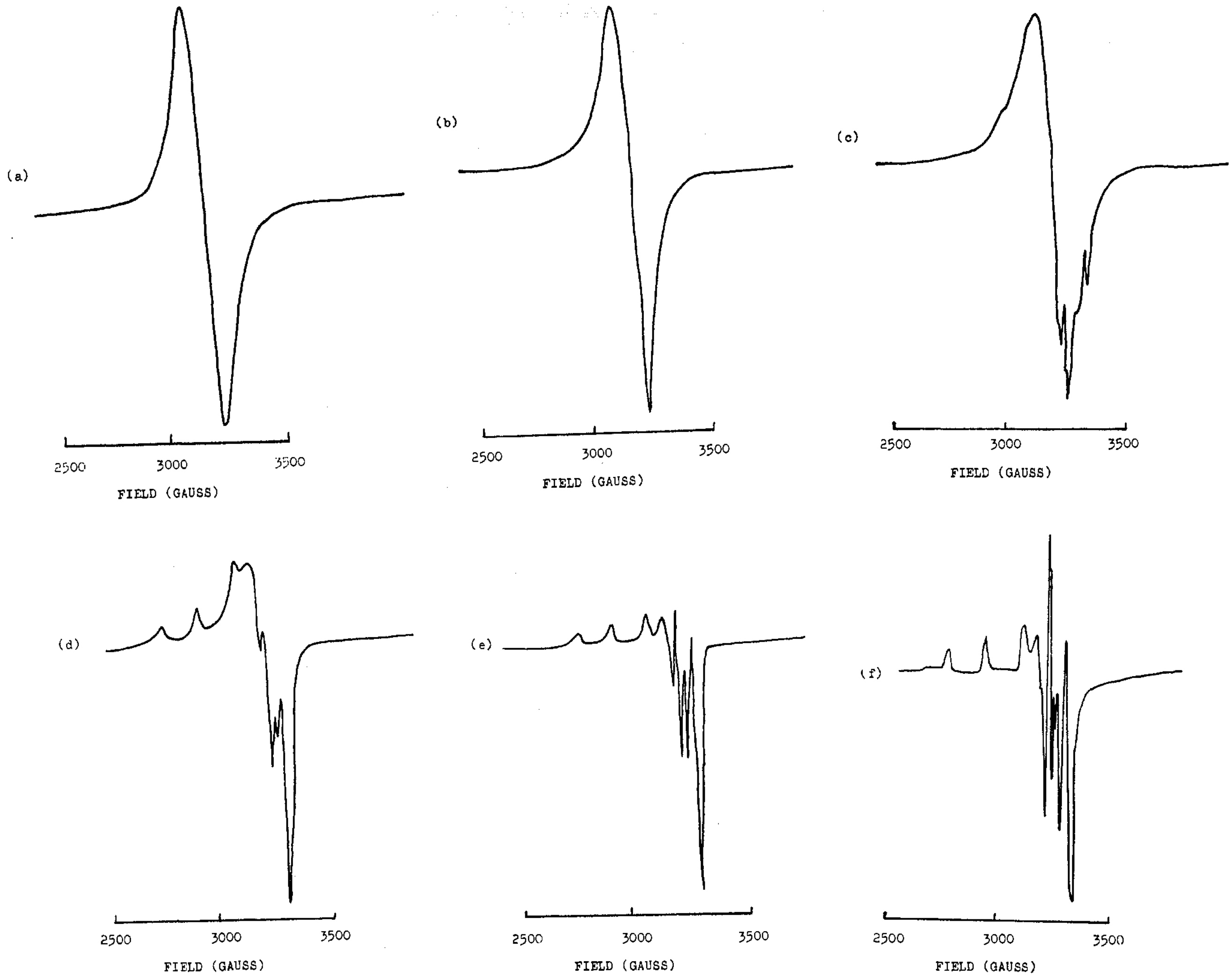

Figure 2.—Esr spectra of 0.05 *M* Cu(ttmb)$_2$ at 77°K and 9.230 GHz in various solvents: (a) dimethyl sulfoxide, (b) petroleum ether (bp 100–120°), (c) chloroform, (d) pyridine, (e) petroleum ether (bp 100–120°) containing 20% by volume of pyridine, and (f) dimethyl sulfoxide containing 20% by volume of chloroform.

monomeric cases while the dipolar and the hyperfine interactions are treated as the perturbations for the dimeric cases. It is possible to obtain analytical formulas for the magnetic fields at which resonance occurs as a function of the orientation of the applied field H with respect to the symmetry axes of the complexes.

The results presented in this paper can be treated using the following model. (1) The two copper(II) ions are in identical sites each of which possesses axial spin Hamiltonians of the form given by eq 1. (We label the separate Hamiltonians H_1 and H_2.) (2) The parallel axes of the g tensors of the two ions are collinear so that the dimer is assumed to have axial symmetry. (3) Dipole–dipole coupling contributes the term

$$\mathcal{H}_d = \frac{\beta^2}{r^3}(g_x^2S_{1x}S_{2x} + g_y^2S_{1y}S_{2y} - 2g_z^2S_{1z}S_{2z}) \quad (3)$$

where r is the copper(II)–copper(II) internuclear separation. (4) Exchange coupling may contribute a term

$$\mathcal{H}_{ex} = -JS_1S_2 \quad (4)$$

which is sufficiently small that no second-order splittings within the triplet states can occur. We write the total spin Hamiltonian for the dimer as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_d + \mathcal{H}_{ex} \quad (5)$$

but in order to appreciate the relative importance of the various terms we rewrite (5) as

$$\mathcal{H} = \mathcal{H}_{Zeeman} + \mathcal{H}_d + \mathcal{H}_{hyperfine} + \mathcal{H}_{ex} \quad (6)$$

(d) Principles of the Computer Simulation of Spectra.—To compute a theoretical line shape for complexes in a frozen glassy state, we must consider contributions from all possible orientations. We assume that the complexes in the samples are randomly oriented. In principle we should clothe the general transition with a suitable line shape function and integrate over all orientations to obtain the result. For dimer problems it is not possible to use analytical integration methods so one approximates the integral by a summation of a finite number of orientations, weighted by a suitable angular factor. A simple case where an analytical calculation was appropriate has been discussed by Pake.[5] Axial cases require a single angle θ ($0 \leq \theta \leq \pi/2$) which H makes with the z or parallel axis of the

[5] G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, New York, N. Y., 1962.

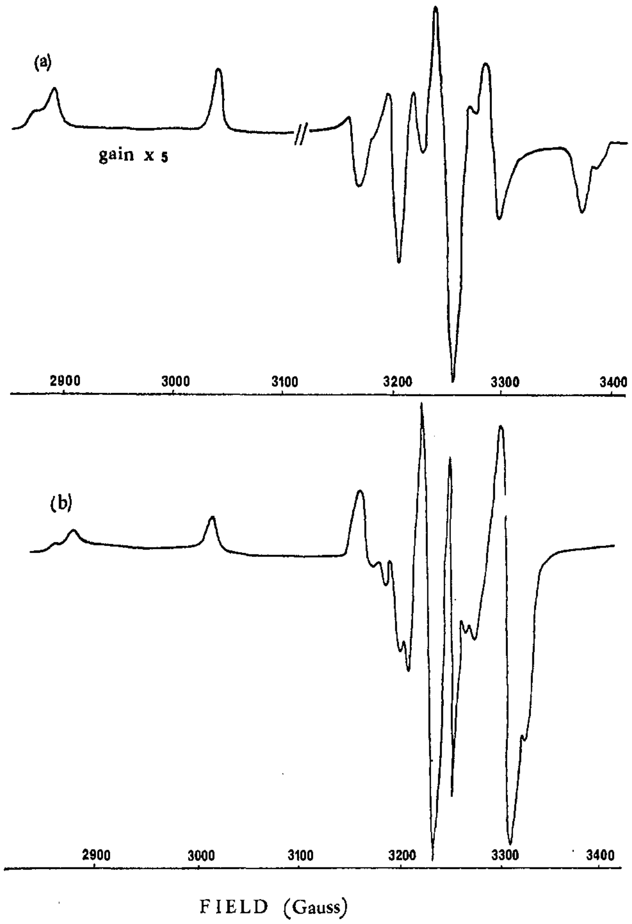

Figure 3.—Esr spectra of copper(II) diethyldithiocarbamate: (a) 0.005 *M* in chloroform containing 60% by volume of toluene at 77°K and 9.140 GHz and (b) 0.005 *M* in chloroform containing 60% by volume of pyridine at 77°K and 9.140 GHz.

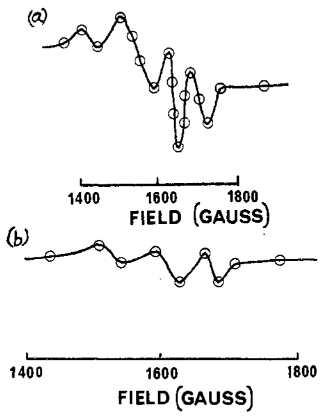

Figure 4.—Esr spectra recorded at high instrument gain in dimethyl sulfoxide containing 20% by volume of chloroform at 77°K and 9.230 GHz: (a) 0.01 *M* Cu(dpmb)$_2$ and (b) 0.05 *M* Cu(ttmb)$_2$. The circles represent the computed curve.

complex. Thus the fraction of complexes whose z axes lie within a cone (θ, $\theta + \Delta\theta$) is approximately $\Delta \cos \theta$. Because $\cos \theta$ varies much more rapidly near 90° than at 0°, we choose equal intervals of $\Delta \cos \theta$ from θ_c to 90°. The value of θ_c is obtained by requiring the values of $\Delta \cos \theta$ on either side of θ_c to be equal or approximately so. The value of this critical angle, θ_c, is 43.6°.

Orthorhombic complexes involve the two spherical polar angles θ and ϕ. The angular distribution of complexes is now $\sim\Delta \cos \theta \Delta\phi$ with θ in the range 0–90° and ϕ in the range 0–90°. Thus to obtain a theoretical line shape, summations are required over the first quadrant only.

The computed line shape is obtained by incrementing the magnetic field over the required range and then by summing up the contributions at each particular value of magnetic field. We use either Lorentzian or Gaussian first-derivative line shapes, correctly weighted by the $\Delta \cos \theta$ or $\Delta \cos \Delta\theta\phi$ factors and a correction for anisotropy of the g tensor. For Gaussian lines we use

$$G = -[(H - H')/\sigma^3] \exp[-(H - H')^2/2\sigma^2] \quad (7)$$

where σ is the peak–peak half-width of the derivative, H' the resonance field of a particular transition, and H the field at which the line shape is being evaluated. In the case of Lorentzian lines we have

$$G = -\sigma(H - H')/[\sigma^2 + (H - H')^2]^2 \quad (8)$$

where σ is the peak–peak half-width of the derivative, H and H' having the same meaning as in the Gaussian case. To allow for the possibility of an anisotropic line width we include the factor $1/\sigma^3$ in (7) and σ in (8) to ensure proper normalization of the line shapes. These factors are vital when the line width is anisotropic.

In practice we take about 90 orientations for θ and approximately 10 orientations in the xy plane for ϕ in orthorhombic cases; however, the required number of these is a function of the degree of anisotropy in the g and hyperfine tensors and the limitation of computer time available.

Such calculations were carried out at the Monash University Computer Centre either on a CDC 3200 or a Burroughs B5500 computer using FORTRAN programs. Output is in the form of a curve produced by the computer line printers. Routines are available for output *via* a CALCOMP graph plotter. By variation of the magnetic parameters used in the simulation of the spectra a unique set was obtained for each experimental spectrum. In the case of the spectra due to dimeric species the main spectral features of the experimental result were fitted to within ±5 G while the peaks in the spectra due to monomeric species were fitted to within ±2 G. The range of values of each magnetic parameter used to achieve the fitting of the experimental curves to within these tolerances is outlined in the relevant tables.

The results obtained for the monomeric copper(II) species studied here were considered from the point of view as to whether the experimental line shapes could best be accounted for by axial or orthorhombic symmetry of the copper(II). The relationship between these two forms is illustrated by Figure 5 which depicts the change of simulated line shapes when the symmetry of the copper(II) ion changes from axial to orthorhombic. The variation in line shape in this case is controlled by the values of g_x, the other parameters remaining constant. The esr spectra at 77°K of the copper(II) chelate of ttmb in pyridine and petroleum ether (bp 100–120°) containing pyridine can be accounted for by an axial Hamiltonian, and the relevant magnetic parameters are shown by Table I. On the other hand, the esr spectra of the copper(II) chelates of dpmb,

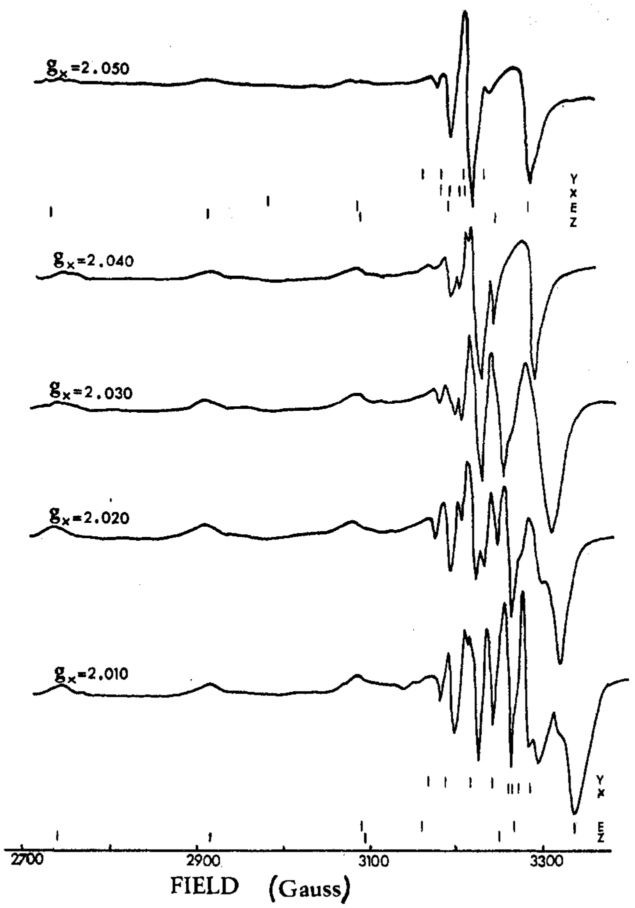

Figure 5.—Computer-simulated monomer spectra illustrating variation from axial to orthorhombic symmetry with changes in g_x, at a microwave frequency of 9.230 GHz. The other parameters remain constant taking the following values: $g_z = 2.188$, $g_y = 2.050$; $A_z = 163$, $A_x = 10$, $A_y = 20$; $\sigma_z = 15$, $\sigma_x = 5$, $\sigma_y = 5$. The stick spectra labeled E, Z, X, and Y correspond to extrema lines (arising from angular variation abnormalities), z, x, and y axes lines, respectively.

TABLE I

Chelate	$g_\parallel$	$g_\perp$	10^4A, cm^{-1}	10^4B, cm^{-1}	σ, G
Cu(ttmb)$_2$ in pyridine	2.204 ±0.001	2.046 ±0.001	155 ± 5	5 ± 5	25
Cu(ttmb)$_2$ in petroleum ether containing 20% pyridine	2.200 ±0.001	2.046 ±0.001	155 ± 5	5 ± 5	25

ttmb, and diethyldithiocarbamate at 77°K in the other solvents used are best accounted for by an orthorhombic Hamiltonian and the results of the line-fitting procedure are shown by Table II. We note that copper-63 and copper-65 hyperfine structure is included specifically for the copper(II) diethyldithiocarbamate case. The parameters of the copper(II) diethyldithiocarbamate have previously been extracted by Gersmann and Swalen using an axial Hamiltonian.[3] However such a treatment does not account for all the lines present and the subtle difference between the experimental line shape and that calculated on the basis of an axial Hamiltonian is explained by the introduction of rhombic terms. Indeed, this departure from axial symmetry is to be expected from an inspection of the crystal structure data.[6] The introduction of pyridine into the copper(II) diethyldithiocarbamate solutions produces changes in the spectrum which indicate a further departure from axial symmetry.

TABLE II

Chelate	g values	Hyperfine constants × 10^4, cm^{-1}	Line widths (σ), G
Cu(dpmb)$_2$ in pyridine	g_z 2.180 ± 0.001	A_z 163 ± 2	σ_z 70
	g_x 2.040 ± 0.001	A_x 20 ± 2	σ_x 80
	g_y 2.050 ± 0.001	A_y 20 ± 2	σ_y 80
Cu(dpmb)$_2$ in dimethyl sulfoxide containing 20% chloroform	g_z 2.180 ± 0.001	A_z 170 ± 2	σ_z 10
	g_x 2.020 ± 0.001	A_x 30 ± 2	σ_x 5
	g_y 2.040 ± 0.001	A_y 30 ± 2	σ_y 5
Cu(ttmb)$_2$ in dimethyl sulfoxide containing 20% chloroform	g_z 2.189 ± 0.001	A_z 165 ± 2	σ_z 15
	g_x 2.044 ± 0.001	A_x 20 ± 2	σ_x 10
	g_y 2.052 ± 0.001	A_y 20 ± 2	σ_y 10
Copper(II) diethyldithiocarbamate in chloroform containing 60% toluene	g_z 2.008 ± 0.001	A_z^{63} 164 ± 1	σ_z 8
	g_x 2.009 ± 0.001	A_z^{65} 175 ± 1	σ_x 4
	g_y 2.021 ± 0.001	A_x^{63} 30 ± 1	σ_y 6
		A_x^{65} 32 ± 1	
		A_y^{63} 48 ± 1	
		A_y^{65} 51 ± 1	
Copper(II) diethyldithiocarbamate in chloroform containing 60% pyridine	g_z 2.120 ± 0.001	A_z^{63} 140 ± 1	σ_z 6
	g_x 2.029 ± 0.001	A_z^{65} 149 ± 1	σ_x 2
	g_y 2.017 ± 0.001	A_x^{63} 24 ± 1	σ_y 5
		A_x^{65} 25 ± 1	
		A_y^{63} 20 ± 1	
		A_y^{65} 26 ± 1	

The magnetic parameters associated with copper(II) when the binding site consists solely of oxygen atoms, as for example in the β-diketones, or solely of sulfur atoms, as in the dialkyldithiocarbamates, have been well documented.[7] The values of the magnetic parameters obtained from the spectra of the Cu(dpmb)$_2$ and Cu(ttmb)$_2$ chelates are close to those obtained for the β-diketone chelates indicating the binding site is dominated by binding to oxygen.

The low-field lines observed in the esr spectra of the Cu^{II}–dpmb and –ttmb chelates are attributed to $\Delta M = 2$ arising from the magnetic dipolar interactions of copper(II) ions in a dimeric species. The results of the computer simulation of these lines is shown by Table III, where it may be noted that the important structural parameter r, the distance between the magnetic point dipoles, taken to be equivalent to the internuclear distance between the copper(II) ions in the dimeric species, is similar for both the monothio-β-diketone chelates.

TABLE III[a]

Chelate	r, Å	$g_\parallel$	$g_\perp$	10^4A, cm^{-1}	10^4B, cm^{-1}	σ, G
Cu(dpmb)$_2$	3.9 ± 0.2	2.34	2.05	220 ± 10	10 ± 5	18
Cu(ttmb)$_2$	4.2 ± 0.2	2.21	2.03	190 ± 10	10 ± 5	18

[a] g values ±0.01.

It may be noted that the g values obtained for the monomeric copper(II) complexes of the monothio-β-diketones are somewhat different from those obtained for their corresponding dimeric forms. A similar situation occurs when comparing the g values of the monomeric copper(II) diethyldithiocarbamate complex with those reported for its dimeric form.[4] This effect is thought to arise from small changes of symmetry which the copper(II) ion undergoes when forming these dimeric chelates.

There is no information available concerning the crystal and molecular structure of the copper(II)

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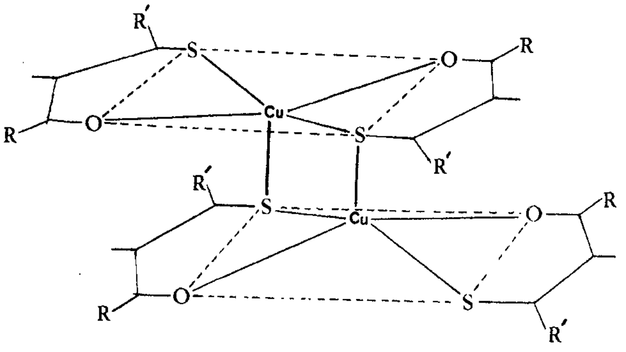
[6] M. Bonamico, G. Dessy, A. Magnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 886 (1965).

[7] H. Landolt and R. Börnstein, "Numerical Data and Functional Relationships in Science and Technology. Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," Vol. 2, Springer-Verlag, Berlin, 1966.

chelates of the monothio-β-diketones. However a preliminary report of relevance as far as the spatial requirements of the ligand are concerned was one made by Shygam, *et al.*,[8] on the X-ray crystal and molecular structure of Pd- and Pt-dpmb chelates. Here, in addition to problems of an interaction between molecules and the structure of the ring containing the metal, the question of cis-trans isomerism is involved for the molecular structure of the unsymmetrical β-diketones. The data indicate that $Pd(dpmb)_2$ has a cis configuration with the angle S_1-Pd-S_2 close to 90° and the Pd-S distances being 2.26 and 2.22 Å. The separation between the copper(II) ions determined by the esr data is compatible with a stacking of the copper(II) chelates in a fashion similar to that found in the crystal structure of copper(II) diethyldithiocarbamate and is represented by structure I. The diethyldithiocarbamate chelate exists as a bimolecular unit in which each pair of centrosymmetrically related copper(II) ions, which share sulfur atoms, are 3.59 Å apart.[6] We have assumed here that the monothio-β-diketone chelates will have an essentially planar structure.



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Appendix

(a) The esr spectra due to monomeric complexes which possess axial symmetry may be accounted for by the spin Hamiltonian

$$\mathcal{H} = \beta[gH_zS_z + g_\perp (H_xS_x + H_yS_y)] + AS_zI_z + B(S_xI_x + S_yI_y)$$

To second order in A and B, normal allowed $\Delta M = 1$ ($M, m \rightarrow M - 1, m$) transitions occur, according to the formula first obtained by Bleaney,[9] at the magnetic field

$$H = H_0 - \left(\frac{K}{g\beta}\right)m - \frac{B^2(A^2 + K^2)}{4K(g\beta)^2H_0}[I(I+1) - m^2] - \frac{AB^2}{2(g\beta)^2H_0K}m(2M - 1) - \left(\frac{A^2 - B^2}{K}\right)^2 \times \left(\frac{g_\| g_\perp}{g^2}\right)^2\left(\frac{\sin^2\theta\cos^2\theta}{2(g\beta)^2H_0}\right)m^2 \quad (9)$$

where $h\nu = g\beta H_0$, $g^2 = g_\|^2\cos^2\theta + g_\perp^2\sin^2\theta$, $K^2g^2 = A^2g_\|^2\cos^2\theta + B^2g_\perp^2\sin^2\theta$, and m and M are the nuclear and electronic quantum numbers, respectively. When $S = {}^1/_2$, because $M = {}^1/_2$, the second to last term in (9) vanishes.

To allow for an anisotropic line width we would use formulas of the type $\sigma^2 = \sigma_\|^2\cos^2\theta + \sigma_\perp^2\sin^2\theta$ or $\sigma^2g^2 = \sigma_\|^2g_\|^2\cos^2\theta + \sigma_\perp^2g_\perp^2\sin^2\theta$. If $g_\|, g_\perp \approx 2$, both formulas give much the same result.

Finally to correct the transition probability for g tensor anisotropy we must include Bleaney's factor[10] $g_\perp^2g_\|^2/(g^2 + 1)$.

(b) For copper(II) complexes where ligand atoms have orthorhombic distribution about the metal ion the appropriate spin Hamiltonian is

$$\mathcal{H} = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z$$

which can be solved in the high-field case correct to second order in A_i to yield $\Delta M = 1$ transitions at the magnetic field

$$H = H_0 - \left(\frac{K}{g\beta}\right)m - \frac{r_1^2 + r_2^2 + r_3^2}{4(g\beta)^2H_0}[I(I+1) - m^2] - \frac{A_xA_yA_z}{2(g\beta)^2H_0K}m(2M - 1) - \frac{r_4^2 + r_5^2}{2(g\beta)^2H_0}m^2 \quad (10)$$

where $g^2 = g_xl_x^2 + g_y^2l_y^2 + g_z^2l_z^2$ and

$$K^2g^2 = A_x^2g_x^2l_x^2 + A_y^2g_y^2l_y^2 + A_z^2g_z^2l_z^2 \quad (11)$$

H_0, m, and M have the same significance as in eq 9. The l_i are the direction cosines of the magnetic field relative to the principal axes of the g and A tensors, and in terms of the polar angles θ and ϕ these are $l_x = \sin\theta\cos\phi$, $l_y = \sin\theta\sin\phi$, and $l_z = \cos\theta$. The r_i are defined as

$$\begin{aligned} r_1 &= Z_zA_\perp/K \\ r_2 &= A_xA_y/A_\perp \\ r_3 &= [A_z(A_y^2 - A_x^2)g_xg_yg_z\sin\phi\cos\phi\cos\theta]/K_gA_\perp g_\perp^2 \\ r_4 &= g_zg_\perp(A_\perp^2 - A_x^2)\sin\theta\cos\theta/K_g^2 \\ r_5 &= [(A_y^2 - A_x^2)g_xg_y\sin\phi\cos\phi\sin\theta]/K_gg_\perp \end{aligned} \quad (12)$$

where

$$\begin{aligned} g_\perp^2 &= g_x^2\cos^2\phi + g_y^2\sin^2\phi \\ A_\perp^2g_\perp^2 &= A_x^2g_x^2\cos^2\phi + A_y^2g_y^2\sin^2\phi \end{aligned} \quad (12a)$$

The expressions in (11) are well known and were discussed, *e.g.*, by Abragam and Bleaney.[11] There are three second-order terms in eq 10 similar to those in eq 9 apart from differences in the coefficients.[12] Also in this case, since $S = {}^1/_2$ and $M = {}^1/_2$, $2M - 1$ vanishes and the second to last term in (8) disappears.

In the event that $A_x \approx A_y \ll A_z$, it might be thought that an adequate second-order perturbation treatment would be possible using eq 2 by putting $B = (A_x + A_y)/2$. This is not recommended for it can lead to a singularity in the second-order correction if $B = 0$ when H is in the xy plane of a complex. The results given in eq 12 and 12a are compatible with those given by Mackey, *et al.*[13] However, Mackey, *et al.*, did not state whether they used second-order terms.

The powder averaged anisotropic transition probability factor required to correct the intensities for

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[8] E. S. Shygam, L. M. Shkol'nikova, and S. E. Livingstone, *J. Struct. Chem. (USSR)*, **8**, 490 (1967).

[9] B. Bleaney, *Phil. Mag.*, **41**, 441 (1951).

[10] B. Bleaney, *Proc. Phys. Soc., London*, **75**, 621 (1960).

[11] A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Oxford University Press, London, Chapter 3, 1970.

[12] The terms in eq 10 are all worked out in different notation by R. M. Golding in his book "Applied Wave Mechanics," Van Nostrand, London, 1969, Appendix G.

[13] J. H. Mackey, M. Kopp, E. C. Tynan, and T. F. Yen, "Electron Spin Resonance of Metal Complexes," Plenum Press, New York, N. Y., 1968, p 51.

g-factor anisotropy[14] for our experimental situation where H is perpendicular to the radiofrequency field is $[g_x{}^2g_y{}^2 \sin^2\theta + g_y{}^2g_z{}^2(\sin^2\phi + \cos^2\theta\cos^2\phi) + g_z{}^2g_x{}^2(\cos^2\phi + \cos^2\theta\sin^2\phi)]/2g^2$. Anisotropy in the line width σ is included in similar fashion to the axial case, $\sigma^2 = \sigma_x{}^2g_x{}^2l_x{}^2 + \sigma_y{}^2g_y{}^2l_y{}^2 + \sigma_z{}^2g_z{}^2l_z{}^2$.

(c) For the esr spectrum due to coupled copper(II) pairs the results may be represented by the spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{hyperfine}} + \mathcal{H}_{\text{d}} + \mathcal{H}_{\text{ex}}$$

Apart from $\mathcal{H}_{\text{ex}}$, the terms in (11) have the relative magnitudes $\mathcal{H}_{\text{Zeeman}} > \mathcal{H}_{\text{d}} > \mathcal{H}_{\text{hyperfine}}$. So we work in a Zeeman representation and consider $\mathcal{H}_{\text{d}}$ and $\mathcal{H}_{\text{hyperfine}}$ together as the perturbation. The matrix elements of $\mathcal{H}_{\text{ex}}$ are also included, but since they do not occur in off-diagonal positions in a coupled representation and serve basically to separate the singlet and triplet states, $\mathcal{H}_{\text{ex}}$ does not influence the way one sets up the perturbation calculations.

The $(2S_1 + 1)(2I_1 + 1)(2S_2 + 1)(2I_2 + 1) = 64$ states for copper(II) pairs are defined initially in an uncoupled representation $|M_1,M_2,m_1,m_2\rangle$. The presence of $\mathcal{H}_{\text{d}}$ and $\mathcal{H}_{\text{ex}}$ in (11) removes the degeneracy of the $|{}^1/_2,-{}^1/_2,m_1,m_2\rangle$ and $|-{}^1/_2,{}^1/_2,m_1,m_2\rangle$ states and leads to a coupled representation in terms of total spin S and corresponding states $|S,M,m_1,m_2\rangle$. Thus, we have the connection between states in the two representations coupled, left side of equation; uncoupled, right side of equation

$$\left.\begin{aligned} |1,1,m_1m_2\rangle &= |{}^1/_2,{}^1/_2,m_1m_2\rangle \\ |1,0,m_1,m_2\rangle &= a|{}^1/_2,-{}^1/_2,m_1,m_2\rangle + \\ &\qquad b|-{}^1/_2,{}^1/_2,m_1,m_2\rangle \\ |1,-1,m_1,m_2\rangle &= |-{}^1/_2,{}^1/_2,m_1,m_2\rangle \end{aligned}\right\}\text{“triplet”} \qquad (13)$$

$$\begin{aligned} |0,0,m_1,m_2\rangle &= c|{}^1/_2,-{}^1/_2,m_1,m_2\rangle + \\ &\qquad d|-{}^1/_2,{}^1/_2,m_1,m_2\rangle \text{ “singlet”} \end{aligned}$$

If hyperfine structure is ignored, $a = b = c = -d = 1/\sqrt{2}$.

The essentials of this treatment have been outlined previously,[15,16] but at that stage the perturbation theory results were really reliable only if $B \ll A$. It has since been established that this restriction is no longer necessary and the results now quoted are the general ones, where

$$\begin{aligned} D_1 &= (\beta^2/4r^3)[g_\perp{}^4\sin^2\theta - 2g_{\|}{}^4\cos^2\theta/g^2] \\ D_2 &= (\beta^2/4r^3)[2g_{\|}{}^2(1 - 2\sin^2\theta) + g_\perp{}^2\sin^2\theta]g_\perp{}^2/g^2 \\ D_3 &= (\beta^2/4r^3)[g_\perp{}^2(g_\perp{}^2 + 2g_{\|}{}^2)\sin^2\theta/g^2] \\ D_4 &= (\beta^2/4r^3)[g_\perp{}^2 + 2g_{\|}{}^2]g_{\|}g_\perp\sin\theta\cos\theta/g^2 \\ R &= (B^2 - A^2)g_{\|}g_\perp\sin\theta\cos\theta/Kg^2 \\ D_1' &= D_1 - {}^1/_4J \qquad\qquad (14) \\ D_2' &= D_2 - {}^1/_2J \\ \phi &= [D_2'^2 + {}^1/_4K^2(m_1 + m_2)^2]^{1/2} \\ a, b &= D_2'/\{D_2'^2 + [\pm\phi + {}^1/_2K(m_1 - m_2)]^2\}^{1/2} \\ c, d &= [\pm\phi + {}^1/_2K(m_1 - m_2)]/\{D_2'^2 + [\pm\phi + \\ &\qquad {}^1/_2K(m_1 - m_1)]^2\}^{1/2} \end{aligned}$$

The a, b, c, and d in (14) are the same as those given in (13). If $J = 0$, then $D_1' = D_1$ vanishes for $\theta' \approx 65°$ depending on the g values, and the various transitions cross over in this region. For $\theta < \theta'$, $H_{1,2}$ refers to the transitions within the triplet while $H_{3,4}$ refers to those which are weakly allowed near $\theta = 0$ involving the singlet state. When $\theta > \theta'$, $H_{1,2}$ and $H_{3,4}$ have their roles reversed. If $|J| \leq h\nu$, the microwave quantum, then $H_{1,2}$ refers to transitions within the triplet for all values of θ.

Resonant Field Position of the $\Delta M = 1$ and $\Delta M = 2$ Transitions.—The steps in the calculation simply involve the transformation of eq 6 into the Zeeman representation and the application of perturbation theory. The resonant field positions for the four possible $\Delta M = 1$ transitions are

$$\begin{aligned} H_{1,2} = H_0[1 &- (2D_4{}^2 + {}^1/_2D_3{}^2)/(g\beta H_0)^2 \mp 2D_1'/g\beta H_0 - \\ &({}^1/_2K(m_1 + m_2) \mp \phi)/g\beta H_0 \mp 2D_4R(m_1 + m_2) \times \\ &(1 + ab)/(g\beta H_0)^2 - {}^1/_2R^2(a^2m_{2,1}{}^2 + b^2m_{1,2}{}^2)/ \\ &(g\beta H_0)^2 - \frac{B^2}{4}\left(\frac{A^2 + K^2}{K^2}\right)[I(I + 1) - \\ &(m_{2,1}{}^2b^2 + m_{1,2}{}^2a^2)]/(g\beta H_0)^2] \qquad (15a) \end{aligned}$$

and

$$\begin{aligned} H_{3,4}(m_1,m_2) = H_0[1 &- (2D_4{}^2 + {}^1/_2D_3{}^2)/(g\beta H_0)^2 \mp \\ &2D_1'/(g\beta H_0) - {}^1/_2[{}^1/_2K(m_1 + m_2) \mp \phi]/(g\beta H_0) \mp \\ &2D_4R(m_1 + m_2)(1 - ab)/(g\beta H_0)^2 - {}^1/_2R^2(a^2m_{1,2}{}^2 + \\ &b^2m_{2,1}{}^2)/(g\beta H_0)^2 - \frac{B^2}{4}\left(\frac{A^2 + K^2}{K^2}\right)[I(I + 1) - m_{1,2}{}^2b^2 + \\ &m_{2,1}{}^2a^2)/(g\beta H_0)^2] \qquad (15b) \end{aligned}$$

The relative transition probabilities are porportional to the square of

$$\left[1 + \frac{D_3}{2g\beta H_0} - \frac{4D_4{}^2}{(g\beta H_0)^2} \mp \frac{D_4R(m_1 + m_2)}{(g\beta H_0)^2}\right]\left(\frac{a + b}{2}\right) \mp \left[\frac{R(m_1 - m_2)(\pm 2D_4 + {}^1/_2R(m_1 + m_2))}{4(g\beta H_0)^2}\right](b - a)$$

for transitions 1 and 2 and

$$\left[1 \pm \frac{D_3}{2g\beta H_0} - \frac{4D_4{}^2}{(g\beta H_0)^2} \mp \frac{D_4R(m_1 + m_2)}{(g\beta H_0)^2}\right]\left(\frac{b - a}{2}\right) \pm \left[\frac{R(m_1 - m_2)(\pm 2D_4 + {}^1/_2R(m_1 + m_2))}{4(g\beta H_0)^2}\right](a + b)$$

for transitions 3 and 4.

Finally we must consider the "forbidden" transition within the triplet which occurs at

$$\begin{aligned} H(m_1,m_2) = H_0[{}^1/_2 &- (2D_4{}^2 + {}^1/_2D_3{}^2)/(g\beta H_0)^2 - \\ &{}^1/_2K(m_1 + m_2)/g\beta H_0 - R^2(m_1{}^2 + m_2{}^2)/(2g\beta H_0)^2 - \\ &\frac{B^2}{4}\left(\frac{A^2 + K^2}{K^2}\right)[2I(I + 1) - (m_1{}^2 + m_2{}^2)]/(g\beta H_0)^2] \end{aligned}$$

This has a relative transition probability of $4D_4{}^2/(g\beta H_0)^2$.

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[14] J. R. Pilbrow, *Mol. Phys.*, **16**, 307 (1969).

[15] R. H. Dunhill, J. R. Pilbrow, and T. D. Smith, *J. Chem. Phys.*, **45**, 1474 (1966).

[16] J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc. A*, 94 (1969).