An Electron Spin Resonance Study of the Structure of Dinuclear Titanium-(III), Vanadyl, and Copper(II) Chelates of Tetrakis(aminomethyl)methane

By **S. G. Carr, P. D. W. Boyd, and T. D. Smith,*** Chemistry Department, Monash University, Clayton, Victoria, Australia, 3168

The triplet-state *X*-band e.s.r. spectra, recorded at sample temperatures of 77 K, due to dinuclear titanium(III), copper(II), and vanadyl ion chelates of tetrakis(aminomethyl)methane which exist in frozen aqueous glycol solution have been interpreted in terms of an interaction spin Hamiltonian which takes into account the symmetry imposed on the paramagnetic ion-pair system by the ligand and which results in a non-parallel alignment of the *g*-tensor axes of the individual paramagnetic ions. Computer simulation of the lineshapes of the triplet-state e.s.r. spectra has been carried out for cases involving isotropic *g*-values and anisotropic *g*-values and in the presence and absence of hyperfine interactions. These calculations are relevant to the determination of the magnetic parameters associated with the dinuclear complexes of titanium(III), copper(II), and vanadyl ions formed by combination with the spiro-amine. The parameter of chief interest is the distance between the magnetic point dipoles which in each case has been related to the internuclear separation of the metal ions in the dinuclear complex by use of molecular models.

RECENT developments in the theory of dipolar coupling between paramagnetic ions of spin $\frac{1}{2}$ in pair systems which exist under conditions of diamagnetic dilution have involved a consideration of the role played by the symmetry of the pair system.[1] The results of these considerations have been expressed in terms of an interaction spin Hamiltonian, the solution of which leads to the ability to compute the lineshape of triplet-state spectra which arise from the magnetic interactions in pair systems of lower than axial symmetry. Comparison of the computed spectra with those observed experimentally enables the recognition, from salient features of the spectra, of circumstances which involve a departure from axial symmetry of the pair system. The fitting of computed lineshapes to experimental spectra enables the determination of the relevant magnetic parameters. Chief interest has been shown in the parameters pertinent to structural considerations of the metal ion-pair system, namely R, the separation of the magnetic point dipoles, and ξ, the angle between the zero-field splitting tensor and the g_z-component of the g-tensor of the individual metal ion. The chemical circumstances which give rise to the formation of such pair systems are varied though a common cause is the dimerisation of centrosymmetric chelate molecules and many examples of this type of interaction occur. Fortunately, X-ray crystallographic studies of such systems have been made and it is possible to compare R and ξ with structural data on the internuclear separation of the metal ions and the angle between the internuclear vector and the g_z axis of the individual ion (*i.e.*, an axis normal to the mean plane of the atoms bonded to the individual metal ion). In a number of cases it has been found that the two sets of structural parameters are compatible, thus lending confidence in the use of e.s.r. data in determining an important aspect of the structure of the dimeric molecule.[2,3] Another common circumstance leading to the formation of metal ion-pair systems whose symmetry may be lower than axial is the formation of dinuclear complexes formed by the combination of metal ions with certain organic ligands. A ligand of

---

[1] P. D. W. Boyd, A. D. Toy, T. D. Smith, and J. R. Pilbrow, *J.C.S. Dalton*, submitted for publication.

[2] A. D. Toy, P. D. W. Boyd, and T. D. Smith, *J.C.S. Dalton*, submitted for publication.

[3] M. D. Hobday, P. D. W. Boyd, and T. D. Smith, *J.C.S. Dalton*, submitted for publication.

particular importance in this respect is tetrakis(aminomethyl)methane whose significance lies with the fact that the spiro-conformation of the methylene groups involves a fixed geometry of the terminal amine groups once they are part of the co-ordination sphere of each metal ion. In these circumstances the pair of ions in the dinuclear complex will have non-parallel alignment of the *g*-tensor axes as indicated by Figure 1. A study of the e.s.r. triplet state spectrum due to the dinuclear copper(II) complex of the spiro-amine has been reported.[4] A preliminary theoretical treatment of the results made possible the computer simulation of the low-field region (*ca.* 1500 G) of the triplet state spectrum due to $\Delta M = \pm 2$ transitions arising from magnetic dipole–dipole coupling of the copper(II) ions in the dinuclear complex. The present investigation deals with the triplet state e.s.r. due to dinuclear complexes containing pairs of titanium(III) ions and vanadyl ions formed by combination of these ions under suitable conditions with the spiro-amine. The role played by the symmetry of the metal ions in these circumstances on the triplet state e.s.r. spectra has been reassessed to make possible a simulation of the complete lineshape the triplet state e.s.r. spectra due to the spiro-amine dinuclear complex of each metal ion system.

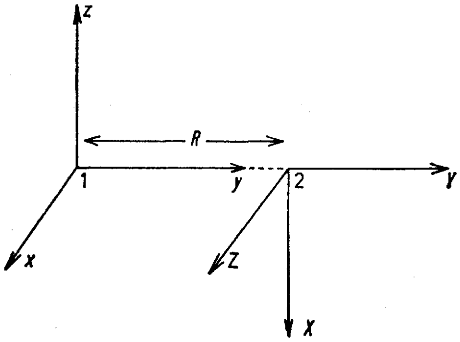

FIGURE 1 Orientations of the principal axes of the *g*-tensor for the metal ions in the spiro-amine dinuclear complex

The *X*-band e.s.r. spectra recorded at sample temperatures of 77 K due to glycol–water solutions containing the metal ion and ligand in 2 : 1 mole ratio at a pH of *ca.* 4, conditions which promote the formation of the dinuclear complexes, is shown in Figure 2. In each case a low-field component of the spectrum was easily observed. The low-field portion of the spectrum, attributable to $\Delta M = \pm 2$ transitions, provides good evidence for the existence of the dinuclear complex in each case.

Quantitative Treatment of the Results.—Pairs of identical ions with non-parallel magnetic axes. Several complications arise in the solution of the spin Hamiltonian for a pair of ions with non-parallel magnetic axes, the most serious of which is the occurrence of matrix elements involving the magnetic field in off-diagonal positions. This problem can be overcome by exact diagonalisation of the Hamiltonian but when hyperfine interactions are present this makes the calculations long. An alternative method, by use of second-order perturbation theory, leads to terms quadratic in H and a solution using this approach leads to a considerable reduction in calculation time. If the frame of reference is taken to be the axes of ion 1, the spin Hamiltonian for the system is (1), where $\mathscr{H}$ is given by equations (2)—(4). The spin Hamiltonian

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 + \mathscr{H}_{\text{int}} \tag{1}$$

$$\mathscr{H}_1 = \beta[g_{\parallel}H_{1z}S_{1z} + g_{\perp}(H_{1x}S_{1x} + H_{1y}S_{1y})] + AI_{1z}S_{1z} + B[I_{1y}S_{1y} + I_xS_{1x}] \tag{2}$$

$$\mathscr{H}_2 = \beta[g_{\perp}H_{1z}S_{2z} + g_{\parallel}H_{1y}S_{2y} + g_{\perp}H_{1x}S_{2x}] + AI_{2x}S_{2x} + B[I_{2y}S_{2y} + I_{2z}S_{2z}] \tag{3}$$

$$\mathscr{H}_{\text{int}} = \mathscr{H}_{\text{dip}} + \mathscr{H}_{\text{ex}} = \beta^2[g_{\parallel}g_{\perp}(S_{1x}S_{2x} + S_{1z}S_{2z}) - 2g_{\parallel}{}^2S_{1y}S_{2y}]/R^3 - JS_1S_2 \tag{4}$$

can be solved by use of non-degenerate perturbation theory to second order, treating the dipolar and hyperfine terms as a perturbation on the Zeeman interaction. The spin Hamiltonian in the Zeeman transformation, with neglect of terms leading to non-secular elements, can be represented by equation (5), with (6)—(16).

$$\begin{aligned}\mathscr{H} = {} & g_1\beta HS_{1z}{}' + g_2\beta HS_{2z}{}' + Z1\beta HS_{2x}{}' + Z2\beta HS_{2y}{}' \\ & + K1I_{1z}{}''S_{1z}{}' + R1S_{1x}{}'I_{1z}{}'' + P1I_{2z}{}''S_{2z}{}' \\ & + P2I_{2x}{}''S_{2z}{}' + P3I_{2y}{}''S_{2z}{}' + P4I_{2z}{}''S_{2x}{}' \\ & + P5I_{2z}{}''S_{2y}{}' + \sum_{p,\,q} D_{pq}S_{1p}S_{2q}\end{aligned} \tag{5}$$

$$g_1 = (g_{\parallel}{}^2 \cos^2\theta + g_{\perp}{}^2 \sin^2\theta)^{\frac{1}{2}} \tag{6}$$

$$g_2 = (g_{\perp}{}^2 \cos^2\theta + g_{\perp}{}^2 \sin^2\theta \sin^2\phi + g_{\parallel}{}^2 \sin^2\theta \cos^2\phi)g_1 \tag{7}$$

$$Z1 = (-g_{\perp} \cos\theta \sin\psi + (g_{\parallel} + g_{\perp}) \sin\theta \cos\psi \sin\phi \cos\phi) \tag{8}$$

$$Z2 = (g_{\perp} - g_{\parallel}) \sin\theta \sin\phi \cos\phi \tag{9}$$

$$K1 = (A^2g_{\parallel}{}^2 \cos^2\theta + B^2g_{\perp}{}^2 \sin^2\theta)^{\frac{1}{2}}/g_1 \tag{10}$$

$$R1 = (B^2 - A^2)g_{\parallel}g_{\perp} \sin\theta \cos\theta/Kg_1{}^2 \tag{11}$$

$$P1 = A \sin\beta \sin\psi \cos^2\phi + B(\sin\beta \sin\psi \sin^2\phi + \cos\beta \cos\psi) \tag{12}$$

$$P2 = A \cos\beta \sin\psi \cos^2\phi + B(\cos\beta \sin\psi \sin^2\phi - \sin\beta \cos\psi) \tag{13}$$

$$P3 = -A \sin\phi \cos\phi \sin\psi + B\sin\phi \cos\phi \sin\psi \tag{14}$$

$$P4 = A \sin\beta \cos\psi \cos^2\phi + B(\sin\beta \cos\psi \sin^2\phi - \cos\beta \sin\psi) \tag{15}$$

$$P5 = -A \sin\beta \cos\phi \sin\phi + B \sin\beta \cos\phi \sin\phi \tag{16}$$

In previous considerations[1] the simple product basis states were used to solve the spin Hamiltonian after transformation by diagonalisation of the inner matrix of basis states $|\tfrac{1}{2} - \tfrac{1}{2}m_1m_2\rangle$ and $|-\tfrac{1}{2}\tfrac{1}{2}m_1m_2\rangle$. In the present case the same difficulty arises but in addition the coefficients of the transformed basis states are now dependent on the magnetic field. This difficulty may

---

[4] T. D. Smith and A. E. Martell, *J. Amer. Chem. Soc.*, 1972, to be published.

be surmounted by transforming the simple product basis states as in equations (17) and (18) where $a =$

$$|\psi_1\rangle = |\tfrac{1}{2}\tfrac{1}{2}m_1m_2\rangle; \quad |\psi_2\rangle = a|\tfrac{1}{2} - \tfrac{1}{2}m_1m_2\rangle + b|-\tfrac{1}{2}\tfrac{1}{2}m_1m_2\rangle \tag{17}$$

$$|\psi_3\rangle = |-\tfrac{1}{2} - \tfrac{1}{2}m_1m_2\rangle; \quad |\psi_4\rangle = c|\tfrac{1}{2} - \tfrac{1}{2}m_1m_2\rangle + d|-\tfrac{1}{2}\tfrac{1}{2}m_1m_2\rangle \tag{18}$$

$b = c = -d = 1/\sqrt{2}$. The matrix elements of the spin Hamiltonian with respect to these basis states for the triplet state only are shown in Table 1.

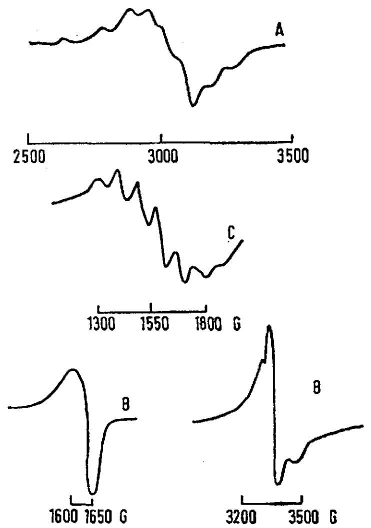

FIGURE 2 X-Band e.s.r. spectra at 77 K of a water–ethylene glycol solution of transition-metal ion (0·1M) and spiro-amine (0·05M) at pH *ca.* 4; A, copper(II); B, titanium(III); C, vanadyl ion

TABLE 1

	$\lvert\psi_1\rangle$	$\lvert\psi_2\rangle$	$\lvert\psi_3\rangle$
$\langle\psi_1\rvert$	$(g_1 + g_2)\beta H/2 + (K1m_1 + P1m_2)/2 + D_{zz}/4 - J/4$	$V1 + V01 + i(V2 + V02)$	$V3 + iV4$
$\langle\psi_2\rvert$	$V1 + V01 - i(V2 + V02)$	$-D_{zz}/4 + V7$	$V5 + V05 + i(V6 + V06)$
	$V3 - iV4$	$V5 + V05 - i(V6 + V06)$	$-(g_1 + g_2)\beta H/2 - (K1m_1 + P1m_2)/2 + D_{zz}/4 - J/4$

$V1 = [D_{xz} + P2m_2 + R1m_1]/2\sqrt{2}$; $V2 = [D_{yz} - P3m_2]/2\sqrt{2}$; $V3 = [D_{xx} - D_{yy}]/4$; $V4 = D_{xy}/2$; $V5 = (R1m_1 + P2m_2 - D_{xz})/2\sqrt{2}$; $V6 = (-D_{yz} - P3m_2)/2\sqrt{2}$; $V7 = (D_{xx} + D_{yy})/4$; $V01 = Z1\beta'H/2$; $V02 = Z2\beta'H/2$; $V05 = V01$; $V06 = V02$; $\beta' = \beta/\sqrt{2}$.

By use of second-order perturbation theory the energies $E1$ and $E3$ of energy levels 1 and 3 can be calculated, as in equations (19) and (20), where $V12 =$

Thus $W = h\nu = E1 - E3$ (19)

$$= (g_1 + g_2)\beta H + (K1m_1 + P1m_2) + V12/W + V34/W + V56/W \tag{20}$$

$VP1^2 + VP2^2$; $V34 = V3^2 + V4^2$; $V56 = VP5^2 + VP6^2$; $VP1 = V1 + V01$, $VP2 = V2 + VP2$, $VP5 = V5 + V05$, and $VP6 = V6 + V06$.

The terms $V12$ and $V56$ contain the magnetic field H and lead to a quadratic equation in H. Solution of this equation leads to only one positive value of H. The transition field for the $\Delta M = \pm 2$ transitions is given by equations (21)—(24).

$$H(1{,}3) = [-Q + (Q^2 - 4PR)^{\frac{1}{2}}]/2P \tag{21}$$

$$P = \beta^2[Z1^2 + Z2^2]/2W \tag{22}$$

$$Q = (g_1 + g_2)\beta + \beta[Z1(V1 + V5) + Z2(V2 + V6)]/W \tag{23}$$

$$R = (K1m_1 + P1m_2) + (V1^2 + V2^2 + V34 + V5^2 + V6^2)/W - W \tag{24}$$

In a similar manner the $\Delta M = \pm 1$ transition fields may be calculated, as in equations (25)—(32). The

$$H(1, 2) = (-T1 + \sqrt{T1^2 - 4T2T3})/2T2 \tag{25}$$

$$H(2, 3) = (-S1 + \sqrt{S1^2 - 4S2S3})/2S2 \tag{26}$$

$$T1 = (g_1 + g_2)\beta/2 + (2V1Z1 + 2V2Z2 - V5Z1 - V6Z2)\beta/W \tag{27}$$

$$T2 = P/2 \tag{28}$$

$$T3 = (K1m_1 + P1m_2)/2 + D_{zz}/2 - V7 + V34/2W + (2V1^2 + 2V2^2 - V5^2 - V6^2)/W - W \tag{29}$$

$$S1 = (g_1 + g_2)\beta/2 + (2V5Z1 + 2V6Z2 - V1Z1 - V2Z2)\beta/W \tag{30}$$

$$S2 = P/2 \tag{31}$$

$$S3 = (K1m_1 + P1m_2)/2 - D_{zz}/2 + V7 + V34/2W + (2V5^2 + 2V6^2 - V1^2 - V2^2)/W \tag{32}$$

transition probabilities for the above transitions are proportional to the square of the matrix element $|\langle\psi_i'|S_{1x} + S_{2x}|\psi_j'\rangle|$ multiplied by a factor $F1$ which accounts for the anisotropy of the g-tensor in the two ions. For the $\Delta M = \pm 1$ transitions transition probabilities are proportional to $F(1,\ 2) = F1(TP1^2 + TP2^2)$ where the terms are defined in equations (33) and (34), and $F(2,\ 3) = F1(TP3^2 + TP4^2)$ where the terms are defined in equations (35) and (36). For $\Delta M = \pm 2$ transitions the probabilities are proportional to $F(1,\ 3) = F1(TP5^2 + TP6^2)$ where the terms are defined by (37) and (38).

$$TP1 = 1{\cdot}0 - (VP1^2 + VP2^2 - VP1\,.\,VP5 + VP2\,.\,VP6)/W^2 + V3/2W \tag{33}$$

$$TP2 = V4/2W + (VP2\,.\,VP5 + VP1\,.\,VP6)/W^2 \tag{34}$$

$$TP3 = 1{\cdot}0 - (VP5^2 + VP6^2 - VP1\,.\,VP5 + VP2\,.\,VP6)/W^2 - V3/2W \tag{35}$$

$$TP4 = V4/2W - (VP1\,.\,VP6 + VP2\,.\,VP5)/W^2 \tag{36}$$

$$TP5 = (VP1 - VP5)/W - (V3 \,.\, VP1 + V4 \,.\, VP2 + V3 \,.\, VP5 + V4 \,.\, VP6)/2W^2 \qquad (37)$$

$$TP6 = (VP6 + VP2)/W - (V3 \,.\, VP2 - V4 \,.\, VP1 + V4 \,.\, VP5 - V3 \,.\, VP6)/2W^2 \qquad (38)$$

the point magnetic dipoles, by Figure 4. The computed lineshapes of the triplet-state spectra shown by Figure 5 are those expected from a pair system involving anisotropic *g*-values and hyperfine interactions when the nuclear spin of each individual paramagnetic ion is $\frac{3}{2}$.

state e.s.r. spectrum in this case. The value of R is closely similar for each dinuclear complex and is compatible with the internuclear separation of the metal ions as deduced from molecular models.

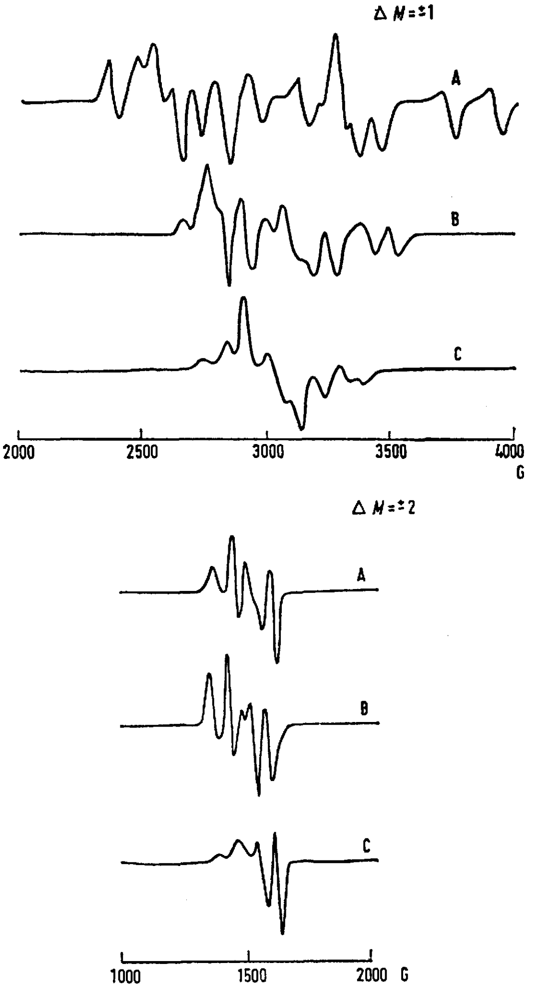

FIGURE 5 Computer-simulated $\Delta M = \pm 1$ and ± 2 spectra for various values of R with values of the other parameters as follows: $g_{\parallel} = 2{\cdot}30$, $g_{\perp} = 2{\cdot}06$, $A = 180 \times 10^{-4}$ cm^{-1}, $B = 10 \times 10^{-4}$ cm^{-1}; R for A, 3·5 Å; B, 4·5 Å; and C, 5·5 Å

EXPERIMENTAL

Solutions containing copper(II) and vanadyl ions were prepared from analysed aqueous stock solutions of copper(II) and vanadyl chlorides. In the experiments involving titanium(III), commercial titanium(III) trichloride was used without further purification. Tetrakis(aminomethyl)methane tetrahydrochloride was prepared by the method of Litherland and Mann.[5] The solvent used in the preparation of solutions for e.s.r. measurements was water–ethylene glycol (20% v/v). Solutions of the metal halides and the ligand were prepared by simple mixing of stock solutions with adjustment of the pH by addition of sodium hydrogen carbonate followed by the e.s.r. measurements. All manipulations and transfer operations were carried out under nitrogen. The e.s.r. spectra were recorded at 77 K as the first derivative of the absorption signal.

TABLE 2

Calculated magnetic parameters for dinuclear species. Errors give range of parameters on which theoretical curves are compatible with observed e.s.r. spectra

Paramagnetic dinuclear complex	Transition	$g_{\parallel}$	$g_{\perp}$	$10^{-4}A$/cm^{-1}	$10^{-4}B$/cm^{-1}	σ/G	R/Å
Titanium(III)	$\Delta M = \pm 1$	1·92 ±0·01	1·92 ±0·01				5·6 ±0·3
Copper(II)	$\Delta M = \pm 1$	2·29 ±0·01	2·06 ±0·01	210 ±10	30 ±10	15	5·7 ±0·3
Vanadium(IV)	$\Delta M = \pm 2$	1·98 ±0·02	1·96 ±0·02	220 ±20	80 ±10	20	5·7 ±0·03

The triplet-state spectra were shown to be independent of the concentration of the metal ion used. A Varian V-4531 100 kHz multipurpose cavity was used in conjunction with a 3 cm spectrometer of conventional design operating in the absorption mode with the klystron locked to the resonant cavity by an automatic frequency controller. All spectra at 77 K were recorded at 9140 MHz.

[2/176 *Received, 28th January,* 1972]

---

[5] A. Litherland and F. G. Mann, *J. Chem. Soc.*, 1938, 1588.