An Electron Spin Resonance Study of the Metal Ion Separations in Dimeric Copper(II) and Vanadyl Chelates of 4,4′,4″,4‴-Tetrasulphophthalocyanine

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

Electron spin resonance measurements involving water–dimethylformamide solutions of the copper(II) and vanadayl chelates of 4,4′,4″,4‴-tetrasulphophthalocyanine carried out at room temperature and 77 K provide good evidence for the formation of dimers. The spectra obtained at 77 K, attributable to dimeric forms of the chelates, arise from triplet state formation. Use of an appropriate spin Hamiltonian enables the simulation of the dimer e.s.r. lineshape. The resulting calculations provide values of the magnetic parameters for the triplet state and allow a determination of the metal-ion separations, which give a measure of the interplanar distance in the dimeric chelates, by use of the magnetic dipole–dipole interaction model. Spectra obtained by use of varying solvent mixtures provide information on the distribution of the chelate species in terms of monomeric, dimeric, and polymeric forms.

THE energetics of the dimerisation of aqueous solutions of 4,4′,4″,4‴-tetrasulphophthalocyanine (tspc) has been investigated by Eyring *et al.*[1,2] using kinetic and thermodynamic data. The dimerisation is exothermic and despite a decrease in entropy is favoured energetically. The dissociation was analysed in terms of an electrostatic model involving charges separated by about 5 Å in the activated complex. This information combined with crystallographic data set the limits of separation of the planar molecules to lie between 3·38 and 5 Å in the dimer unit. The visible spectra of argon matrix-isolated phthalocyanines has been studied by Lucia *et al.*[3] who attributed the results obtained in more concentrated solutions to arise from interacting pairs. The coupling of transition dipoles was invoked to correlate the observed spectrum with copper(II) phthalocyanine pair configurations. Calculations with use of non-bonded atom potentials were carried out to find the most stable relative orientation of the two molecules for various intermolecular distances. For distances between 4 and 5 Å the fully eclipsed 'sandwich' configuration was most stable while at shorter distances the two planes were twisted to attain maximum stability. Thus in these and related studies concerned with dimer formation of planar molecules firm knowledge of the interplanar separation contributes essential information to the understanding of the dimerisation process.

Recent progress in the quantitative treatment of the e.s.r. spectra of systems involving spin–spin interactions between metal ions where the major contribution to zero field splitting is the magnetic dipole–dipole interaction has provided a means for the determination of the distance between the magnetic point dipoles which can be equated to the internuclear separation of the ions.[4] In the present investigation e.s.r. spectroscopy has been used to examine dimers formed from sulphonated phthalocyanine chelates in solution and frozen solution and from the spectra obtained the internuclear distance between the ions, in this case copper(II) and vanadyl ions, calculated.

RESULTS

The e.s.r. spectrum of an aqueous solution of the copper(II)tspc chelate at room temperature consists of a weak isotropic line at *g ca.* 2. At 77 K again an isotropic signal was obtained at *g ca.* 2. The addition of dimethylformamide to form solvent mixtures containing up to 50% (v/v) of dimethylformamide had little effect on the signal observed at 77 K in the *g ca.* 2 region though a signal could now be detected at *g ca.* 4. Increasing the amount of dimethylformamide to 75% (v/v) of the solvent mixture gave the spectrum shown in Figure 1. In these circumstances a resolution of the signal at *g ca.* 2 occurs while the signal at *g ca.* 4 is clearly discerned. The low-field component of the spectrum is attributable to $\Delta M = \pm 2$ transitions arising from the triplet state formed by coupling of the copper(II) ions in a dimeric form of the copper(II)tspc

---

[1] Z. A. Schelly, R. D. Farina, and E. M. Eyring, *J. Phys. Chem.*, 1970, **74**, 617.

[2] Z. A. Schelly, D. J. Harward, P. Hemmes, and E. M. Eyring, *J. Phys. Chem.*, 1970, **74**, 3040.

[3] E. A. Lucia, F. D. Verderane, and G. Taddei, *J. Chem. Phys.*, 1970, **52**, 2307.

[4] (*a*) P. D. W. Boyd, T. D. Smith, J. H. Price, and J. R. Pilbrow, *J. Chem. Phys.*, 1972, in the press; (*b*) T. D. Smith, T. Lund, J. R. Pilbrow, and J. H. Price, *J. Chem. Soc.* (*A*), 1971, 2936.

chelate while the signal at *g ca.* 2 indicates that the corresponding $\Delta M = \pm 1$ transition may also be observed. In solutions containing still further amounts of dimethylformamide (90% v/v) the spectrum in the *g ca.* 2 region shows the presence of a highly resolved spectrum similar to that observed by Rollman and Iwamoto[5] in dimethyl sulphoxide due to monomeric species though a very weak $\Delta M = 2$ transition was still present.

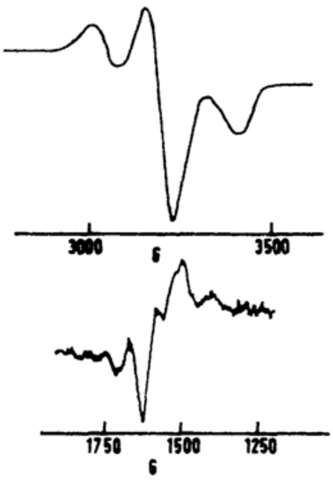

FIGURE 1 The *X*-band e.s.r. spectrum due to the copper(II) tspc chelate (0·01M) in 75% dimethylformamide–water mixture at 77 K; ν = 9140 MHz

The e.s.r. spectrum of an aqueous solution containing 0·01M-vanadyl tspc chelate at room temperature is shown in Figure 2 which depicts the effect of additions of dimethylformamide to the solvent mixture. The corresponding spectra at 77 K are shown in Figure 3; optimum conditions for observations of the multi-line system at *g ca.* 2 are found in solutions with 50% (v/v) of dimethylformamide. The complex spectrum at *g ca.* 2 is due almost entirely to $\Delta M = \pm 1$ transitions from the dimeric vanadyl tspc chelate. The observation of a low-field line at *g ca.* 4 due to a $\Delta M = \pm 2$ transition confirms the assignment of the *g ca.* 2 line. In solutions containing 75% (v/v) of dimethylformamide the spectrum at *g ca.* 2 shows lines clearly due to monomeric vanadyl species. In a 50% dimethylformamide–water solution containing a ten-fold excess of nickel(II)tspc chelate over that of copper(II) or vanadyl chelates, the spectra observed were those due to uncoupled vanadyl or copper(II) ions.

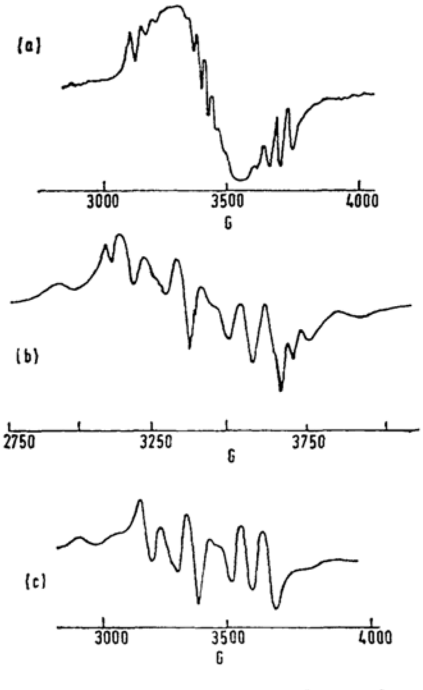

FIGURE 2 The *X*-band e.s.r. spectrum due to the vanadyl tspc chelate in various solvent mixtures at room temperature: (a) 0·04M in water, ν = 9501 MHz; (b) 0·02M in 50% dimethylformamide–water, ν = 9502 MHz; (c) 0·01M in 75% dimethylformamide–water, ν = 9504 MHz

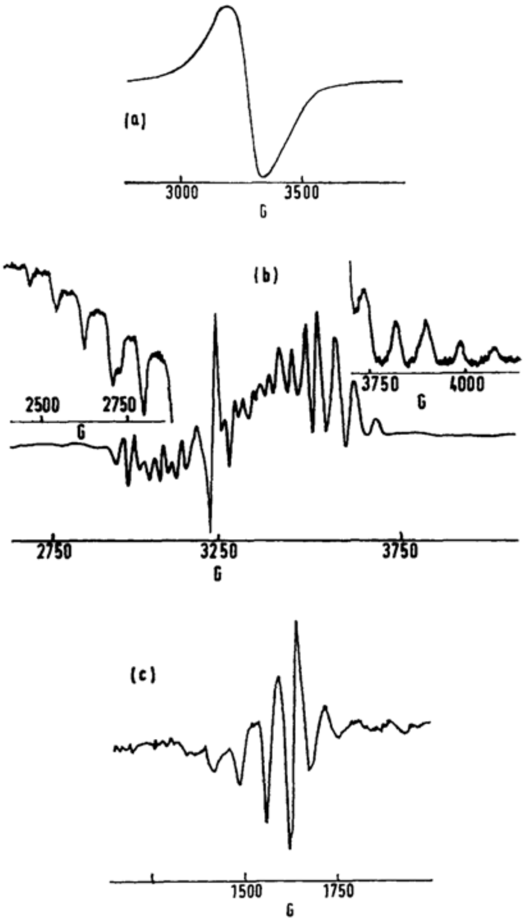

FIGURE 3 The *X*-band e.s.r. spectrum due to the vanadyl tspc chelate in various solvent mixtures at 77 K: (a) 0·04M in water, ν = 9137 MHz; (b) 0·02M in 50% dimethylformamide–water, ν = 9138 MHz; (c) 0·01M in 75% dimethylformamide–water, ν = 9138 MHz

Theoretical Considerations of the Spectra Due to Interacting Ions of Spin ½.—The interaction of the paramagnetic ions of $S = \frac{1}{2}$ in the dimeric species will give rise to a singlet ($S = 0$) and triplet ($S = 1$) states. As discussed pre-

---

[5] L. D. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 1455.

viously[4] this situation is represented by the spin Hamiltonian (1), where $\mathscr{H}_1$ and $\mathscr{H}_2$ are the individual ion spin

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 + \mathscr{H}_{\text{int}} \qquad (1)$$

Hamiltonians which take the form (2). $\mathscr{H}_{\text{int}}$ represents

$$\mathscr{H}_i = g_{i\parallel}\beta H_{iz}S_{iz} + g_{i\perp}\beta(H_{ix}S_{ix} + H_{iy}S_{iy}) + A_iS_{iy}I_{iz} + B_i(S_{ix}I_{ix} + S_{iy}I_{iy}) \text{ where } i = 1,2 \qquad (2)$$

the interaction Hamiltonian for the two paramagnetic ions and consists[6] of (1) isotropic exchange, $-JS_1S_2$, (2) magnetic dipole–dipole interactions, and (3) anisotropic exchange terms. The isotropic exchange serves to separate the singlet and triplet states while the effect of (2) and (3) is to separate levels within the triplet state. In the case of copper(II) and vanadyl ions when the isotropic exchange is small the anisotropic exchange is small compared with the magnetic dipole–dipole interaction and hence the major contribution to zero field splitting within the triplet state arises from the dipolar term.

In the cases considered here we assume that the two ions are in identical sites of axial symmetry and hence the interaction spin Hamiltonian is (3), where the anisotropic

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

exchange terms are considered to be negligible. This is equivalent to using a term of the form (4) where $D =$

$$\mathscr{H}_{\text{int}} = -JS_1S_2 + D(S_z{}^2 - \tfrac{1}{3}S(S + 1) \qquad (4)$$

$-\beta^2/R_3(g_\parallel{}^2 + \frac{1}{2}g_\perp{}^2)$ is the zero field splitting term within the triplet state. However, for reasons which have to do with the line simulation procedures we use the former representation. (The possibility of non-axial symmetry was considered and calculations such as those described in previous work showed that the dimer is axial to within ±20°.[7]) For the systems involving interacting pairs of copper(II) ions the transition fields have been previously calculated.[8] For similar systems involving the vanadyl ion it is necessary to take into account terms involving B and AB/K.[4] Again transition fields can be calculated by use of non-degenerate time-independent perturbation theory to second order in perturbations of the Zeeman interaction for both $\Delta M = \pm 1$, $\Delta m_1 = 0$, $\Delta m_2 = 0$, and forbidden $\Delta M = \pm 2$ transitions after transformation of the basis functions to remove near degeneracy of states $|\frac{1}{2} - \frac{1}{2}m_1m_2\rangle$ and $|-\frac{1}{2}\frac{1}{2}m_1m_2\rangle$. Transition probabilities can be calculated from first-order functions with a factor accounting for the anisotropy of the g tensor $g_\perp{}^2(1 + g_\parallel{}^2/g^2)$. In all the calculations in the present investigation terms involving B and AB/K were included for both copper(II) and vanadyl cases. The computed lineshapes were obtained by incrementing the magnetic field over the required range and summing the contributions for each particular value of magnetic field by use of either Lorentzian or Gaussian first-derivative line-shapes correctly weighted by $\Delta \cos \theta$ as described previously. Such calculations were carried out at the Monash University Computer Centre on a CDC 3200 computer with Fortran programs.

For the copper(II)tspc chelate in aqueous solutions the isotropic signal is due to coupling of a large number of copper(II) ions. Similar spectra have been found for higher aggregates of Uroporphyrin III by Blumberg and Peisach.[9] The origin of this line is discussed by Pake.[10]

Dimeric copper(II)tspc chelate observed in 75% dimethylformamide–water exhibits two peaks in the g *ca.* 2 region due to the perpendicular (x, y) parts of the $\Delta M = \pm 1$ transition but the parallel (z) part of the spectrum was not resolved. At low field a well resolved $\Delta M = \pm 2$ signal was observed. The two portions of the spectrum were fitted by use of an axial model for the dimer. This yielded identical parameters from both $\Delta M = \pm 1$ and $\Delta M = \pm 2$ parts of the spectrum where they could be compared. The simulated line-shape for the observed spectrum is shown in Figure 4. The central part of the $\Delta M = \pm 1$ signal in the observed spectrum is due to remaining polymer signal.

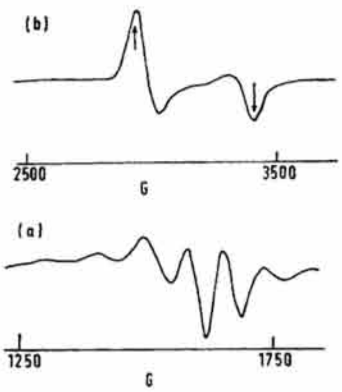

FIGURE 4 Simulated line-shape of the e.s.r. spectrum due to the dimeric copper(II)tspc chelate: (a) $\Delta M = \pm 2$ signal; $g_\parallel = 2{\cdot}20$, $g_\perp = 2{\cdot}04$, $A = 0{\cdot}02$ cm^{-1}, $B = 0{\cdot}002$ cm^{-1}, $D = 0{\cdot}038$ cm^{-1}, $R_{\text{Cu–Cu}} = 4{\cdot}3$ Å, $\sigma = 20$ G: (b) $\Delta M = \pm 1$ signal; $g_\perp = 2{\cdot}04 \pm 0{\cdot}01$, $D = 0{\cdot}038$ cm^{-1}, $R_{\text{Cu–Cu}} = 4{\cdot}3 \pm 0{\cdot}1$ Å. For the computation of the spectra in the case of the $\Delta M = \pm 1$ signal parameters obtained for the $\Delta M = \pm 2$ were used, except for $g_\perp$ and D, as only the perpendicular peaks, indicated by arrows, were resolved in the experimental spectrum

For aqueous solutions of the vanadyl tspc chelate the isotropic signal arises from a similar mechanism to that of the copper complex. The dimeric vanadyl tspc chelate observed in 50% dimethylformamide–water gives a multi-line spectrum at room temperature similar to that observed in vanadyl tartrates[11,12] at low pH. Aside from the multi-line spectrum unresolved side bands can be seen at *ca.* ±500 G from the centre of the spectrum. At 77 K the salient features of the spectrum due to the dimer are the complex $\Delta M = \pm 1$ signal with a broad underlying

---

[6] B. Bleany and A. Abragam, 'Paramagnetic Resonance of Transition Ions,' Oxford Univ. Press, 1970.

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

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

[9] W. E. Blumberg and J. Peisach, *J. Biol. Chem.*, 1965, 240, 870.

[10] G. E. Pake, 'Paramagnetic Resonance,' Benjamin, New York, 1962.

[11] R. H. Dunhill and T. D. Smith, *J. Chem. Soc.* (*A*), 1968, 2189.

[12] L. C. Dickinson, R. H. Dunhill, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 922.

envelope together with a relatively intense line at *ca.* 3250 G. The experimental lineshape in this region can be explained as follows: The $\Delta M = \pm 2$ transition can be fitted by use of an axial model as described previously.[4] The parallel and perpendicular parts of the $\Delta M = \pm 1$ transitions overlap extensively because of the similarity of $g_{\parallel}$ and $g_{\perp}$. The broad envelope of the $\Delta M = \pm 1$ signal arises from the overlapping of the parallel and perpendicular parts of the spectrum. At higher gain a number of lines are observed well away from the centre of the spectrum. These are due to parallel components of the $\Delta M = \pm 1$ signal. Figure 5 shows the $\Delta M = \pm 1$ signal calculated along the parallel and perpendicular axes and the total simulated spectrum. The fitting of the $\Delta M = \pm 1$ and $\Delta M = \pm 2$ signals enables convergence on a good set of magnetic parameters for the dimer. The sharp signal at *ca.* 3250 G is due to residual monomer signal. The complete simulation of the experimental spectrum was achieved by the summation of spectra due to dimeric species and *ca.* 1% of the monomer. The parameters used to simulate the monomer spectrum were as follows: $g_{\parallel}$ 1·96, $g_{\perp}$ 1·99, $A = 0{\cdot}0145$ cm^{-1}, $B = 0{\cdot}006$ cm^{-1}, and $\sigma = 15$ G. In the final selection of parameters the distances between the point magnetic dipoles which can be equated to the internuclear distances between the metal ions are 4·3 ± 0·2 Å for the copper(II) dimer and 4·5 ± 0·1 Å for the vanadyl dimer. The interionic distance is closely similar in each dimer and the extra distance in the vanadyl dimer may be attributed to the vanadyl ion sitting slightly out of the plane of the phthalocyanine molecule. The interplanar separation which may be equated to the interionic separation is seen to be little influenced by the nature of the dipositive cation though the distribution of the various species in solution is markedly different.

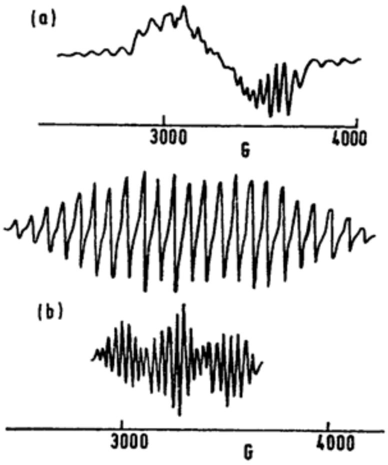

FIGURE 5 Simulated line-shape of the e.s.r. spectrum due to the dimeric vanadyl tspc chelate: (a) $\Delta M = \pm 1$ signal; $g_{\parallel} = 1{\cdot}96 \pm 0{\cdot}01$, $g_{\perp} = 1{\cdot}99$, $A = 0{\cdot}014$ cm^{-1}, B = 0·006 cm^{-1}, $D = 0{\cdot}028$ cm^{-1}, $R = 4{\cdot}5 \pm 0{\cdot}1$ Å, $\sigma = 15$ G. (Parameters used to simulate the $\Delta M = \pm 2$ signal; $g_{\parallel} = 1{\cdot}96$, $g_{\perp} = 1{\cdot}99$, $A = 0{\cdot}014$ cm^{-1}, $B = 0{\cdot}028$ cm^{-1}, $D = 0{\cdot}028$ cm^{-1}, $R_{\text{V-V}} = 4{\cdot}5$ Å, $\sigma = 15$ G.) (b) Computed $\Delta M = \pm 1$ signals along z axis and x, y axis showing major contributions to the total line-shape

DISCUSSION

The results clearly indicate that although the copper(II) and vanadyl tspc dimeric chelates possess closely similar interplanar separations their distribution of species amongst monomeric, dimeric, and polymeric forms is different. In the case of the vanadyl tspc chelate in aqueous solution dimers are present but most of the vanadyl chelate is polymeric. In solutions containing up to 50% by volume of dimethylformamide most of the vanadyl chelate is dimeric while further increases in the percentage of dimethylformamide present in the solvent mixture gives rise to formation of substantial amounts of monomer. In aqueous solutions of copper(II)tspc chelate a polymeric form predominates and persists in solvent mixtures containing up to 50% (v/v) of dimethylformamide. Only in solutions containing up to 75% of dimethylformamide is the dimer signal clearly discerned so that in the copper(II) chelate the polymeric form is less easily broken down to simpler species.

Several studies of dimeric tspc and metal chelates in aqueous solution at low concentration (10^{-5}M or less) have measured the equilibrium constants for dimer formation.[13] From these studies the stability of the tspc dimers was found to be $\mathrm{Cu^{II}} > \sim \mathrm{H_2} > \mathrm{Fe} > \sim \mathrm{VO} \sim \mathrm{Zn^{II}} > \mathrm{Co}$. The role of the metal ion in determining the instability of the dimer is thought to be due to competition between water molecules and phthalocyanine molecules for other phthalocyanine molecules such that the water molecules bond to the metal ion in the axial sites. At greater concentrations in aqueous solutions higher aggregates form.

The nature of bonding in dimers and aggregates of this type has been the subject of a number of studies concerned mainly with thermodynamic properties.[14,15] Factors contributing to the formation of aggregates in aqueous solution include London dispersion forces between the readily polarisable aromatic systems on the phthalocyanine ring and water structure effects.[15] In the dimerisation equilibrium of the cobalt(II)tspc chelate the zero activation energy of the dissociation reaction was considered by Eyring *et al.*[1] to be noteworthy, indicating that in the course of separation of the constituents of the dimer to a distance corresponding to that in the activated complex the repelling and binding forces are approximately in balance. On the basis of a simple electrostatic model the separation between the two parallel planes in the activated complex was estimated to be *ca.* 5 Å. In the circumstances considered here the interplanar distance will be closely similar to the internuclear metal ion separation which is 4·3 Å in the copper(II) chelate and 4·5 Å in the vanadyl chelate. The relevant distance in the dimeric cobalt(II)tspc chelate is very likely to be closely similar to these values such that the movement, and thus the

---

[13] H. Sigel, P. Waldmeier, and B. Prijs, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 161.

[14] K. K. Rohatgi and G. S. Singhai, *J. Phys. Chem.*, 1966, **70**, 1695.

[15] P. Mukerjee and A. K. Ghosh, *J. Amer. Chem. Soc.*, 1970, **92**, 6419.

expenditure of energy, of the planar molecules to the estimated separation in the activated complex would be expected to be small, a view consistent with the findings of a zero activation energy of dissociation in the dimeric cobalt(II)tspc chelate.

EXPERIMENTAL

The tetrasodium salts of the copper(II) and nickel(II) chelates of 4,4′,4″,4‴-tetrasulphophthalocyanine were prepared and purified by the method of Weber and Busch.[16] The corresponding vanadyl chelate was prepared by a similar procedure from hydrated vanadyl sulphate.

X-Band e.s.r. measurements were carried out at room temperature and 77 K on aqueous solutions in the concentration range 0·01—0·04M and near-saturated solutions (<0·04M) for mixed solvent solutions. The spectrometer was as previously described.[4]

[1/1972 *Received, 25th October, 1971*]

---

[16] J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.