Electron Spin Resonance Study of Titanium(III) Trichloride in Pyridine Solutions

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The *X*-band e.s.r. spectra of titanium(III) trichloride in pyridine solution at room temperature and 77 K provide evidence to show that the molecular species formed in greatest amount is a dimeric form of the bispyridinetitanium-(III) chloride complex which is characterised both in the liquid phase and at 77 K by triplet-state spectra. The observed spectra at 77 K is best accounted for by consideration of an interaction spin Hamiltonian which involves an angular dependence of the zero-field splitting term. Computer simulation of the experimental line-shapes has enabled a determination of the magnetic parameters associated with the various titanium(III) trichloride–pyridine complexes. The determination of these parameters in the case of the dimeric species includes an evaluation of the internuclear separation and the symmetry properties of the pair of titanium(III) ions which have been used to indicate their structure.

THE dissolution of titanium(III) chloride in pyridine at room temperature results in the formation of a red-brown solution, of the nature of which little is known. A green trispyridine complex has been reported by Fowles and Hoodless.[1] Later, as part of a study dealing with the polymerisation of propylene by various amine adducts of titanium(III) chloride Pirogov and Cirkov prepared the adduct, TiCl$_3$,pyridine, a violet solid and the light yellow solid, TiCl$_3$,2(pyridine), both of which were found to be less active in the polymerisation of propylene than the tris-complex.[2] An investigation by Garassi and Danielli[3] confirmed the existence of the solid TiCl$_3$,pyridine, while Zikmund *et al.*[4,5] monitored the range of solid products to be obtained by sampling a solid phase of titanium(III) chloride in contact with n-hexane containing various amounts of pyridine noting that as the reaction proceeded the colour of the solid phase changed from the violet colour attributable to the monopyridine complex to the green of the tris-complex. A similar study involving chemical, i.r., and *X*-ray analysis of the products formed from a reaction mixture consisting of solid titanium(III) chloride in contact with an n-hexane solution of pyridine at 60 °C showed that only the complex TiCl$_3$,3(pyridine) was formed.[6]

Here e.s.r. spectroscopy has been used to assist in establishing the nature of the species formed in greatest amount when titanium(III) chloride is dissolved in pyridine solutions at room temperature.

RESULTS AND DISCUSSION

The solutions used consisted of titanium(III) chloride (0·01 and 0·1M) dissolved in pyridine containing 20% by volume of benzene which was included to improve the resolution of the spectra. The *X*-band e.s.r. spectra were recorded at sample temperatures of 77 K and room temperature; a typical result is shown in Figure 1. The spectrum recorded at sample temperatures of 77 K possesses a low field (1500 G) component attributable to $\Delta M = \pm 2$ transitions which could arise from magnetic dipole–dipole coupling between the titanium(III) ions in a dimeric species. The line-shape of the spectrum in the mid-field region (*ca.* 3000 G) is consistent with this conclusion and is interpreted as being a component of the triplet state spectra arising from $\Delta M = \pm 1$ transitions. The sharp line at 3300 G is attributable in these circumstances to a small percentage of titanium(III) chloride species being in the monomeric state.

The simple conclusion to be drawn from these results is that the dissolution of titanium(III) chloride in pyridine at room temperature results in the formation of a dimeric form of the titanium(III) chloride pyridine complex which at room temperature and in frozen solution

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[1] G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 1963, 33.

[2] O. N. Pirogov and N. M. Girkov, *Vysokomol. Soedineniya*, 1965, **7**, 491.

[3] G. Garrasi and E. Danielli, *Chemica e Industria*, 1965, **47**, 307.

[4] M. Zikmund, R. Foniok, and A. Valent, *Chem. Zvesti*, 1965, **19**, 854.

[5] M. Zikmund, A. Valent, M. Blàzekovă, and E. Stepniĭkorá, *Chem. Zvesti*, 1966, **20**, 775.

[6] Y. Fakashi, *Bull. Chem. Soc. Japan*, 1967, **40**, 999.

accounts for most of the titanium(III) chloride species present.

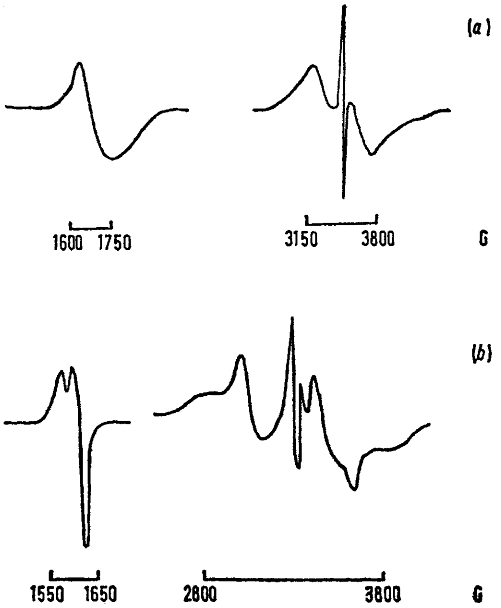

FIGURE 1 *X*-Band e.s.r. spectra due to a pyridine–benzene (20% by volume) solution of titanium(III) chloride (0·1M); (*a*) room temperature, (*b*) 77 K

Quantitative Treatment of the Results.—The distance between the titanium(III) ions and the symmetry of the paramagnetic ion-pair system, may be gained by an adequate consideration of the observed triplet state spectrum. Thus the various symmetry arrangements of the paramagnetic ion-pair system which merit consideration is shown by Figure 2 which depicts the lowering of axial symmetry of the system to achieve, in the limit, orthorhombic or monoclinic symmetry. If we assume in the first instance that the titanium(III) ion-pair system possesses axial symmetry the spin Hamiltonian for the pair may be written:

$$\mathscr{H} = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[D_z^2 - \tfrac{1}{3}S(S+1)] + E\,(S_x^2 - S_y^2)$$

The simulation of e.s.r. line-shapes by computer using the assumption of axial symmetry has been described previously and involved the calculation of the line-shapes due to the $\Delta M = \pm 2$ and $\Delta M = \pm 1$ transitions.[7] It was found that despite the widest variation of the values of the magnetic parameters all attempts to fit the low field peak of the $\Delta M = \pm 2$ signal failed. It was concluded that the observation of the peak at 1564 G indicated that the symmetry of the titanium(III) ion-pair system was lower than axial. Whether this involves a slight lowering or a gross departure from axial symmetry was decided by considering first a non-parallel alignment of the pair of paramagnetic ions as indicated by Figure 3. Here the two ions are in identical sites of axial symmetry. Since the magnetic axes are no longer parallel, ion (1) is taken as the frame of reference to which ion (2) is related. The magnetic interaction between the two titanium(III) ions may be represented by the following spin Hamiltonian:

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

where $\mathscr{H}_1 = \beta[g_{\|}H_{1z}S_{1z} + g_{\perp}(H_{1x}S_{1x} + H_{1y}S_{1y})]$

and $\mathscr{H}_2 = \beta[g_{\perp}H_{1z}S_{2z} + g_{\perp}H_{1y}S_{2y} + g_{\|}H_{1x}S_{2x}]$

and where $\mathscr{H}_{\text{int}}$ becomes

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

The computer simulation of line-shapes based on this form of the spin Hamiltonian in cases where exchange coupling can be neglected has been described previously, and once more, despite a wide variation of the values of the magnetic parameters, the low field peak of the

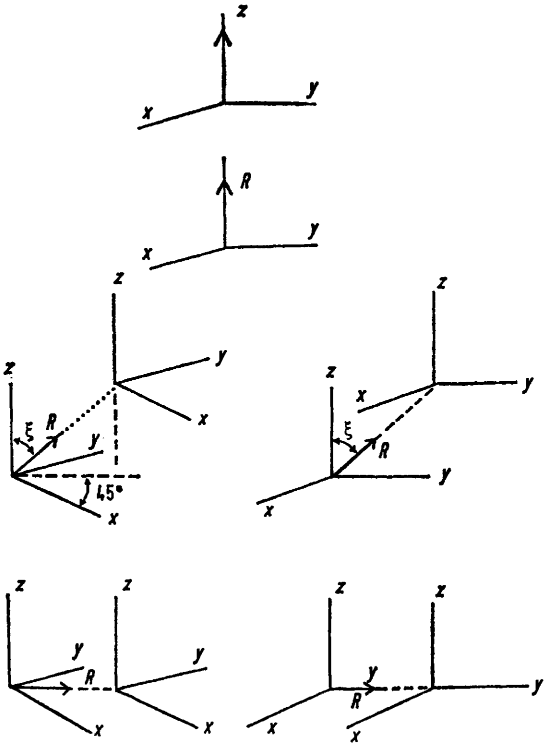

FIGURE 2 Orientations of the principal axes of the *g* tensor for titanium(III) ion pair systems of axial, orthorhombic, and monoclinic symmetry

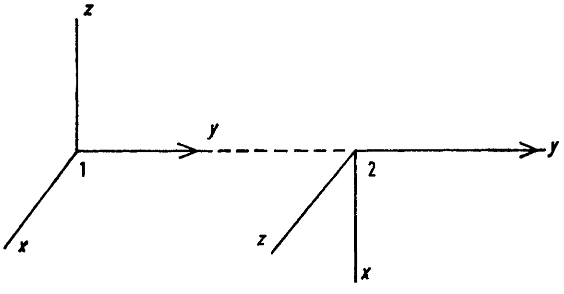

FIGURE 3 Orientations of the principal axes of the *g* tensor in a non-parallel alignment in the dimeric complex

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[7] T. D. Smith, T. Lund, and J. R. Pilbrow, *J. Chem. Soc.* (*A*), 1971, 2786.

$\Delta M = \pm 2$ signal could not be simulated. In these and subsequent calculations the value of J used was -20 cm^{-1} which is sufficient to separate the singlet and triplet states though not large enough to make a significant contribution to the zero-field splitting term.

Finally, the departures from axial symmetry represented by Figure 2 were investigated. Here the internuclear vector makes an angle ξ with the z axis of ion (1). The spin Hamiltonian representing the interaction between the pair of titanium(III) ions under these conditions may be written:

$$\mathscr{H} = g_{\|}\beta H_z(S_{1z} + S_{2z}) + g_{\perp}\beta[H_x(S_{1x} + S_{2x}) + H_y(S_{1y} + S_{2y})] + \mathscr{H}_{\text{dip}} - JS_1S_2$$

After transformation the dipolar interaction may be represented as follows:

$$\mathscr{H}_{\text{dip}} = \frac{\beta^2}{R^3}g_{\perp}^2 + \frac{\beta^2}{R^3}g_{\perp}^2(1 - 3\sin^2\xi) + \frac{\beta^2}{R^3}g_{\|}^2(1 - 3\cos^2\xi) - 6\frac{\beta^2}{R^3}g_{\|}g_{\perp}\sin\xi\cos\xi$$

The energy levels within the triplet state, the transition fields, and the computer simulation of the line-shape appropriate to these symmetry conditions have been described for pairs of copper(II) ions previously and was adapted to the needs of the present investigation.[8] It was found that the variations of ξ proved to be critical in reproducing the observed $\Delta M = \pm 2$ spectrum and typical results are shown by Figure 4. The final selection of parameters was made by obtaining the best fit of the $\Delta M = \pm 1$ and $\Delta M = \pm 2$ signals and are as follows: For the $\Delta M = \pm 1$ signal $R = 3{\cdot}6 \pm 0{\cdot}05$ Å, $g_{\|} = 2{\cdot}04 \pm 0{\cdot}02$, $g_{\perp} = 1{\cdot}93 \pm 0{\cdot}02$, $\xi = 45 \pm 7°$, and $\sigma = 30$ G. In the computer simulation of the line-shape each transition was given an isotropic Gaussian shape factor. Explicitly the Gaussian function is proportional to $\exp[-(H - H^1)^2/2\sigma^2]$, where σ is half the peak–peak width of the differential of the Gaussian, H^1 the centroid of a given transition, and H a general point on the curve.

The sensitivity of the parameters is such that a 0·10 increase in the distance R causes a 40 G upfield shift of the line at 2700 G and a 40 G downfield shift of the line at 2880 G, whereas the line at 3000 G is shifted 20 G upfield and the line at 3620 G is shifted 20 gauss downfield. An increase of 0·01 in $g_{\|}$ causes a downfield shift of 10 G of the outer lines, *i.e.* 2700 and 3870 G and an increase of 0·03 in $g_{\perp}$ causes a 20 G downfield shift of the whole spectrum.

For the $\Delta M = \pm 2$ signal $R = 3{\cdot}6 \pm 0{\cdot}20$, $g_{\|} = 2{\cdot}04 \pm 0{\cdot}02$, $g_{\perp} = 1{\cdot}96 \pm 0{\cdot}02$, $\xi = 45 \pm 7°$, and $\sigma = 16$ G. Here a 0·10 increase in the value of R causes an upfield shift of 5 G of the whole spectrum, an increase of 0·02 in $g_{\|}$ causes the line at 1565 G to shift to 1550 G and an increase of 0·01 in $g_{\perp}$ causes the line at 1600 G to move downfield 10 G.

To account for every feature of the observed e.s.r. spectrum which includes the sharp signal at 3300 G due to monomeric species, the complete simulation of the experimental spectrum was achieved by summation of spectra due to dimeric species and *ca.* 3% of the monomer. The parameters used to simulate the monomer spectrum were as follows: $g_{\|} = 1{\cdot}96 \pm 0{\cdot}01$, $g_{\perp} = 1{\cdot}96 \pm 0{\cdot}01$. These parameters may be compared with the values of $g_z = 1{\cdot}95 \pm 0{\cdot}01$, $g_y = 1{\cdot}86 \pm 0{\cdot}01$, and $g_x = 1{\cdot}89 \pm 0{\cdot}01$ obtained from the e.s.r. spectrum at 77 K recorded by us due to the trispyridine complex formed by dissolution of the green complex $\mathrm{TiCl_3}$,3(pyridine) in pyridine solution or by warming the red-brown solution formed by dissolution of titanium(III) chloride in pyridine at room temperature. The transformation to the green species is slow at room temperature and once achieved the reaction cannot be reversed in solution. The comparison of the parameters indicates that the monomer in equilibrium with the dimeric species is not the trispyridine complex. From the similarity of the product isolated from the brown solution and the yellow bispyridine complex or the similarity of the brown solution and one obtained by dissolution of the bispyridine complex in

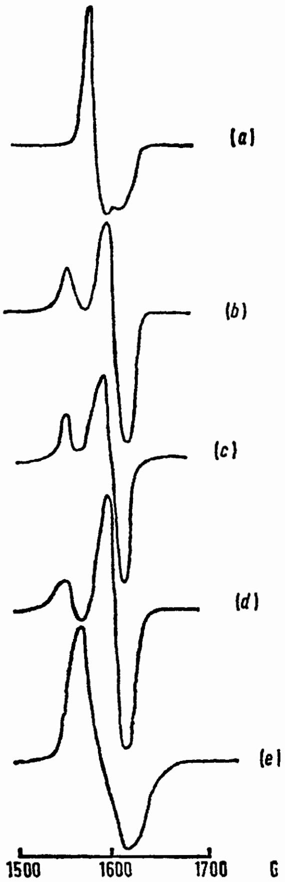

FIGURE 4 Computer simulated $\Delta M = \pm 2$ spectra (case 1) for various values of ξ with values of the other parameters as follows: $g_{\|} = 2{\cdot}04$, $g_{\perp} = 1{\cdot}93$; ξ for (*a*) = 0, (*b*) = 30, (*c*) = 45, (*d*) = 50, (*e*) = 90°

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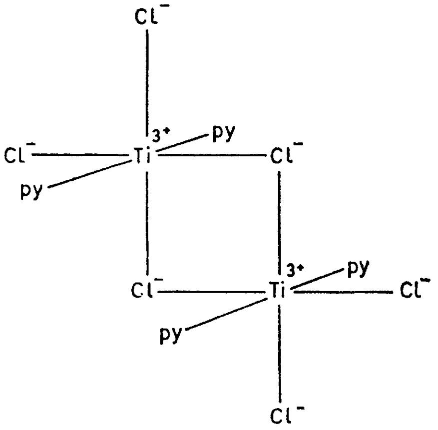
[8] S. G. Carr, P. D. W. Boyd, and T. D. Smith, *J.C.S. Dalton*, **1972**, 1491.

pyridine, it is concluded that the brown solution contains a dimeric form of the bispyridine complex in equilibrium with a small amount (*ca.* 3%) of the monomeric form of the complex $TiCl_3$,2(pyridine). The structural form of the dimeric species could be envisaged to be determined by the sharing of an octahedral face formed by three chloride ions, an edge consisting of two chloride ions, or bridging by a single chloride ion between the two titanium(III) ions. The structural information obtained from an *X*-ray crystallographic study of the anion $Ti_2Cl_9^{3-}$ shows that sharing of three chloride ions occurs and results in a 3·12 Å separation of the paramagnetic ions while the symmetry of the arrangement is closely similar to one involving non-parallel axes.[9] Thus this structure is viewed as an unlikely one for the dimeric pyridine complex formed in frozen pyridine solution. A structure which would be compatible with our determination of the internuclear separation of the titanium(III) ions and their symmetry in the pair system of the pyridine complex is shown by (I) which involves the sharing of an octahedral edge. A usual consequence of the magnetic dipole–dipole coupling between paramagnetic ions of $S = \frac{1}{2}$ in magnetically dilute pair systems such as those formed by dimeric or binuclear paramagnetic ion complexes is the disappearance of the e.s.r. signal from samples of the paramagnetic ion species in the liquid phase. In the few cases where a signal has been observed and where the signal can be easily identified as being due to the species in which coupling occurs, the observation is invariably associated with a structural rigidity of the dimeric or binuclear complex. The room temperature spectrum due to the dimeric titanium(III) chloride pyridine complex is so far unique in making possible the observation of the low-field component due to $\Delta M = \pm 2$ transitions. The observation of the complete triplet state in the liquid phase provides at least circumstantial evidence for structure (I) and is in keeping with the apparent requirement of structural rigidity which in this case arises from the sharing of an octahedral edge.



(I)

The lines observed at 3148 and 3776 G were used to determine *D*, the zero-field splitting term at room temperature and from the expression $D = g_{av}^2 \cdot \frac{\beta^2}{R^3}$ the internuclear distance between the titanium(III) ions was calculated to be 3·4 Å, using the weighted average of the *g* values computed from the data obtained from frozen solutions namely $g_{av} = 1{\cdot}97$. This distance is compatible with that obtained for the dimeric species in frozen solution indicating that the structure of the dimeric titanium(III) pyridine complex is the same in the liquid and frozen solution.

EXPERIMENTAL

Titanium(III) chloride was purchased and used without further purification. The solvents were dried and freshly distilled before use. All transfer operations and solution preparations were carried out under nitrogen. The e.s.r. measurements were carried out at room temperature and 77 K using a Varian 100 kHz multipurpose cavity in conjunction with a 3 cm spectrometer of conventional design. All the spectra at 77 K were recorded at a microwave frequency of 9079 MHz, while those at room temperature were recorded at a microwave frequency of 9499 MHz.

[2/377 *Received*, 21*st February*, 1972]

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[9] G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, 1957, **10**, 466.