Contribution from the Department of Chemistry,
University of Leicester, Leicester LEl 7RH, United Kingdom

An Electron Spin Resonance Study of Solutions of Titanium(III) Chloride in Various Organic Bases

J. B. Raynor and A. W. L. Ball

Received August 31, 1972

Electron spin resonance spectra have been recorded for solutions of titanium(III) chloride in a wide range of organic bases. In some cases, several species coexisted in solution, a doublet state monomer and a triplet state dimer. Hyperfine coupling to $^{47,49}Ti$ was detected for the monomers and the zero field parameters measured for the dimers. Suggestions are made as to the nature of the species in solution.

Introduction

Titanium(III) chloride dissolves in a wide range of organic bases and in many cases, adducts can be isolated.[1,2] Neutral complexes of the form $TiCl_3L_n$ where $n = 1,2$ or 3 have been characterised in the solid state, but little is known about whether such adduct formation is maintained in solution. Magnetic susceptibility measurements of the bulk solid shows that is many cases the magnetic moment is lower than usual for monomeric titanium(III) complexes. This has been interpreted in terms of an antiferromagnetic interaction arising from close proximity of pairs of Ti^{3+} ions.[3] Electron spin resonance measurements have been made on solutions of titanium(III) chloride in methanol,[4] ethanol,[5] glycerine,[5] ethylenediamine,[6] acetonitrile,[7] and the spectra assigned to monomeric species. However, with certain organic acids, salicylamine and 8-hydroxyquinoline, Smith *et al*[8] have obtained evidence for the formation of dimeric species in solution.

We have reinvestigated some of these systems and found evidence for dimer formation in solution. From the e.s.r. spectra, we have in these cases, obtained values for the *D* and *E* zero field parameters. The effect of diluting the solutions in pyridine with benzene and methanol was studied in order to monitor the equilibrium between monomer and dimer.

Experimental Section

Solvents were the best commercially available and dried over Molecular Sieves before use. Titanium(II) chloride was suplied by Alfa Inorganics, Inc. E.s.r. measurements were carried out on Varian E3 and V-4502 spectrometers at room temperature and at 77K.

Results

Fluid solution spectra. Measurements made at room temperature of titanium(III) chloride in various bases all gave isotropic spectra with well-resolved hyperfine coupling to ^{47,49}Ti. The results are summarised in Table I. A typical spectrum is illustrated in Figure 1.

Table I. Room temperature e.s.r. data for $TiCl_3$ dissolved in various organic bases.

Base	g_{av}	$A_{iso}(^{47,49}Ti)$ (gauss)
CH_3OH	1.97	16.0
C_5H_5N	1.96	16.0
$C_5H_5N+C_6H_6$	1.96	15.5
CH_3CN	1.94	20.5
$C_6H_5CH_2CN$	1.94	19.5
$(C_2H_5)_3N$	1.96	16.0
$C_5H_{11}N$	1.96	16.0
β-picoline	1.96	16.0
α-picoline	1.96	16.0

Frozen solutions spectra. All the spectra showed features around $g=2$ but some exhibited various additional lines. These were interpreted in terms of mixtures of both monomeric doublet state and dimeric triplet state species. The (usually) stronger signals around $g=2$ could generally be interpreted in terms of an axially symmetrical monomer and principal values of the *g*-tensor were readily assigned. In some cases there was a slight splitting of the perpendicular feature indicating a small rhombic distortion. Weak features on either side of the main signal arose

---

(1) G.W.A. Fowles and R.A. Hoodless, *J. Chem. Soc.*, 33 (1963).
(2) R.J.H. Clark, *The Chemistry of Titanium and Vanadium*, Elsevier, Amsterdam (1968).
(3) D.J. Machin, K.S. Murray and R.A. Walton, *J. Chem. Soc. (A)*, 195 (1968).
(4) W. Giggenbach and C.H. Brubacker, *Inorg. Chem.*, *8*, 1131 (1969); N.S. Garif'yanov, E.I. Semenova, and N.S. Usacheva, *J. Struct. Chem.*, *3*, 570 (1962); E.L. Waters and A.H. Maki, *Phys. Rev.*, *125*, 233 (1962).
(5) N.S. Garif'yanov, E.I. Semenova, *Soviet Physics. J.E.T.P.*, *14*, 243 (1962).
(6) R.J.H. Clark and M.L. Greenfield, *J. Chem. Soc. (A)*, 409 (1967).
(7) G.D. McDonald, M. Thompson, and E.M. Larson, *Inorg. Chem.*, 7, 648 (1968).
(8) T.D. Smith, T. Lund, and J.R. Pilbrow, *J. Chem. Soc. (A)*, 2786 (1971).

from hyperfine coupling to ^{47,49}Ti nuclei. Table II summarises the data for the monomeric species.

Table II. E.s.r. data for TiCl$_3$ dissolved in various organic bases at 77K. Monomeric species only.

Base	g-tensor	Hyperfine coupling (gauss)
CH$_3$OH	1.88, 1.90, 1.98	—, 35, <5
CH$_3$CN	1.84, 1.89, 1.98	—, 30, <5
C$_6$H$_5$CH$_2$CN	1.85, 1.89, 1.98	—, 29, <5
(C$_2$H$_5$)$_3$N	1.86, 1.89, 1.96	none observed
C$_5$H$_{11}$N	1.86, 1.89, 1.96	none observed
β-picoline	1.92, 1.96, 1.96	28, —, —
C$_5$H$_5$N (red)	1.96, 1.96, 1.96	—, 27, —
C$_5$H$_5$N + C$_6$H$_6$ (red)	1.92, 1.99, 1.98	—, 27.5, —
C$_5$H$_5$N (yellow)	1.93, 1.86, 1.86	—, —, —
C$_5$H$_5$N + C$_6$H$_5$ (yellow)	1.93, 1.86, 1.86	—, —, —
C$_5$H$_5$N + CH$_3$OH	1.86, 1.94, 1.96	—, 25, —[a]

The dashes indicate that no estimate could be made of h.f.s. from the linewidth. [a] a hyperfine splitting of 2G observed on the m_I = 5/2 line.

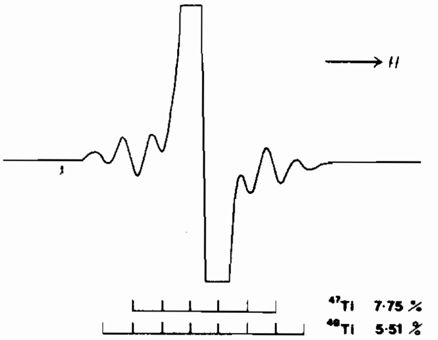

Figure 1. Room temperature e.s.r. spectrum of TiCl$_3$ dissolved in pyridine/methanol mixture.

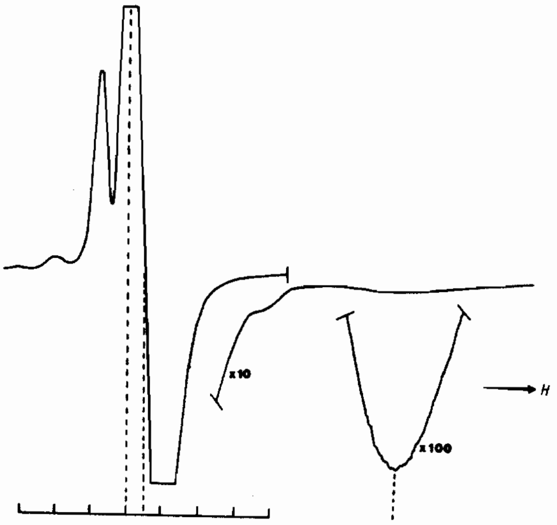

Figure 2. E.s.r. spectrum of the red frozen solution of TiCl$_3$ in pyridine/methanol mixture at 77K. The vertical dotted lines indicate the centres of the three g features. The Ti h.f.s. is reconstructed for the middle g - feature.

In those systems where absorptions other than those around $g = 2$ were observed, they were interpreted in terms of an $S = 1$ system, the theory of which has been worked out by Wasserman, Snyder and Yager.[9] For systems of low symmetry and where the dipole-dipole interactions are large (but less than $g\beta H_o$) the zero field parameters may be obtained from the exact solutions of the Hamiltonian

$$H = \beta H . g . S + DS_z^2 + E(S_x^2 - S_y^2) - \frac{2}{3}D \qquad (1)$$

namely

$$\begin{aligned} H_{x1}^2 &= (g/g_x)^2 (H_o - D' + E')(H_o + 2E') \\ H_{x2}^2 &= (g/g_x)^2 (H_o + D' - E')(H_o - 2E') \\ H_{y1}^2 &= (g/g_y)^2 (H_o - D' - E')(H_o - 2E') \\ H_{y2}^2 &= (g/g_y)^2 (H_o + D' + E')(H_o + 2E') \qquad (2) \\ H_{z1}^2 &= (g/g_z)^2 (H_o - D')^2 - E'^2 \\ H_{z2}^2 &= (g/g_z)^2 (H_o - D')^2 - E'^2 \end{aligned}$$

where $D' = D/g\beta$ and $E' = E/g\beta$ and the subscripts 1 and 2 refer to the low field and high field transitions respectfully (*i.e.* $|+1\rangle \longleftrightarrow |0\rangle$ and $|-1\rangle \longleftrightarrow |0\rangle$

However, the anticipated absorptions incorporating parallel and perpendicular features symmetrically placed about H_o were only obeserved in one instance. A satisfactory analysis for the other cases could be made assuming $D > H_o$ whereupon the $\Delta M = 2$ transition is no longer visible.[9,10] The H_{x1} and H_{y1} fetaures are also lost and H_{z2} line ($|-1\rangle \longleftrightarrow |0\rangle$). Thus only one absorption is observed at fields less than H_o and the high field absorptions are as expected. Often, though, these are very weak, especially the parallel feature H_{z2}.

Table III summarises the field positions of the e.s.r. absorptions of the frozen solutions at 77K.

TiCl$_3$ + pyridine (red solution). Addition of titanium(III) chloride to pyridine resulted in the formation of a dark red solution which after a few minutes went paler and became yellow-green. The various colours of pyridine solutions have been attributed to species of the type TiCl$_3$. *n* C$_5$H$_5$N where $n = 1$ (violet[11]), $n = 2$ (yellow[11]) and $n = 3$ (green[1]). When the solution was prepared and frozen rapidly at 77K, the e.s.r. spectrum showed an intense isotropic line at 3295G ($g = 1.96$) flanked by weak lines, due to hyperfine interaction with ^{47,49}Ti with a spacing of about 27G.

When the red solution was diluted with benzene, the spectrum showed g-anisotropy and hyperfine splitting asociated with one of the g features. The hyperfine splitting associated with the other two g-features was estimated to be small from the narrow linewidth.

TiCl$_3$ + pyridine (yellow solution). The e.s.r. spectrum of the red solution after it had faded to a pale yellow-green colour was significantly different from that of the parent solution. The intense anisotropic features around 3400G were characterised by $g_\parallel = 1{,}93$ $g_\perp = 1.86$, but any hyperfine coupling

---

[9] E. Wasserman, L.C. Snyder, and WA.. Yager, *J. Chem. Phys.*, *41*, 1763 (1964).

[10] J.R. Wasson, C.I. Shyr, and C. Trapp, *Inorg. Chem.*, 7, 469 (1968).

[11] M. Zikmund, A. Valent, M. Blazekova, and E. Stepniikora, *Chem. Zvestia*, *20*, 775 (1966); G. Gerrassi and E. Danielli, *Chim. Ind. (Milan)*, *47*, 307 (1965).

Table III. E.s.r. spectra of $TiCl_3$ dissolved in various organic bases at 77K. Doublet species only.

Base	Field position of lines and assignment (gauss)		zero field parameters (gauss)	monomer absorption around $g = 2$
β-picoline (yellow)	1110	(z_2')	$D=4500$	strong
	1250	(z_2')	$D=4640$	
	1645	$(\Delta m=2)$		
C_5H_5N (yellow)	1480	(z_2')	$D=4880$	strong
	5350	(x_2)	$E=207$	
	5970	(y_2)		
	8220	(z_2)		
$C_5H_5N+C_6H_6$ (yellow)	1250	(z_2') (species 3)	$D=4650$	strong
	2480	(y_1)		
	2660	(x_1)	$D=1160$	
	3580sh	(x_2)	$E=70$	
	3815	(y_2)		

sh = shoulder.

was broadened beyond detection. This spectrum was attributed to a monomeric species. There was, in addition, a well resolved absorption at 1480G, a weak full line at 5350G, and weak half lines at 5970 and 8220G. These absorptions were interpreted in terms of a system with large $D(>H_o)$ and small E. The lines at 5350 and 5970 were assigned to x_2 and y_2 and the lines at 1480 and 8220G to the two z_2 absorptions. The best fit values of D and E were $D = 4880G$ and $E = 207G$.

When the solution was made up in the presence of an equal amount of benzene, the spectrum was quite different. There were sharp absorptions at 1250, 2480, 2660 and 3815G and a shoulder at 3580G. The absorptions at 2480, 2660 and 3815 were assigned to four of the six $\Delta M = 1$ absorptions expected for a $S = 1$ system. They were assigned to the y_1, x_1, x_2 and y_2 lines respectively (eqn 2), from which $D = 1160G$ and $E = 70G$. Unfortunately the lines z_1 and z_2 were not seen, but since their intensity is likely to be an order of magnitude less than the perpendicular features, they could easily be lost in the noise level. The absoprtion at 1250G is postulated as arising from a third species with a much larger D $(>H_o)$ equal to about 4650G.

On the other hand, when the solution was made up in the presence of methanol, the spectrum showed considerable g-anisotropy with well resolved hyperfine coupling $^{47,49}Ti$ on the middle line. The $m_I = +^5/_2$ line was split into a triplet (2G) (Figure 3) presumably due to the interaction with ^{14}N of one pyridine. Whilst this was well resolved in one sample, it was not reproducible and suggested that line widths were very sensitive to the relative concentrations of the components.

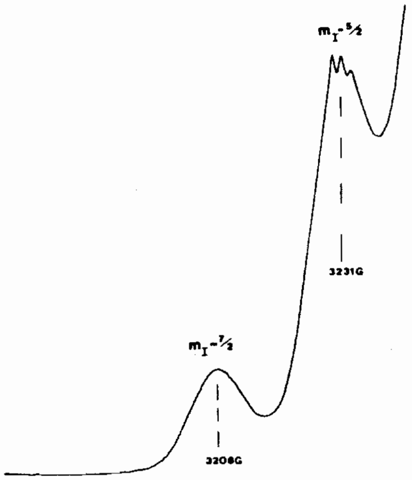

Figure 3. Part of the spectrum of $TiCl_3$ in pyridine + methanol at 77K showing the resolved triplet on the $m_I = 5/2$ line

$TiCl_3$ + pyridine (green solution). Very dilute solutions of titanium(III) chloride in pyridine were green rather than yellow with a simple e.s.r. spectrum comprising features around $g = 2$ arising from a monomeric species.

$TiCl_3$ + other bases. The e.s.r. spectra at 77 K of titanium(III) chloride in α-picoline, methanol, piperidine, dimethylsulphoxide, acetonitrile, benzonitrile and triethylamine were all very similar. They all consisted of an absorption at around $g = 2$ which was sometimes so weak as to be virtually non-existent. The results are summarised in Tables II and III. The spectrum in β-picoline was more complex and consisted of strong absorptions at 1250 and 1645G together with a weaker absorption at 1110G and a very strong signal around $g = 2$. The absence of other lines makes the analysis uncertain, but we tentatively propose that the solution contains several different types of dimeric species wih different large D values each contributing to the lines at 1110 and 1250, whereas the line at 1645G could be the $\Delta M = 2$ absorption of a weakly interacting dimer.

Discussion

The e.s.r. spectra of the monomeric species in most cases show a strongly anisotropic g-tensor with discernable hyperfine coupling only associated with one *g-feature*. The symmetry of the species contributing to the spectra must be rhombic, although in most cases, the distortion from axial is not great. All g-values are <2 and this shows that the unpaired electron is in a non bonding d-orbital and mixing (by spin-orbit coupling) with unfilled d-orbitals which are close-by. The formula of the complexes in solution is probably of the type *trans*-$TiCl_3L_3$ since the *cis*-isomer will have axial symmetry. Species with empirical formula $TiCl_nL_{(6-n)}$ are possible, but the large excess of base present is unlikely to make n greater than 3. The only system to have been studied before is the $TiCl_3$-C_2H_5OH system[12] and our anisotropic spectra for $TiCl_3$-CH_3OH are similar to those of $[TiCl_2(C_2H_5OH)_4]^+$. No hyperfine coupling were observed in the ethanol systems.

The values obtained for A_{iso} (Ti) are typical for Ti^{3+} complexes. The anisotropic tensor cannot be calculated with great accuracy because only the largest experimental value is known. This ranges from 25-35G. From the line width of the other *g*-features, it is concluded that the other two hyperfine couplings must be $<10G$. Taking e.g., $A_{iso} = -16G$ and $A_1 = -30G$, then $A_2 + A_3$ must total $-18G$. Although there is no absolute evidence that the hyperfine tensor is axial, it cannot be far from axial since if either A_2 or A_3 were much greater than 9G, then hyperfine structure would be observed. If the hyperfine tensor is taken as roughly axial, then $A_{aniso} = -14G$ and this gives an entirely reasonable spin density of 90% in the 3*d* orbital since the anisotropic hperfine coupling for an electron entirely in a 3*d* orbital on Ti^{3+} is calculated to be 15.6G.[13] The negative sign and magnitude of A_{aniso} is entirely consistent with an electron in a non-bonding d_{xy} orbital.

From the spectra of the yellow pyridine solution, it is apparent that the species present are different from those in the red solution. Dilution of the yellow solution with benzene leaves the monomer signal unchanged, ($g_{\|} > g_{\perp}$) and it seems probable that the complex in solution is $TiCl_3(C_5H_5N)_3$ since this compound has been characterised by Fowles and Hoodless.[1] The *g*-values are consistent with this formulation.

The red solution differs in that $g_{\|} > g_{\perp}$. The change is not as drastic as it may seem since only a small increase in the separation between hte $d_{xz,yz}$ and d_{xy} levels could accomplish this, as follows from the relevent equation (3)

$$g_{\|} = 2 - \frac{8\lambda}{\Delta E(d_{x^2-y^2} - d_{xy})}$$

$$g_{\perp} = 2 - \frac{2\lambda}{\Delta E(d_{xz,yz} - d_{xy})} \qquad (3)$$

This could come about by a structure involving increased π-bonding which would destabilise the non-bonding $d_{xz,yz}$ orbitals.

From the spectra of the triplet state species, which appeared to coexist with the monomeric doublet state species, the zero field parameters were obtained by using equations 1 and 2. Only in two cases could both D and E be determined simultaneously; in the other cases only D could be estimated and it was assumed E was very small.

Interpretation of D is frought with difficulties. D involves the sum of terms arising from magnetic dipole-dipole interactions and anisotropic spin-spin exchange interactions and is given by equation 4.[14]

$$D = D_{dip} + D_{ex}$$

i.e.

$$D = -(2g_{\|}^2 + g_{\perp}^2)\beta^2/2r^3 + {}^1/_8 J\{{}^1/_4(g_{\|} - 2)^2 - (g_{\perp} - 2)^2\} \qquad (4)$$

where r is the interelectronic distance.

It is imposible to distinguish between these contributions to D unless r or J is known; in our case, neither is known nor can they be estimated readily. For small values of r which occur when the pair of ions are in close proximity, the dipolar contribution is large, whereas the exchange contribution can have more or less any value. It is only when $r > 60$ nm that the dipolar contribution becomes negligible ($<$ 100G) and then $D = D_{ex}$. We are thus, unfortunately, unable to determine the interionic distance from the e.s.r. measurements unless it can be shown that the dipolar interactions is the dominant coupling mechanism.

Experimental values of D were all around 4500-4800G except in one case, when the solvent was pyridine+benzene, whereupon the yellow solution had $D = 1160G$. The only known Ti-Ti bond lengths, determined by X-ray diffraction, are α-$TiCl_3$[15] (double chlorine bridged), 35.4 nm; β-$TiCl_3$[16] (triple chlorine bridged), 29.1 nm; and $Ti_3Cl_9^{3-}$, 31.2 nm.[17] It is unlikely that a dimeric complex with pyridine would have a Ti-Ti separation less than 30 nm, and in such cases, the dipolar contribution to D would be 1030G assuming $g = 2$. For the single case of $TiCl_3$ in pyridine+benzene in this work, $D = 1160G$ and the results could indicate that the exchange contribution is small and that $D_{dip} = 1160G$ with $r = 29$ nm. If this is so, then the structure of the dimer is likely to be of the form $L_3TiCl_3'TiL_3$ analagous to $Ti_2Cl_9^{3-}$. For all the other cases where D is very large, there must be considerable exchange coupling with strong antiferromagnetic interactions.

---

[12] W. Giggenbach and C.H. Brubaker, *Inorg. Chem.*, *8*, 1131 (1969).

[13] B.A. Goodman and J.B. Raynor, *Adv. Inorg. Radiochem.*, *13*, 135 (1970).

[14] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions*, Clarendon, Oxford (1970), p. 508.

[15] W. Klemm and E. Krose, *Z. Anorg. Allgem. Chem.*, *253*, 209 (1947).

[16] G. Natta, P. Corradini, and G. Allegra, *J. Polymer Sci.*, *51*, 399 (1961); J.A. Cras, *Nature*, *194*, 678 (1962).

[17] G.J. Wessel and D.J.W. Iido, *Acta Cryst.*, *10*, 466 (1957).