

An Electron Spin Resonance Study of Dimeric Titanium(III) Complexes

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The e.s.r. spectra of dimethylformamide solutions of the titanium(III) complexes of mandelic, malic, citric, cyclopentane-1,2,3,4-tetracarboxylic, 5-sulphosalicylic, 5-chlorosalicylic, *p*-aminosalicylic, and phthalic acids, salicylamide and 8-hydroxyquinoline have been observed. The results provide evidence for the formation of dimeric species from the observation of spectra at 77 K due to $\Delta M = 1$ transition in the *g* ca. 2 region and in most cases the observation of low-field components of the spectra at *g* ca. 4. The solution of an appropriate spin Hamiltonian which includes the magnetic dipole-dipole interaction between the titanium ions makes possible the computer simulation of the line shapes of the spectra associated with the dimeric species. By this procedure the magnetic parameters of the titanium(III) pairs have been evaluated, the parameter of chief interest being the distance between the metal ions in the dimeric complexes. This information has been used to suggest possible structures of these dimers.

RECENT investigations of the e.s.r. spectra of copper(II) complexes with a variety of ligands have revealed the existence of dimeric species, where the exchange interaction makes a negligibly small contribution to the triple state transitions and the magnetic interaction can be considered to be essentially dipolar in character.¹⁻⁹ Quantitative treatment of the data leads to the determination of the distance between the point dipoles which have been regarded as equivalent to the internuclear separation of the metal ions. The frequent occurrence of dimeric forms for copper(II) complexes has prompted a search amongst complexes of other transition-metal ions and the present investigation deals with the results obtained for those of titanium(III).

Compared with copper(II) far fewer physicochemical investigations of the titanium(III) chelates have been reported. Few of these have indicated that dimer formation takes place in titanium(III) complexes. Kyker and Schraur¹⁰ reported the isolation and characterisation of the reduction product of di[bis-(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)] which contains titanium in the formal oxidation state three. The magnetic susceptibility data was interpreted in terms of a localised intramolecular exchange interaction between the titanium ions, giving rise to the relatively high value of *J* of -378 cm^{-1} . Measurements of the magnetic susceptibility of polycrystalline bis-(π -cyclopentadienyl)titanium(III) chloride reveals the presence of singlet and triplet states in thermal equilibrium with *J* = -192 cm^{-1} with the assumption of a titanium-titanium separation of ca. 3.5 \AA .¹¹ A halogen-bonded dimeric compound of titanium(III) was prepared by refluxing titanium(III) chloride with acetylacetone.¹²

Titanium(III) complexes of carboxylic, hydroxycarb-

oxylic, and substituted benzoic acids can be prepared in dimethylformamide (DMF) solution by addition of the base triethylamine to a DMF solution of titanium(III) chloride and the particular ligand. This particular group of ligands was found to give rise to dimeric species with copper(II) making them eminently suitable for the search for similar dimeric complexes involving titanium(III). Accordingly the present investigation involves the e.s.r. study of DMF solutions of the titanium(III) complexes of mandelic, malic, citric, cyclopentane-1,2,3,4-tetracarboxylic, 5-sulphosalicylic, 5-chlorosalicylic, *p*-aminosalicylic and phthalic acids, salicylamide and 8-hydroxyquinoline.

RESULTS

The room-temperature X-band e.s.r. spectrum of DMF solutions containing 1:3 mol ratios of titanium(III) chloride (0.1M) and mandelic acid (0.3M) gives an easily detected signal which decreases in intensity upon addition of triethylamine. In frozen solution at 77 K the spectrum obtained at *n* = 3, where *n* is the number of mol of triethylamine added per mol of titanium, consists of a somewhat ill-defined signal at *g* ca. 4 with a line at *g* ca. 2 which could be distinguished from that due to monomeric species. However at *n* = 6, as indicated by Figure 1, a clearly defined signal at *g* ca. 4 is observed, attributed to the $\Delta M = 2$ transitions arising from the magnetic dipole-dipole interactions of the titanium(III) ions in a dimeric species. At *g* ca. 2 the spectrum is predominantly due to the corresponding $\Delta M = 1$ transition. Additions of triethylamine to DMF solutions containing titanium(III) and malic, citric, or cyclopentane-1,2,3,4-tetracarboxylic acids lead in each case to diminutions of the intensities of the room-temperature signals while the spectra obtained at 77 K indicate the presence of low-field lines at *g* ca. 4. The spectra in each case are shown in Figure 1.

The intensity of the room-temperature signals obtained from DMF solutions of titanium(III) chloride (0.1M) and

¹ R. H. Dunhill, J. R. Pilbrow, and T. D. Smith, *J. Chem. Phys.*, 1966, **45**, 1474.

² J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 94.

³ J. F. Boas, J. R. Pilbrow, C. R. Hartzell, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 572.

⁴ J. F. Boas, J. R. Pilbrow, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 723.

⁵ J. F. Boas, J. R. Pilbrow, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 721.

⁶ A. D. Toy, J. R. Pilbrow, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 1029.

⁷ J. F. Boas, J. R. Pilbrow, G. J. Troup, C. Moore, and T. D. Smith, *J. Chem. Soc. (A)*, 1969, 965.

⁸ A. D. Toy, J. R. Pilbrow, and T. D. Smith, *Austral. J. Chem.*, 1970, **11**, 2278.

⁹ S. G. Carr, J. R. Pilbrow, and T. D. Smith, *J. Chem. Soc. (A)*, 1970, 723.

¹⁰ G. S. Kyker and E. P. Schraur, *Inorg. Chem.*, 1969, **8**, 2306.

¹¹ R. L. Martin and G. Winter, *J. Chem. Soc.*, 1965, 4709.

¹² A. Pflugmacher, H. J. Carduck, and M. Zucketto, *Naturwiss.*, 1958, **45**, 490.

5-sulphosalicylic acid (0.3M) varied little for various additions of triethylamine. At 77 K the weak low-field line was observed when $n = 9$ while the component of the

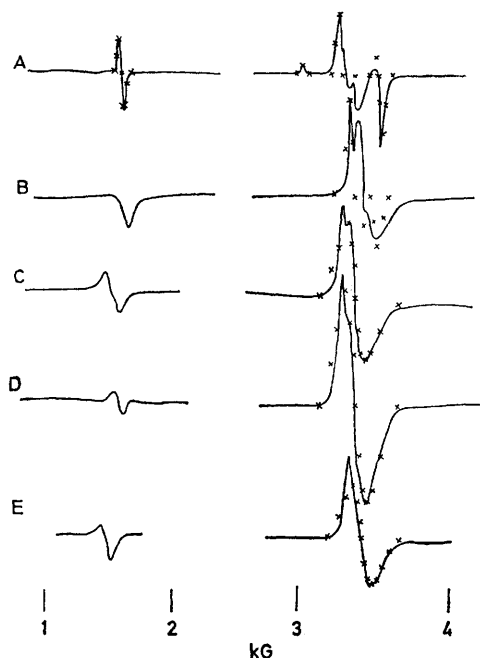


FIGURE 1 X-band e.s.r. due to DMF solutions at 77 K containing TiCl_3 (0.1M) and the following (A) mandelic acid (0.3M), $n = 6$; (B) malic acid (0.1M), $n = 2$; (C) citric acid (0.1M), $n = 3$; (D) citric acid (0.1M), $n = 4$; (E) cyclopentane-1,2,3,4-tetracarboxylic acid. Crosses represent the computer simulation of the lineshape using the parameters outlined in the Table

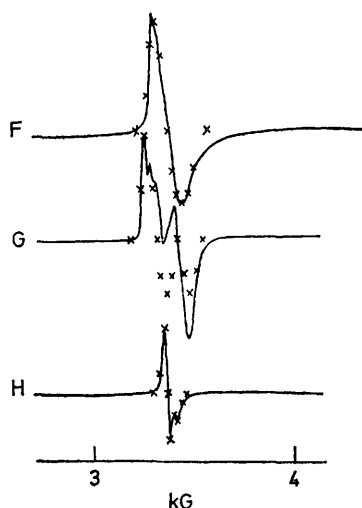


FIGURE 2 X-band e.s.r. due to DMF solutions at 77 K containing TiCl_3 (0.1M) and the following (F) 5-sulphosalicylic acid (0.3M), $n = 0$; (G) 5-sulphosalicylic acid (0.3M), $n = 3$; (H) 8-hydroxyquinoline (0.3M), $n = 3$. Crosses represent the computer simulation of the lineshape using the parameters outlined in the Table

spectrum at $g \text{ ca. } 2$ is as shown in Figure 2. When $n = 6$ in this system the spectrum at $g \text{ ca. } 2$ is as shown by curve F.

¹³ J. H. Price, J. R. Pilbrow, K. S. Murray, and T. D. Smith, *J. Chem. Soc. (A)*, 1970, 968.

Similar spectra to that shown by curve F of Figure 2 at 77 K were obtained for DMF solutions containing 5-chlorosalicylic acid (0.3M) at $n = 3$ and 6, *p*-aminosalicylic acid (0.3M) at $n = 3$ and 6, phthalic acid (0.3M) at $n = 1$ to 3, and salicylamide (0.3M) at $n = 2$. Dimethylformamide solutions containing titanium(III) chloride (0.1M) and 8-hydroxyquinoline give an easily detected signal which narrows somewhat upon addition of triethylamine. At 77 K at $n = 3$ the signal observed in the $g \text{ ca. } 2$ region is as shown in Figure 2.

When two neighbouring titanium(III) ions interact, as occurs when dimeric complexes are formed, the Hamiltonian for the pair may be written:

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

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) \quad (1)$$

where \mathcal{H}_1 and \mathcal{H}_2 are each of the form (1). \mathcal{H}_{int} , representing the interaction energy between the two ions, has the form:^{1,2,13}

$$D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + J S_1 \cdot S_2 \quad (2)$$

where $S = S_1 + S_2$, if the ions are in sites of the same symmetry. D may be the sum of both dipolar and exchange coupling contributions such that

$$D = D_{\text{ex}} - (g_{\parallel}^2 + \frac{1}{2}g_{\perp}^2) \frac{\beta^2}{r^3}$$

Here the second term results from the magnetic dipole-dipole interaction and is appropriate in this particular form only if the g tensors of the two ions are aligned, and if the ions lie on the common z axis.¹ Thus, for the coupled pair of titanium ions, a singlet state ($S = 0$) and a triplet state ($S = 1$) are formed, which in the absence of a hyperfine interaction will not be mixed.¹³ Only the transitions within the triplet need be considered in this case, and so the spin Hamiltonian for the pair can be written:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$$

where $S = 1$.

The situation now reached is similar to that previously discussed for the case of coupled copper(II) ions and the method for the simulation of e.s.r. lineshapes by computer can be used for the simulation of the spectra of coupled pairs of titanium(III) ions.¹³ In fact, since there is no hyperfine interaction to mix the singlet with the triplet, the direct diagonalisation procedure may be used without restriction according to the value of J , and without consequent recourse to the perturbation methods described previously.^{1,2} A series of computed spectra which illustrate the effect of increasing the separation between the titanium(III) point dipoles is shown by Figure 3. The g values chosen are typical of those values encountered in the present investigation. The parameters obtained from the computer simulation of the line shapes of the various spectra obtained in the present investigation are given in the Table.

It could be considered that the weak lines observed at $g \text{ ca. } 4$ in many of the systems studied here could arise from a resonance within an excited doublet. To eliminate this possibility, lineshapes were simulated using a spin Hamiltonian with g values appropriate to the doublet, that is $g_{\parallel} \text{ ca. } 4$ and $g_{\perp} \text{ ca. } 0$.¹⁴ However, the peak height of the signal

¹⁴ A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970.

at g ca. 4 was very much less than the peak height of the doublet spectrum due to uncoupled titanium(III) such that it could be predicted that the low-field doublet spectrum would be undetectable by the spectrometer used here. Thus, the signals detected at g ca. 4 can be confidently assigned to $\Delta M = 2$ transitions arising in the triplet formed

if the signal is sufficiently resolved, it is possible to distinguish monomer from dimer, since the spectra are qualitatively different. For the monomer, in the region near $g = 2$, the 'peak' appears on the low-field side of the main line, whereas for the dimer the 'peak' appears on the high-field side. Thus, the powder spectrum of $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$

TABLE

System	g_{\parallel} ± 0.02	g_{\perp} ± 0.01	D/cm^{-1} ± 0.001	$r/\text{\AA}$ ± 0.2	σ/G
TiCl_3 (0.1M) + mandelic acid (0.3M) $n = 6$	1.99	1.92	0.024	4.7	20
TiCl_3 (0.1M) + malic acid (0.1M) $n = 2$	1.99	1.92	0.014	5.6	30
TiCl_3 (0.1M) + citric acid (0.1M) $n = 3$ or 4	1.99	1.89	0.010	6.3	70
TiCl_3 (0.1M) + cyclopentane-1,2,3,4-carboxylic acid $n = 2$ or 3	1.99	1.87	0.007	7.1	60
TiCl_3 (0.1M) + 5-sulphosalicylic acid $n = 6$	1.97	1.92	0.009	6.5	40
	1.99	1.93	0.015	5.5	30
TiCl_3 (0.1M) + 5-chlorosalicylic acid (0.3M) $n = 3$	1.97	1.92	0.009	6.5	40
TiCl_3 (0.1M) + <i>p</i> -aminosalicylic acid (0.3M) $n = 3$ or 6	1.97	1.92	0.009	6.5	40
TiCl_3 (0.1M) + salicylamide (0.3M) $n = 3$	1.97	1.92	0.009	6.5	40
TiCl_3 (0.1M) + phthalic acid (0.3M) $n = 1$ or 2	1.97	1.92	0.009	6.5	40
TiCl_3 (0.1M) + 8-hydroxyquinoline (0.3M) $n = 3$	1.99	1.95	0.004	8.6	15

by essentially magnetic dipolar coupling of the titanium(III) ions.

To aid the interpretation of the complex spectra which arise from a mixture of monomeric and dimeric titanium(III) spins, the lineshapes for uncoupled titanium ions were simulated using magnetic parameters close to those used in

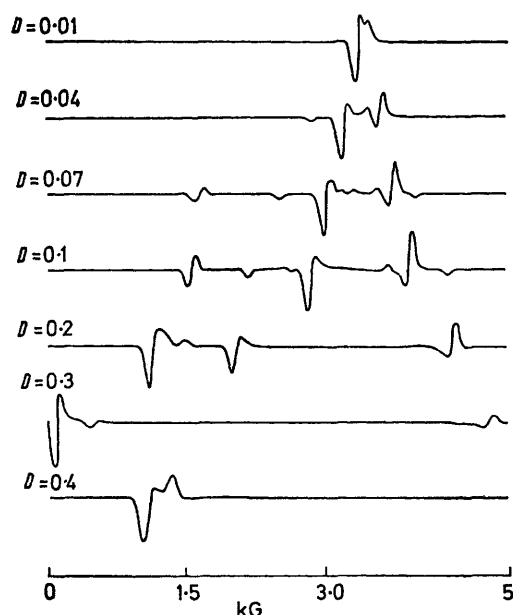


FIGURE 3. Calculated e.s.r. spectra for coupled Ti^{3+} pairs, for $g_{\parallel} = 1.99$, $g_{\perp} = 1.90$, $\sigma = 40$ G, $\nu = 9150$ MHz and various values of D .

the simulation of the spectra due to dipolar coupled titanium(III) ions. Thus a spectrum at 77 K such as that obtained from a DMF solution of titanium chloride (0.1M) and salicylamide (0.3M) when $n = 3$ can be seen to be due predominantly to monomeric species, while the spectrum due to a DMF solution containing titanium(III) chloride (0.1M) and mandelic acid (0.3M) at $n = 3$ is once more due to a mixture of monomeric and dimeric species, although in this case the component due to the dimeric species is more clearly discernible. Even for small values of D ,

reported by Avvakumov *et al.*,¹⁵ we would interpret as resulting from the interaction between titanium(III) ions in adjacent unit cells. This explanation we would consider more plausible than their assignment of $g_{\perp} > g_{\parallel}$ or the use of three g values, especially since the spectrum becomes symmetrical in the diluted salt. The absence of hyperfine interactions which have the effect of broadening the signals allows the $\Delta M = 1$ transition to be more readily and precisely used in identifying triplet-state phenomena than is the case in similar circumstances involving copper(II). On the other hand the low field $\Delta M = 2$ component is less reliable for obtaining magnetic parameters though its presence is useful in providing good evidence for the existence of dimeric species.

DISCUSSION

From the point of view of interpreting the titanium(III)–titanium(III) separation in terms of the functional groups of the ligand responsible in forming the dimeric species, the structural simplicity of the mandelate anion provides a good starting point since the binding site consists of the ionised hydroxy and carboxylic acid groups whose spatial arrangement is closely defined by the central carbon atom to which each is bonded. The actual disposition of each titanium(III) ion in a co-ordination state involving the ionised hydroxy-group and carboxyl groups in a head-to-tail arrangement, similar to that proposed for copper(II), is uncertain, since the metal ion to ligand atom bond angles are not known but the distance of 4.7 Å observed when enough base has been added to release all the protons in the system could be compatible with such an arrangement. The distances observed in the systems involving derivatives of salicylic acid are somewhat longer and again involve the hydroxy and carboxylic acid groups, though these functional groups are now separated by the carbon–carbon bond of the aromatic nucleus which adds ca. 1.5 Å to the distance between them. The common distance of ca. 6.5 Å observed

¹⁵ V. I. Avvakumov, N. S. Garifyanov, S. G. Salikhov, and E. I. Semanova, *Fiz. Tverd. Tela*, 1961, **3**, 2111.

for the titanium(III)–titanium(III) separation observed in these systems as well as with salicylamide and phthalic acid is in accord with this entire distance provided that the binding site is otherwise unchanged.

The somewhat longer distance of 7.1 Å observed with cyclopentane-1,2,3,4-tetracarboxylic acid could be envisaged as the result of a further increase in the separation of the binding site where the structure would be similar to that proposed for the copper(II) complex with this ligand.¹³ The greatest titanium–titanium separation observed in the quinolin-8-olato-complex. Though the assignment of the transition and the structural information must be used with caution, it can be said with certainty that the distance of 8.6 Å observed in this system is far too great to involve a simple head-to-tail arrangement of the ligand binding sites, which would lead to a distance of less than half of that actually observed. It is tentatively proposed that the dimer

unit involves some sort of interaction arising from a planar arrangement of the ligands attached to each titanium ion.

EXPERIMENTAL

The titanium trichloride, mandelic, malic, citric, cyclopentane-1,2,3,4-tetracarboxylic, 5-sulphosalicylic, 5-chlorosalicylic, *p*-aminosalicylic acids, salicylamide and phthalic acids and 8-hydroxyquinoline were purchased and used without further purification. The dimethylformamide and triethylamine were freshly distilled, dried and purged with nitrogen until free of oxygen. All transfer operations and solution preparations were carried out under nitrogen. E.s.r. measurements were recorded as previously described¹ 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 were recorded at a microwave frequency of 9150 MHz.

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