Physicochemical Study of Titanium(III) Mononuclear, Dinuclear, and Dimeric Polyaminocarboxylates Formed in Aqueous and Frozen Aqueous Solution

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Potentiometric and e.s.r. studies have proved the existence of dimeric and dinuclear titanium(III) complexes of some polyaminocarboxylic acids. The ligands studied include ethylenediaminetetra-acetic acid (EDTA), 3,6-dioxaoctane-1,8-diamine-*NNN′N′*-tetra-acetic acid (EGTA), diethylenetriaminepenta-acetic acid (DTPA), and triethylenetetra-aminehexa-acetic acid (TTHA). Although they are structurally similar, the nature of their titanium(III) chelates is quite diverse. Potentiometric titration data has shown that titanium(III) will form 2:1 and 1:1 chelates with EGTA, DTPA, and TTHA which are stable over a wide pH range. E.s.r. measurements at 77 K on solutions containing the dinuclear 2:1 titanium(III) EGTA, DTPA, or TTHA chelates reveal the presence of $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transitions arising from a triplet state involving an essentially magnetic dipolar interaction between the two titanium(III) ions in the dinuclear chelates. Similar measurements show that signals are also observed at room temperature which are again presumably due to the triplet state. E.s.r. measurements on solutions containing titanium(III) and EGTA or TTHA in 1:1 mole ratio similarly show the presence of $\Delta M_s = \pm 2$ transitions, at significantly different field positions than for the 2:1 chelate, indicating the formation of a dimeric species. A $\Delta M_s = \pm 2$ signal is not observed in the case of DTPA indicating that the mononuclear chelate is the major species formed under 1:1 conditions. Solutions containing titanium(III) and EDTA in 1:1 mole ratio give rise to $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ signals at 77 K providing unequivocal evidence for the formation of dimeric species. From a survey of e.s.r. spectral data and comparison of results obtained on similar systems, structures have been proposed for the dimeric and dinuclear complexes formed in solution.

ELECTRON spin resonance measurements have been made on the copper(II) chelates of 3,6-dioxaoctane-1,8-diamine-*NNN′N′*-tetra-acetic acid (EGTA),[1] diethylenetriaminepenta-acetic acid (DTPA), and triethylenetetra-aminehexa-acetic acid (TTHA).[2] In each case dinuclear chelates are formed and it was the purpose of the measurements to determine the structural relationships of the copper(II) ion pair systems formed in the dinuclear chelates. The measurements showed that the stereochemical arrangement of the pair system depended to a marked extent on the nature of the ligand used. It is of interest therefore to extend these structural determinations to other transition metal ions which possess suitable e.s.r. properties. Such an opportunity is presented by titanium(III). It is the aim of the present investigation to study the chelates formed by titanium(III) with the polyaminocarboxylic acids and to provide structural information concerning any dimeric or polynuclear complexes that are formed in solution. To aid the interpretation of the results the chelates formed in the reaction of titanium(III) with ethylenediametetra-acetic acid (EDTA) have also been studied.

The titanium(III) chelates of some other ligands, including EDTA and DTPA, have been investigated.[3-6] The nature of the chemical bonding in these titanium(III) chelates was discussed by using the *g* values, hyperfine coupling constants, and the maximum absorption wavelengths in the visible absorption spectra.

RESULTS

Potentiometric pH titration provides useful information about the formation of the chelates in solution, the pH range over which they are fully formed, and the possible role of hydrolysis of the chelates or free aquametal ions. The interaction of the metal ions with the ligand molecules in solution in principle can give rise to a distribution of metal chelates ranging in composition from polynuclear chelates to those with ligand to metal ratios greater than 1 : 1 at any relative concentration of metal ion and ligand molecules. It is expected, however, that solutions with metal ion to ligand mole ratios of 2 : 1 will favour the formation of dinuclear chelates in systems where the chelates are stable. When the ligand concentration is increased, the formation of complexes containing greater amounts of the ligand may be favoured provided they are sufficiently stable.

Using pH measurements alone, the formation of the chelates brought about by mixing solutions of the metal

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[1] S. G. Carr, P. D. W. Boyd, and T. D. Smith, *J.C.S. Dalton*, 1972, 907.

[2] T. D. Smith and A. E. Martell, *J. Amer. Chem. Soc.*, 1972, **94**, 4123.

[3] B. R. McGarvey, *J. Chem. Phys.*, 1963, **38**, 388.

[4] S. Fujiwara and M. Codell, *Bull. Chem. Soc. Japan*, 1964, **37**, 49.

[5] S. Fujiwara, K. Nagashima, and M. Codell, *Bull. Chem. Soc. Japan*, 1964, **37**, 773.

[6] T. Watanabe and S. Fujiwara, *J. Magnetic Resonance*, 1970, **2**, 103.

ion and the free ligand is signalled by a lowering of pH of the solution. Measurement of pH at various stages of addition of base gives a measure of the total number of protons generated by the system. This deceptively simple process results in a reaction mixture of metal ion and ligand species, all of whose components have to be considered if thermodynamic data concerning the equilibrium processes are to be determined. Thus, the role for the anion, which accompanies the metal ion, may itself complicate the system by forming metal ion complexes which have to be taken into consideration in computing concentrations of metal ion. The chemical forms of the base should be chosen so as to reduce possible combination of the accompanying cation with the ligand anion. In studies designed to extract thermodynamic data these difficulties are reduced to minimal effects by using metal perchlorates as metal ion sources, and tetra-alkylammonium hydroxide as the base. However in the present circumstances, where the reaction mixture leads to the formation of extremely stable polyaminocarboxylate complexes of titanium(III), the chloride anion present is expected to have little effect on the distribution of titanium(III) chelate species which will compete favourably for their existence with the sodium ions introduced by the use of sodium hydroxide as base. A more significant property of the system to consider is the role played by the hydrolytic properties of the titanium(III) species. In the pH range of *ca.* 2·5—3·0, the formation of the chelate competes with the hydrolysis of the titanium(III) cation. Thus if the chelates possess low thermodynamic stability, the protons generated by the system could arise from the hydrolysis of the metal cations as well as from the formation of the polyaminocarboxylate chelate. However once again the high thermodynamic stability associated with the combination of triply charged cations with these ligands leads to the expectation that hydrolysis of the metal ion will be small compared with formation of the metal chelate in this pH region, and that the protons generated by the system will largely result from replacement from the ligand. At higher pH's the chelates themselves may undergo a hydrolytic process. In most circumstances this would occur in a pH region beyond that where ligand protons are released. In the case of multidentate ligands, particularly those with different functional groups acting as donor sites, it could prove difficult to distinguish between a hydrolytic reaction of the chelate and proton replacement from the ligand as the process occurring during base addition.

Potentiometric pH titrations were carried out on solutions containing $1\cdot0 \times 10^{-3}$M-EDTA (disodium salt), -EGTA, -DTPA, or -TTHA and $1\cdot0 \times 10^{-3}$M- and $2\cdot0 \times 10^{-3}$M-titanium(III) chloride. Titration data of the EDTA disodium salt alone, and in the presence of one and two mole equivalents of titanium(III), are shown in Figure 1. Comparison of curves 1 and 2 shows that chelate formation takes place prior to addition of base. The steep inflexion at $a = 3$ (a = mol sodium hydroxide added per mol ligand) indicates that the formation of the titanium(III)–EDTA chelate is accompanied by the process of hydrolysis of the chelate, a dual process which is complete by pH *ca.* 5·0. The formation and subsequent hydrolysis process may be summarised as follows:

$$H_2L_{(1)}{}^{2-} + Ti^{3+} \rightleftharpoons TiL_{(1)}{}^{1-} + 2H^+ \text{ and}$$

$$TiL_{(1)}{}^{1-} + H_2O \rightleftharpoons Ti(OH)L_1{}^{2-} + H^+$$

where $L_{(1)}$ is the tetra-negative anion of the ligand. When the titanium(III) to ligand mole ratio is 2 : 1, curve 3 is obtained. Precipitation of titanium(III) hydroxide occurs at low pH, leaving a clear solution whose colour is the same as the solution containing titanium(III) and EDTA in 1 : 1 mole ratio. The pH at which the precipitation appeared to be complete is marked by the arrow on curve 3 in Figure 1. We conclude that a dinuclear chelate is not formed in this case and that the excess of titanium(III) generates three extra protons in the system as follows

$$Ti^{3+} + 3H_2O \rightleftharpoons Ti(OH)_3 \downarrow + 3H^+$$

which together with those protons generated from the hydrolysed titanium(III) chelate accounts for the steep change of curvature at $a = 6$ on curve 3.

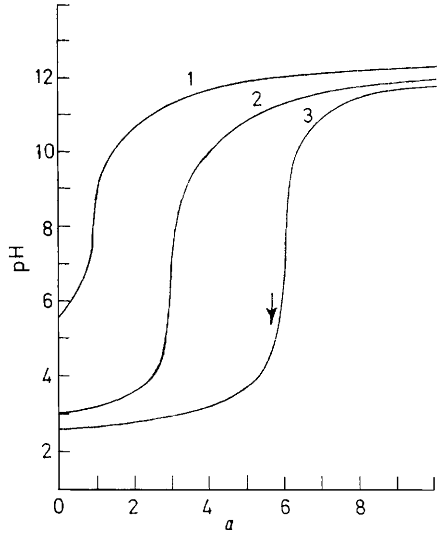

FIGURE 1 pH Titration of 100 ml of aqueous solution containing (1) EDTA, disodium salt ($1\cdot0 \times 10^{-3}$M); (2) titanium(III) chloride ($1\cdot0 \times 10^{-3}$M), EDTA disodium salt ($1\cdot0 \times 10^{-3}$M); (3) titanium(III) chloride ($2\cdot0 \times 10^{-3}$M), EDTA disodium salt ($1\cdot0 \times 10^{-3}$M), with 0·1M-NaOH

The titrations involving EGTA shown by Figure 2, curve 2, and obtained from a solution containing titanium(III) and EGTA in 1 : 1 mole ratio, show a steep inflexion which is complete by $a = 4$. If at this point it is considered that all the protons originate from the ligand, the formation of the 1 : 1 chelate may be represented as follows:

$$Ti^{3+} + H_4L_{(2)} \rightleftharpoons TiL_{(2)}{}^{1-} + 4H^+$$

Curve 3 is obtained from titration of a solution containing titanium(III) and EGTA in 2 : 1 mole ratio respectively.

Precipitation of titanium(III) hydroxide takes place at pH *ca.* 10, so that the ligand is capable of maintaining all the titanium(III) in solution under conditions where, if it were not bound to the ligand, precipitation as the hydroxide would occur. This is the key information required to show that a dinuclear chelate is formed under these circumstances. These are the conditions where the ligand would be expected to employ all its carboxylic and functional groups releasing four protons. Curve 3 of Figure 2 shows that the total number of protons released is close to six, indicating the presence of a hydrolytic process.

The total chemical change involving the formation of the dinuclear chelate and its subsequent hydrolysis may be represented as follows:

$$2\mathrm{Ti}^{3+} + \mathrm{H}_4\mathrm{L}_{(2)} \rightleftharpoons \mathrm{Ti}_2(\mathrm{OH})_2\mathrm{L}_{(2)} + 6\mathrm{H}^+$$

The dinuclear chelate is hydrolysed further at higher pH resulting in precipitation of the hydroxide.

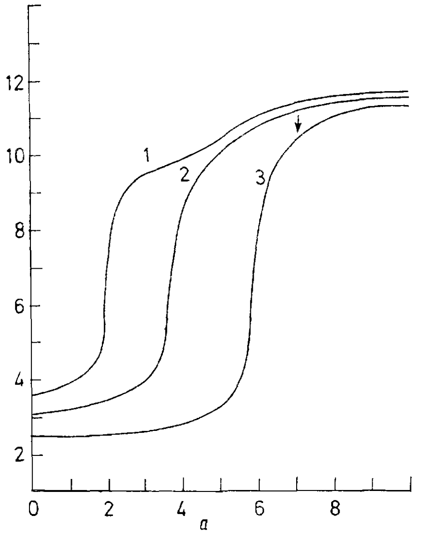

FIGURE 2 pH Titration of 100 ml of aqueous solution containing (1) EGTA (1·0 × 10^{-3}M); (2) titanium(III) chloride (1·0 × 10^{-3}M), EGTA (1·0 × 10^{-3}M); (3) titanium(III) chloride (2·0 × 10^{-3}M), EGTA (1·0 × 10^{-3}M), with 0·1M-NaOH

Titration of an aqueous solution containing titanium(III) chloride and DTPA in an equimolar ratio results in the pH-titration curve 2 of Figure 3, which indicates the formation of a stable chelate. If it is assumed that all the protons generated originate from the ligand, the formation of a 1 : 1 chelate will proceed as follows:

$$\mathrm{Ti}^{3+} + \mathrm{H}_5\mathrm{L}_{(3)} \rightleftharpoons \mathrm{TiL}_{(3)}{}^{2-} + 5\mathrm{H}^+$$

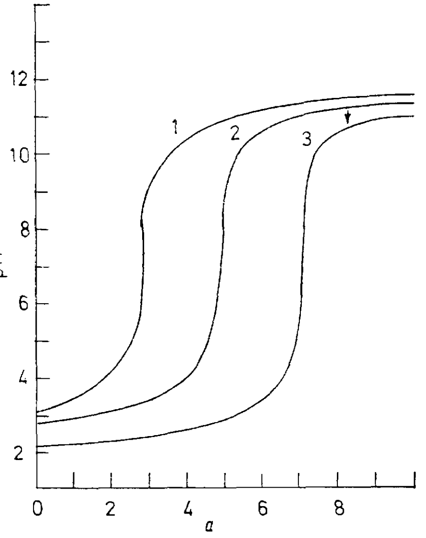

FIGURE 3 pH Titration of 100 ml of aqueous solution containing (1) DTPA (1·0 × 10^{-3}M); (2) titanium(III) chloride (1·0 × 10^{-3}M), DTPA (1·0 × 10^{-3}M); (3) titanium(III) chloride (2·0 × 10^{-3}M), DTPA (1·0 × 10^{-3}M); with 0·1M-NaOH

Curve 3 of Figure 3 shows that DTPA is capable of forming a dinuclear chelate which undergoes hydrolysis giving rise to a sharp inflexion at $a = 7$. If it may be assumed that all the protons generated arise from the ligand, the formation and subsequent hydrolysis of the dinuclear chelate may be represented as follows:

$$2\mathrm{Ti}^{3+} + \mathrm{H}_5\mathrm{L}_{(3)} \rightleftharpoons \mathrm{Ti}_2(\mathrm{OH})_2\mathrm{L}^-{}_{(3)} + 7\mathrm{H}^+$$

Alternative formulations exist involving a greater contribution of protons from hydrolysis of the metal ion with protons remaining on the ligand. However it may be noted that DTPA possesses one more carboxylic acid group than EGTA and that this corresponds to the experimental observation that the formation of the dinuclear DTPA chelate shifts the pH titration curve by just this amount.

Titration data for solutions containing titanium(III) and TTHA is shown by Figure 4. Similar results to those obtained using EGTA and DTPA are observed for TTHA. When the aqueous solution contains equimolar amounts of titanium(III) trichloride and TTHA curve 2 of Figure 4 shows that at pH *ca.* 7, $a = 6$, and at this point the formation of a 1 : 1 chelate could result as follows:

$$\mathrm{Ti}^{3+} + \mathrm{H}_6\mathrm{L}_{(4)} \rightleftharpoons \mathrm{TiL}_{(4)}{}^{3-} + 6\mathrm{H}^+$$

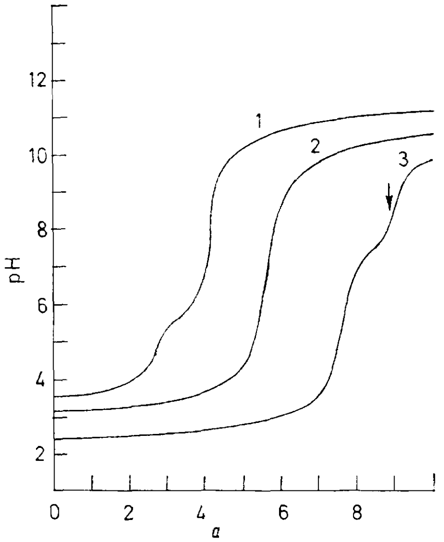

FIGURE 4 pH Titration of 100 ml of aqueous solution containing (1) TTHA (1·0 × 10^{-3}M); (2) titanium(III) chloride (1·0 × 10^{-3}M), TTHA (1·0 × 10^{-3}M); (3) titanium(III) chloride (2·0 × 10^{-3}M), TTHA (1·0 × 10^{-3}M), with 0·1M-NaOH

However below this point protonated forms of the 1 : 1 chelate are likely to occur and this may well be the case in the systems involving DTPA and EGTA. Curve 3 of Figure 4 furnishes evidence for the formation of a dinuclear chelate.

To summarise at this point, the potentiometric data has shown that all the ligands form 1 : 1 chelates with titanium(III) which are stable over a wide pH range. The ligands EGTA, DTPA, and TTHA form dinuclear chelates with titanium(III), all of which undergo the process of hydrolysis and give rise to titanium(III) hydroxide and the mononuclear chelate at high pH.

Electron Spin Resonance Measurements. The *X*-band e.s.r. spectra were recorded at sample temperatures of

77 K and room temperature. To facilitate observation of the singlet–triplet state spectra it is necessary to increase the concentration of titanium(III) chloride and ligand to 0·1M levels. The pH of each solution was varied prior to examination of the e.s.r. spectra. The spectral data, in conjunction with those from pH titration, are used to identify the species formed in major amount in solution and frozen solution. It must be recognised that the freezing process may in some cases partially alter the distribution and molecular form of the chelates.

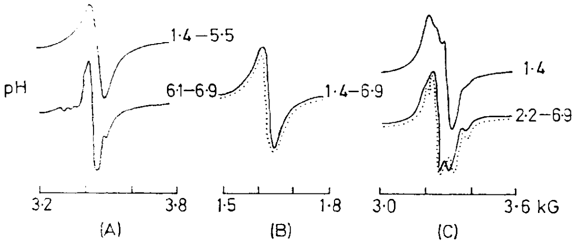

FIGURE 5 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium(III) chloride (0·1M), EDTA (0·1M) at various pH's; 5A, room temperature; 5B, C, 77 K. The dotted curves show the computed spectra using the parameters outlined in the Table

Typical e.s.r. spectra of solutions containing titanium(III) and EDTA in a 1 : 1 mole ratio at room temperature are shown in Figure 5A. The intensity of the signals is the same throughout the pH range 1·4 to 5·5; at pH 5 the line narrows and smaller peaks attributed to hyperfine effects due to the isotopes

$$^{49}\text{Ti}\left(I = \frac{7}{2}\right) \text{ and } ^{47}\text{Ti}\left(I = \frac{5}{2}\right)$$

are observed. This is the pH region where hydrolysis of the titanium(III)–EDTA chelate is expected to occur. At sample temperatures of 77 K the e.s.r. spectrum possesses a low field (1500 G) component depicted by Figure 5B. This signal is attributed to a $\Delta M_s = \pm 2$ transition arising in the singlet–triplet state as a result of the magnetic point dipolar–dipolar coupling between two titanium(III) ions. It is proposed that this occurs due to the dimerisation of the 1 : 1 chelate in the frozen aqueous solution. However there is no evidence for the formation of dimeric species in aqueous solution at room temperature. The spectrum in the $g = 2$ region consists of an unresolved somewhat broadened lineshape. The process of dimerisation may be accompanied by a more general solute aggregation which often depends on the solvent composition. It was found that the addition of 20% by volume of ethylene glycol brought about a resolution of this signal depicted by Figure 5C. Under these circumstances, the signal could be discerned to be the $\Delta M_s = \pm 1$ signal. It was established from potentiometric pH titration of 1 : 1 mole ratio titanium(III) chloride EDTA aqueous solutions containing 20% by volume ethylene glycol, that the 1 : 1 chelate formed as described previously. Further the room temperature signals were quite unchanged by the addition of ethylene glycol as was the case for the low field $\Delta M_s = \pm 2$ signal. Thus the only effect brought about by the ethylene glycol is a significant improvement in resolution of the signal depicted by Figure 5C. The addition of ethylene glycol to form 20% by volume of the solvent composition was found to have an equally beneficial effect on the singlet–triplet state spectra in the $g = 2$ region due to solutions containing titanium(III) and EGTA, DTPA, and TTHA as was found previously for the dinuclear copper(II)–EGTA chelate.

In the calculations of the magnetic and structural parameters derived from singlet–triplet state spectra, it is possible to determine the parameters from the $\Delta M_s = \pm 2$ transitions alone, thus making it unnecessary to seek optimum conditions for the observation of the $\Delta M_s = \pm 1$ signals. However since the computer lineshape simulation of the $\Delta M_s = \pm 1$ signal is more sensitive to variation of the internuclear separation of the magnetic dipolar coupled titanium(III) ions, the structural parameters gain in reliability if the experimental $\Delta M_s = \pm 1$ signal is available.

The e.s.r. spectra of solutions containing 0·1M-titanium(III) chloride and 0·5M-EGTA at various pH values and at room temperature consisted of a single isotropic line whose intensity did not change with change of pH. The spectra obtained at sample temperatures of 77 K are shown by Figure 6. Low field (1500 G) signals, attributable to $\Delta M_s = \pm 2$ transitions arising from magnetic dipole–dipole coupling between the titanium(III) ions in the dinuclear chelate, are observed. The extra low field line observed in the pH range 2·3 to 4·5 has been observed previously and is attributed to a distortion from axial symmetry.[7] The spectrum obtained at room temperature for solutions containing 0·1M-titanium(III) chloride and 0·1M-EGTA at various pH's consists of a single isotropic line. This spectrum is similar to that obtained under 2 : 1 mole ratio conditions. The presence of low field (1500 G) signals at sample temperatures of 77 K (Figure 7) indicates the presence of coupling between titanium(III) ions.

However close examination of the respective low field spectra shows a marked change both in intensity and field positions in the spectra obtained under 2 : 1 mole ratio reactant conditions. It appears therefore that, as in the case of the formation of the titanium(III)–EDTA chelate, a dimeric form of the 1 : 1 chelate is present in frozen solution. However, the signal observed in the *g ca.* 2 region (Figure 7) indicates that a monomeric form of the 1 : 1 chelate is also present in frozen solution.

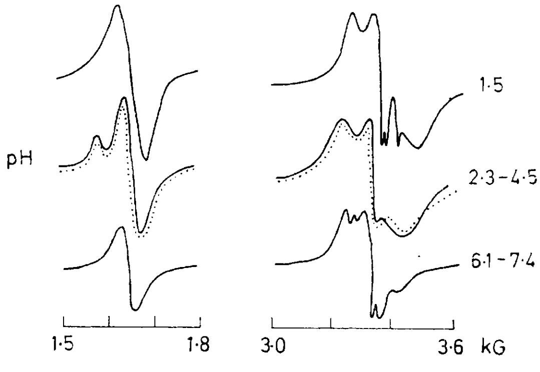

FIGURE 6 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium(III) chloride (0·1M), EGTA (0·05M) at various pH's, 77 K. The dotted curves show the computed spectra using the parameters outlined in the Table

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[7] S. G. Carr and T. D. Smith, *J.C.S. Dalton*, 1972, 1887.

DTPA also possesses the capacity to form polynuclear chelates. The spectra obtained at room temperature for solutions containing 0·1M-titanium(III) chloride and 0·05M-DTPA are shown in Figure 8A. Instead of a simple signal line spectrum, as observed in the case of EDTA and EGTA, characteristic of a dinuclear complex, several extra lines are observed, which increase in intensity with increasing pH. These extra lines are also observed, although slightly more intense, under 1 : 1 conditions. This phenomenon has been observed previously in studies involving mononuclear titanium(III) chelates [6] and attributed to a hyperfine effect involving the isotopes of titanium, ^{49}Ti ($I = \frac{7}{2}$), ^{47}Ti ($I = \frac{5}{2}$).

The fact that this effect is slightly more pronounced under 1 : 1 mole ratio conditions and at high pH indicates that it is probably due to the formation of a mononuclear chelate. The spectra of solutions containing 0·1M-titanium(III) chloride and 0·1M-DTPA verify this where a $\Delta M_s = \pm 2$ spectrum is observed at 77 K, and the signal observed in the *g ca.* 2 region is typical of those observed for monomeric titanium(III) complexes.

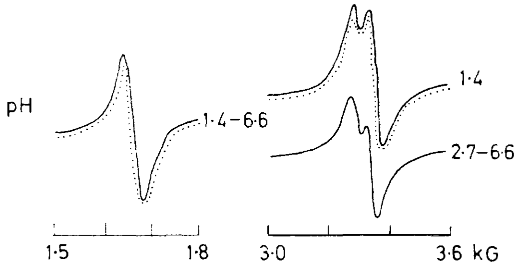

FIGURE 7 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium(III) chloride (0·1 M), EGTA (0·1M) at various pH's, 77 K. The dotted curves show computed spectra using the parameters outlined in the Table

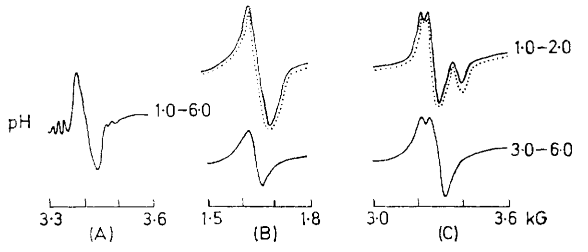

FIGURE 8 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium(III) chloride (0·1M), DTPA (0·05M) at various pH's; A, room temperature, B, C, 77 K. The dotted curves show computed spectra using the parameters outlined in the Table

The spectra obtained at sample temperatures of 77 K for the 2 : 1 mole ratio solutions are shown in Figure 8B and 8C. The presence of low field (1500 G) signals over a wide pH range provides unequivocal evidence for the formation of a dinuclear chelate in frozen solution. Both the loss in intensity of the low field signal as well as the loss of structure on the corresponding spectra in the *g ca.* 2 region confirm that, as the pH of the solution is increased, the concentration of the monomeric chelate in solution increases.

The spectrum obtained at room temperature for solutions containing 0·1M-titanium(III) chloride and 0·05M-TTHA consists of a single isotropic signal whose intensity varies little with change in pH. The corresponding spectrum obtained at sample temperatures of 77 K is shown in Figure 9. Singlet–triplet state spectra are observed providing evidence for the formation of the dinuclear chelate in frozen solution. The spectrum obtained from solutions containing the reactants in 1 : 1 mole ratio indicate the presence of magnetic dipole–dipole coupling between titanium(III) ions due to the formation of a dimeric form of the 1 : 1 chelate (Figure 10).

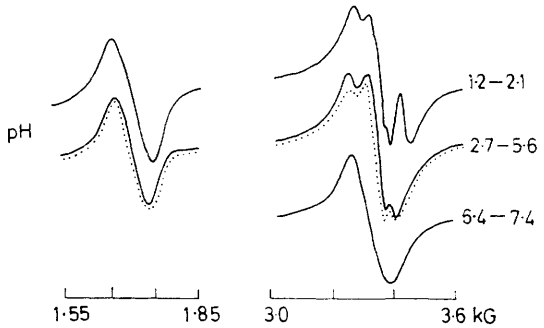

FIGURE 9 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium(III) chloride (0·1M), TTHA (0·05M) at various pH's, 77 K. The dotted curves show computed spectra using the parameters outlined in the Table

Information concerning the structures of the dinuclear and dimeric species can be obtained by computer simulation of the appropriate signals observed experimentally. The parameter of chief interest in these studies is the internuclear separation of the titanium(III) ions in the pair systems of the dinuclear and dimeric chelates. Its reliability is assessed by finding the range over which comfortable fits are obtained subject to suitable variation of the parameters. Convergence of parameters when both $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ curves can be fitted independently is helpful in justifying the model assumed. The effect on the computed lineshapes of the symmetry of the pair system of transition metal ions ($S = \frac{1}{2}$) has been described previously.[1,8,9] The Table contains the results from the curve fitting procedures and summarises the best values of the parameters concerned which have an adequate fit to the observed signals. The main spectral features of the observed signals were fitted to within ±5 G. The spectra selected for quantitative treatment correspond to conditions where potentiometric pH titration data and

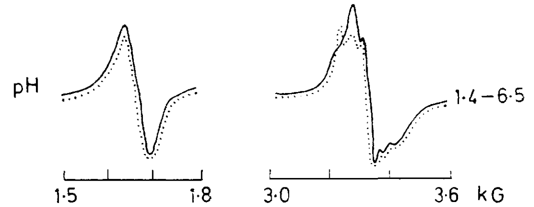

FIGURE 10 *X*-Band e.s.r. spectra due to aqueous solutions containing 20% v/v ethylene glycol, titanium (III) chloride (0·1M), TTHA (0·1M) at various pH's, 77 K. The dotted curves show computed spectra using the parameters outlined in the Table

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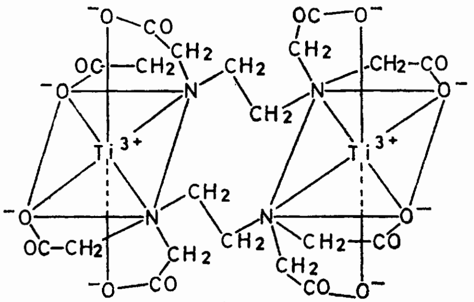
[8] P. D. W. Boyd, A. D. Toy, T. D. Smith, and J. R. Pilbrow, *J.C.S. Dalton*, **1973**, 1549.

[9] S. G. Carr, T. D. Smith, and J. R. Pilbrow, *J.C.S. Faraday II*, **1974**, 497.

e.s.r. measurements indicate that most of the titanium(III) is in one particular chelate form.

A structure which is compatible with our determination of the internuclear separation of the titanium(III) ions and their symmetry in the pair system of the dimeric EDTA chelate is shown by structure (I). This structure involves an orthorhombic symmetry of the pair system in which each EDTA chelate ligand anion is shared between the two titanium(III) ions.

System	ΔM_s Transition	r (Å)	g_x	g_y	g_z	ξ^0	Symmetry of pair system
$TiCl_3$ (0·1M) + Na_2EDTA (0·1M)	±1	6·70 ± 0·05	1·960 ± 0·020	1·960 ± 0·020	1·990 ± 0·020	90	Orthorhombic
pH 2·2	±2	6·70 ± 0·50	1·960 ± 0·010	1·960 ± 0·010	1·990 ± 0·010	90	
$TiCl_3$ (0·1M) + EGTA (0·1M)	±2	6·00 ± 0·50	1·920 ± 0·010	1·920 ± 0·010	1·960 ± 0·010	0	Axial
pH 3·6							
$TiCl_3$ (0·1M) + EGTA (0·05M)	±1	6·05 ± 0·05	1·915 ± 0·010	1·915 ± 0·010	2·060 ± 0·010	30	Monoclinic
pH 3·8	±2	6·00 ± 0·60	1·915 ± 0·010	1·915 ± 0·010	2·070 ± 0·010		
$TiCl_3$ (0·1M) + DTPA (0·05M)	±1	5·70 ± 0·05	1·958 ± 0·005	1·958 ± 0·005	1·980 ± 0·005	0	Axial
pH 1·8	±2	5·80 ± 0·50	1·960 ± 0·005	1·960 ± 0·005	1·980 ± 0·005	0	
$TiCl_3$ (0·1M) + TTHA (0·1M)	±1	6·70 ± 0·10	1·930 ± 0·005	1·930 ± 0·005	1·960 ± 0·005	90	Orthorhombic
pH 3·3	±2	6·80 ± 0·50	1·925 ± 0·005	1·925 ± 0·005	1·955 ± 0·005		
$TiCl_3$ (0·1M) + TTHA (0·05M)	±1	6·50 ± 0·05	1·920 ± 0·005	1·920 ± 0·005	1·970 ± 0·005	90	Orthorhombic
pH 4·7	±2	6·70 ± 0·50	1·910 ± 0·005	1·910 ± 0·005	1·970 ± 0·005	90	

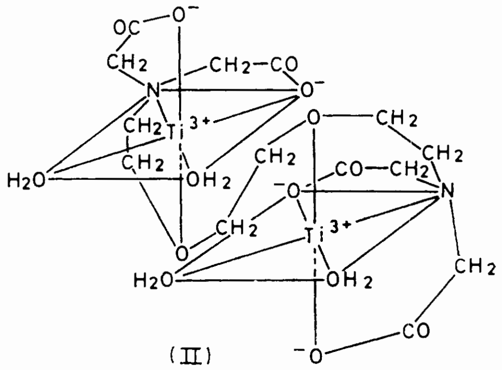

(I)

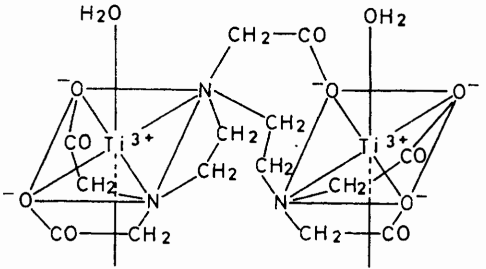
In this structure, and the ones to follow, the main objective is to show a conformation of the ligand anion that would lead to the internuclear metal ion separation shown by the Table. We do not have exact knowledge about the binding site, except to say that the nitrogen atoms and carboxylate groups are at distances which molecular models show would enable them to take part in binding of the metal ion. However in aqueous solution, the carboxylate group alone may be involved in chelation with the remaining co-ordination sites occupied by solvent molecules. The hydrolysis of the titanium(III) chelate does not affect the structural parameters. In considering the role of the solution of the chelate, preferential occupation of a co-ordination site by ethylene glycol may be the explanation for its role in giving better resolved singlet–triplet operation by reducing the possibility of a more ill-defined solute aggregation which occurs in pure water.

Several structures are possible for the dinuclear EGTA chelate. The presence of an extra line in the low field (1500 G) position of the singlet–triplet state spectrum indicates a lowering of the symmetry of the pair system. Structure (II) depicts a structure which accommodates the symmetry properties and presents no difficulty in construction from molecular models. This structure involves the ether linkages of EGTA in the co-ordination of the titanium(III) ions, resulting in a distance of 6·0 Å between the metal ions.

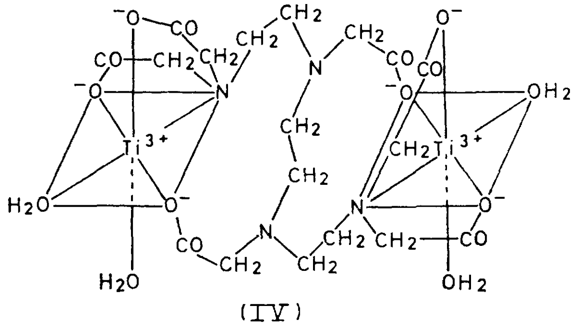
The structural possibilities offered by DTPA when forming a dinuclear chelate are as numerous as those with EGTA. However, a structure involving an axial symmetry of the titanium(III) pair system, as shown in structure (III), provides the only case in which the metal ion separation is compatible with that determined by computer simulation of the appropriate e.s.r. lineshape. This structure involves the sharing of the terminal groups of DTPA and places the titanium(III) ions at a distance of *ca.* 6 Å. This arrangement indicates that possibly one ethylene bridge and one acetate group are involved in bridging the two titanium(III) ions in the dinuclear complex.

Two major structural possibilities are presented by the binding sites of TTHA when forming a dinuclear complex.[2] The first of these involves an open form of the chelate in which the terminal groups bind the titanium(III) ions and the ligand is in an extended form. The metal ion separation in this structure is *ca.* 8 Å and therefore would not be expected to give rise to the observed experimental results. Structure (IV), on the other hand, involves a shorter internuclear separation between the titanium(III)


(II)


(III)

ions as well as an orthorhombic symmetry of the titanium(III) pair system. In this structure the central two nitrogens are not co-ordinated to either titanium(III) ion.



(IV)

EXPERIMENTAL

The source of titanium(III) was commercially available titanium(III) chloride. The ligands, EDTA (disodium salt), EGTA, DTPA, and TTHA were obtained from the Dojindo Pharmaceutical Laboratory, Kumamoto, Japan. The e.s.r. measurements at room temperature and 77 K were made on a conventional *X*-band spectrometer using a Varian multipurpose cavity with 100 kHz modulation and a microwave frequency of 9·080 GHz. All solution preparation and transfer operations were carried out under an atmosphere of nitrogen. Aqueous solutions used for e.s.r. measurements contain 20% by volume of ethylene glycol, added to improve the glass-forming properties and avoid solute aggregation in the process of freezing. Measurements of pH were made using a Radiometer 22 pH meter fitted with a glass electrode and saturated calomel electrode.

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