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The synthesis, structure and nuclear magnetic resonance properties of some titanium relatives of Amavadin: [Δ-Ti(*R*,*R*-hidpa)$_2$]$^{2-}$, [Δ,Λ-Ti(*R*,*R*-hidpa)$_2$]$^{2-}$ and [Δ,Λ-Ti(hida)$_2$]$^{2-}$ [H$_3$hidpa = 2,2′-(hydroxyimino)dipropionic acid, H$_3$hida = *N*-hydroxyiminodiacetic acid]

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The compound [TiO(acac)$_2$] (acac = acetylacetonate) reacts with *N*-hydroxyiminodiacetic acid (H$_3$hida) or (*R*,*R*)-2,2′-(hydroxyimino)dipropionic acid (*R*,*R*-H$_3$hidpa) to yield [Ti(hida)$_2$]$^{2-}$ or [Ti(*R*,*R*-hidpa)$_2$]$^{2-}$, respectively. The anion [Ti(*R*,*R*-hidpa)$_2$]$^{2-}$ has been obtained from H$_2$O in the presence of Ca^{2+} as [Ca(H$_2$O)$_4$][Ca(H$_2$O)$_5$]$_3$-[Δ-Ti(*R*,*R*-hidpa)$_2$]$_4$·2H$_2$O **3** which crystallises in the space group $P2_1$ (no. 4) with a = 14.258(2), b = 16.516(3), c = 19.169(3) Å, β = 110.907(9)°; least-squares refinement of 6082 reflections and 1126 variables converged with agreement factors of R = 0.069 and R' = 0.054. The anions possess the co-ordination geometry identified for other Amavadin-style complexes, *viz*. eight-co-ordination achieved by the ligation of two mutually *trans* and staggered η^2-NO groups and four unidentate carboxylate oxygen atoms; Ti–N(NO) 2.04(1)–2.10(1), Ti–O(NO) 1.962(9)–2.001(9), Ti–O(CO$_2$) 2.024(9)–2.100(9), N–O 1.38(1)–1.44(1) Å. The lattice of compound **3** comprises of parallel zigzag strands of alternating [Δ-Ti(*R*,*R*-hidpa)$_2$]$^{2-}$ and [Ca(H$_2$O)$_x$]$^{2+}$ (x = 4 or 5) linked interstrand by Ca$^{\mathrm{II}}$ binding to carboxylato-oxygen atoms and intra- and inter-strand by hydrogen bonding from the H$_2$O molecules to the oxygen atoms of the anions. The anions are obtained exclusively in the Δ-helical form and this has enabled ^{1}H and ^{13}C NMR studies to follow epimerisation at the Ti$^{\mathrm{IV}}$ centre to produce a mixture of the Δ- and Λ-helical forms. Carbon-13 NMR spectroscopy has been used to investigate the interaction of the carboxylato groups of [Ti(hida)$_2$]$^{2-}$ with solvents.

Vanadium is accumulated in mushrooms of the genus *Amanita* to ⩽400 ppm[1] as Amavadin which is constituted[2–5] as the complex [V(*S*,*S*-hidpa)$_2$]$^{2-}$, where *S*,*S*-H$_3$hidpa = HON[CH(Me)-CO$_2$H]$_2$, (*S*,*S*)-2,2′-hydroxyiminodipropionic acid. This co-ordination environment leads to chirality at the vanadium, and Amavadin as isolated consists of an approximately equimolar mixture of the Δ- and Λ-helical forms of [V(*S*,*S*-hidpa)$_2$]$^{2-}$.[3–5] The presence of V$^{\mathrm{IV}}$ is clearly indicated by EPR spectroscopy[3,5,6] and the centre may be reversibly oxidised to the V$^{\mathrm{V}}$ level;[3–5,7] thus, the species belongs to the group of transition-metal centres in biology which exhibit one-electron reversible redox behaviour. We have explored the chemistry of H$_3$hidpa and that of its achiral analogue *N*-hydroxyiminodiacetic acid, HON(CH$_2$CO$_2$H)$_2$(H$_3$hida),[8] with other early transition metals, including Mo$^{\mathrm{V}}$,[9,10] Nb$^{\mathrm{V}}$ and Ta$^{\mathrm{V}}$,[11] Ti$^{\mathrm{IV}}$ and Zr$^{\mathrm{IV}}$,[12] and developed other chemistry with relatives of these ligands.[13,14] These studies have included the synthesis and structural characterisation of {[Ca(H$_2$O)$_4$][Δ,Λ-Ti(hida)$_2$]·2H$_2$O}$_n$.[12] Herein, we report an extension of this latter chemistry to include a study of the Ti$^{\mathrm{IV}}$–hidpa system and ^{1}H and ^{13}C NMR studies of [Ti(hida)$_2$]$^{2-}$ and [Ti(hidpa)$_2$]$^{2-}$ complexes in solution.

Experimental

Solvents were used as supplied or distilled under dinitrogen using standard methods. Chemicals were supplied by either Aldrich Chemical Company Ltd. or Janssen Chimica. The pro-ligands (*R*,*R*)-2,2′-(hydroxyimino)dipropionic acid (*R*,*R*-H$_3$hidpa) and *N*-hydroxyiminodiacetic acid (H$_3$hida) were synthesised using a modified[11] version of that described by Koch and co-workers[15] and purified using their procedure. Chemical analyses were performed by the University of Manchester Microanalytical Laboratory. Infrared spectra were recorded on a ATI Mattson Genesis Series FTIR spectrometer. Negative-ion FAB mass spectra were recorded using a KRATOS Concept 1S spectrometer (matrix nitrobenzyl alcohol); 300 MHz ^{1}H and ^{13}C 75 MHz NMR spectra were measured using a Bruker AC 300 spectrometer, 500 MHz ^{1}H NMR spectra were recorded on a Varian Unity 500 spectrometer.

Preparation of {[Ca(H$_2$O)$_4$][Ti(hida)$_2$]·2H$_2$O}$_n$ 1

The compound [TiO(acac)$_2$] (acac = acetylacetonate) (0.131 g, 0.5 mmol) was added to a solution of H$_3$hida (0.148 g, 1 mmol) in H$_2$O (10 cm^3). The resultant mixture was stirred at room temperature for 16 h. Calcium chloride (0.055 g, 0.5 mmol) was added and the solution stirred for a further 10 min. The volume was reduced under vacuum on a rotary evaporator to *ca*. 3 cm^3, filtered into a glass tube and a layer of Pr^{i}OH (15 cm^3) carefully added. After several days standing in the dark, at room temperature, colourless bipyramidal crystals of [Ca(H$_2$O)$_4$][Ti(hida)$_2$]·2H$_2$O[12] formed. Yield 0.159 g, 65% (Found: C, 19.9; H, 4.1; N, 5.5. Calc. for C$_8$H$_{20}$CaN$_2$O$_{16}$Ti: C, 19.7; H, 4.1; N, 5.7%). IR/cm^{-1}, KBr disc: 2980, 2924 ($\nu_{\mathrm{C-H}}$); 1631, 1600 ($\nu_{\mathrm{C=O}}$); 1385 ($\nu_{\mathrm{C-O}}$); 1116 ($\nu_{\mathrm{N-O}}$). ^{1}H NMR (D$_2$O, 298 K): δ 4.73 (H$_2$O); 4.35, 4.21, 4.09, 4.03 (4 d, 8 H, $^2J_{\mathrm{H-H}} = -16$ Hz, CH$_2$). ^{13}C NMR (D$_2$O, 298 K): δ 178.21, 178.01 (CO$_2^-$); 61.65, 61.40 (CH$_2$).

Preparation of [NMe$_4$]$_2$[Ti(hida)$_2$]·1.5H$_2$O 2

The compound [TiO(acac)$_2$] (0.131 g, 0.5 mmol) was added to a solution of H$_3$hida (0.148 g, 1 mmol) in H$_2$O (10 cm^3). The resultant mixture was stirred at room temperature for 16 h. The solution was neutralised by the addition of [NMe$_4$][OH] (20–25% w/w solution in H$_2$O). The solvent was removed under reduced pressure. The residue was dissolved in MeOH (3 cm^3) and precipitated with Et$_2$O (30 cm^3). The white precipitate was

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Table 1 Crystallographic data for $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4\cdot 2H_2O$ **3**

	3
	$C_{48}H_{106}Ca_4N_8O_{61}Ti_4$
M	2123.3
Crystal colour, habit	Colourless
Crystal dimensions (mm)	0.05 × 0.20 × 0.55
Crystal system	Monoclinic
Space group	$P2_1$ (no. 4)
a/Å	14.258(2)
b/Å	16.516(3)
c/Å	19.169(3)
β/°	110.907(9)
U/Å^3	4216(2)
Z	2
D_c/g cm^{-3}	1.672
μ/cm^{-1}	7.27
Diffractometer	Rigaku AFC5R
Radiation (λ/Å)	Mo-Kα (0.710 69)
T/°C	19.0 (±1)
Scan type	ω-2θ
Scan rate/° min^{-1} (in ω)	8.0
Scan width/°	0.94 + 0.30tanθ
$2\theta_{max}$/°	55.3
Transmission factors	0.8311–0.9992
No. of reflections measured	12 741
No. of observations	6082 [$I > 2.50\sigma(I)$]
No. of variables	1126
Residuals: R^a,R'^b	0.069, 0.054
Goodness of fit indicator	1.90

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [(\Sigma(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{\frac{1}{2}}$.

filtered off and dried under vacuum. Yield 0.187 g, 73% (Found: C, 37.7; H, 7.0; N, 10.7. Calc. for $C_{16}H_{35}N_4O_{11.5}Ti$: C, 37.3; H, 6.8; N, 10.9%). IR/cm^{-1}, KBr disc: 3033, 2963, 2920 (ν_{C-H}); 1629 ($\nu_{C=O}$); 1380 (ν_{C-O}); 1116 (ν_{N-O}). Mass spectrum (negative FAB): m/z 414 ($\{[NMe_4][Ti(hida)_2]\}^-$); 341 ($\{H[Ti(hida)_2]\}^-$). ^{1}H NMR ($CD_3OD$, 298 K): δ 4.90 (H_2O); 4.28, 4.13, 3.91, 3.89 (4 d, 8 H, $^2J_{H-H} = -16$ Hz, CH_2); 3.36 (CD_3OD); 3.21 (s, 24 H, $[NMe_4]^+$). ^{13}C NMR (CD_3OD, 298 K): δ 177.40, 177.15 (CO_2^-); 62.34, 61.96 (CH_2); 56.02 ($[NMe_4]^+$); 49.00 (CD_3OD).

Preparation of $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4\cdot 2H_2O$ 3

The compound was prepared and crystallised as for **1** using $[TiO(acac)_2]$ (0.131 g, 0.5 mmol), R,R-H_3hidpa (0.177 g, 1 mmol) and $CaCl_2$ (0.55 g, 0.5 mmol). The product was identified by X-ray diffraction studies (see below). Yield: 0.142 g, 54% (Found: C, 27.5; H, 4.9; N, 5.0. Calc. for $C_{48}H_{106}Ca_4N_8O_{61}Ti_4$: C, 27.2; H, 5.0; N, 5.3%). IR/cm^{-1}, KBr disc: 2992, 2945 (ν_{C-H}); 1620 ($\nu_{C=O}$); 1385 (ν_{C-O}); 1124 (ν_{N-O}); 983 (ν_{C-Me}). ^{1}H NMR (D_2O, 298 K): δ 4.74 (DHO); 4.48, 4.00 (2 q, 4 H, $^3J_{H-H} = 7.5$, CH); 1.47, 1.43 (2 d, 12 H, $^3J_{H-H} = 7.5$ Hz, CH_3). ^{13}C NMR (D_2O, 298 K): δ 181.68, 180.77 (CO_2^-); 67.18, 64.09 (CH); 15.22, 12.51 (CH_3).

Preparation of $[NMe_4]_2[Ti(R,R\text{-hidpa})_2]\cdot H_2O$ 4

The compound was prepared as for **2** using $[TiO(acac)_2]$ (0.131 g, 0.5 mmol) and R,R-H_3hidpa (0.178 g, 1 mmol). Yield: 0.188 g, 67% (Found: C, 43.1; H, 7.7; N, 9.4. Calc. for $C_{20}H_{42}N_4O_{11}Ti$: C, 42.7; H, 7.5; N, 10.0%). IR/cm^{-1}, KBr disc: 3012, 2981, 2938, (ν_{C-H}); 1622 ($\nu_{C=C}$); 1384 (ν_{C-O}); 1128 (ν_{N-O}); 979 (ν_{C-Me}). Mass spectrum (negative FAB): m/z 470 ($\{[NMe_4][Ti(R,R\text{-hidpa})_2]\}^-$); 397 ($\{H[Ti(R,R\text{-hidpa})_2]\}^-$). ^{1}H NMR ($CD_3OD$, 298 K): δ 4.89 (H_2O); 4.38, 4.26, 3.95, 3.90 (4 q, 4 H, $^3J_{H-H} = 7.1$, CH); 3.50 (q, Et_2O); 3.32 (CD_3OD); 3.21 (s, $[NMe_4]^+$); 1.64, 1.56, 1.43 (3 d, 12 H, $^3J_{H-H} = 7.1$ Hz, CH_3). ^{13}C NMR (CD_3OD, 298 K): δ 181.30, 180.95, 179.57, 179.53 (CO_2^-), 68.11, 67.73, 64.01, 63.47 (CH); 66.67 (Et_2O); 56.04 ($[NMe_4]^+$); 49.00 (CD_3OD); 15.48 (Et_2O); 15.28, 14.89, 12.46 (CH_3).

Cyclic voltammetric experiments were undertaken on complexes **1** and **3** under standard cyclic voltammetric conditions (0.2 M KCl–H_2O solution at room temperature using a platinum bead working electrode). Scans were run in the available window between +1.0 and −1.0 V *vs.* saturated calomel electrode (SCE) and for both compounds no electrochemical processes were observed.

Structure of complex 3

Colourless crystals of **3** were obtained from an aqueous solution of the reaction mixture layered with Pr^{i}OH. The crystals were sensitive to solvent loss and so were mounted in sealed glass capillaries. A summary of the crystallographic data is presented in Table 1. Azimuthal scans of several reflections indicated that transmission factors ranging from 0.83 to 1.00 were observed and suitable absorption corrections were applied. The data set was corrected for Lorentz and polarisation effects. The structure of **3** was solved by direct methods using SHELXS and expanded using DIRDIF.[16] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in idealised positions (C–H = 0.95 Å) and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement, function minimised $\Sigma w(|F_o| - |F_c|)^2$, was based on 6082 observed reflections [$I > 2.50\sigma(I)$] and 1126 variable parameters and converged with $R = 0.069$ and $R' = 0.054$. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.98 and −0.77 e Å^{-3}, respectively. Both the Δ- and Λ-helical forms were refined and the Δ-helical configuration at Ti gave a slightly lower R' value than that obtained using the alternative Λ-helical form ($R = 0.069$, $R' = 0.055$). The result obtained gave all of the chiral carbon atoms the R conformation which is consistent with the use of R,R-H_3hidpa in the synthesis and therefore acts as a 'lock' on the structure (see below). All calculations were performed using the TEXSAN crystallographic software package.[17]

CCDC reference number 186/737.

Results and Discussion

The choice of $[TiO(acac)_2]$ for the starting material in these syntheses proved to be convenient; it is probable that acac acts as a base helping to deprotonate the pro-ligands H_3hida and R,R-H_3hidpa. The yields of compounds **1**–**4** were reasonably good and the materials were readily obtained essentially analytically and spectroscopically pure. Negative-ion FAB mass spectrometry and IR spectroscopy demonstrated that compounds **1** and **2** contain the $[Ti(hida)_2]^{2-}$ anion and that compounds **3** and **4** contain the $[Ti(hidpa)_2]^{2-}$ anion. Unlike their V[3–5,7] and Mo[9,10] counterparts, the Ti systems are redox inactive.

Structure of complex 3

This compound crystallises in the chiral space group $P2_1$ with the asymmetric unit having the composition $[Ca(H_2O)_4]$-$[Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4\cdot 2H_2O$. The Ti^{IV} centres each comprise a 1 : 2 complex with R,R-hidpa^{3-} (Fig. 1) with a co-ordination geometry very similar to that established for V^{IV} in Amavadin[3–5] and for V^{IV},[3–5,8,14] Nb^V and Ta^V,[11] Mo^V,[9,10] and Ti^{IV},[12] in related systems. Each Ti^{IV} is co-ordinated to two mutually *trans* and staggered η^2-NO groups and four unidentate carboxylate oxygen atoms, giving eight-co-ordination of the metal. The crystal structure refinement was consistent with the presence of the Δ-helical form at all the Ti^{IV} centres and R chirality at all of the chiral carbon atoms. This conclusion is in agreement with the synthetic procedure, as the all-R isomer of H_3hidpa was employed and the alternative chiral refinement would give rise to $[\Lambda\text{-}Ti(S,S\text{-hidpa})_2]^{2-}$ centres.

Table 2 Selected bond distances (Å) and angles (°) for the M^{IV} centres in $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4\cdot 2H_2O$ **3** and two related hidpa complexes (estimated standard deviations in parentheses)

	Ti(1)	Ti(2)	Ti(3)	Ti(4)	$[Ca(H_2O)_4]$ $[Ti(hida)_2]$[12]	$H_2[\Lambda\text{-}V(R,R\text{-hidpa})_2]$[5]
M–O (η^2-NO)	1.975(9)	1.977(10)	1.983(9)	2.001(9)	1.975(5)	1.924(5)
	1.962(9)	1.983(9)	1.982(9)	1.967(9)	1.943(4)	1.945(5)
M–N	2.10(1)	2.06(1)	2.07(1)	2.05(1)	2.071(5)	1.998(6)
	2.05(1)	2.04(1)	2.07(1)	2.05(1)	2.078(5)	2.024(6)
N–O	1.41(1)	1.40(1)	1.40(1)	1.38(1)	1.419(6)	1.375(8)
	1.40(1)	1.38(1)	1.42(1)	1.44(1)	1.401(7)	1.396(8)
M–O (CO_2^-)	2.047(8)	2.084(9)	2.045(8)	2.048(8)	2.079(5)	2.084(5)
	2.082(9)	2.065(8)	2.061(9)	2.075(9)	2.087(5)	2.060(5)
	2.070(9)	2.089(9)	2.100(9)	2.093(9)	2.077(5)	2.036(6)
	2.078(9)	2.049(9)	2.024(9)	2.052(9)	2.089(5)	2.097(5)
O–M–N	40.4(3)	40.4(3)	40.3(3)	39.8(3)	40.6(2)	41.0(2)
	40.7(3)	40.0(4)	40.9(3)	41.8(3)	41.0(2)	41.0(2)
M–O–N	74.4(6)	73.1(6)	73.1(6)	71.9(6)	73.1(3)	72.4(4)
	73.2(6)	72.4(6)	72.9(6)	72.4(6)	74.9(3)	72.0(3)
M–N–O	65.2(6)	66.5(6)	66.7(5)	68.4(6)	65.9(3)	66.6(3)
	66.1(5)	67.6(6)	66.2(5)	65.9(5)	64.5(3)	66.4(3)
Dihedral angle between the two {M–N–O} groups	93.0	94.6	92.4	91.0	92.7	91.6
Dihedral angle between the {M–N–O} planes and the $\{MO_4\}$ plane	88.4	88.3	88.4	88.0	88.9	90.7
	91.6	91.5	90.4	91.0	92.3	90.5
Displacement of the bonding O atoms from the $\{MO_4\}$ plane	0.38 [O(1)]	0.35 [O(15)]	0.36 [O(39)]	0.36 [O(49)]	0.36 [O(1)]	0.38 [O(1)]
	0.50 [O(5)]	0.47 [O(11)]	0.46 [O(35)]	0.46 [O(45)]	0.51 [O(5)]	0.50 [O(5)]
	−0.50 [O(6)]	−0.46 [O(16)]	−0.46 [O(34)]	−0.47 [O(44)]	−0.51 [O(6)]	−0.50 [O(6)]
	−0.37 [O(10)]	−0.35 [O(20)]	−0.35 [O(30)]	−0.35 [O(40)]	−0.35 [O(10)]	−0.37 [O(10)]

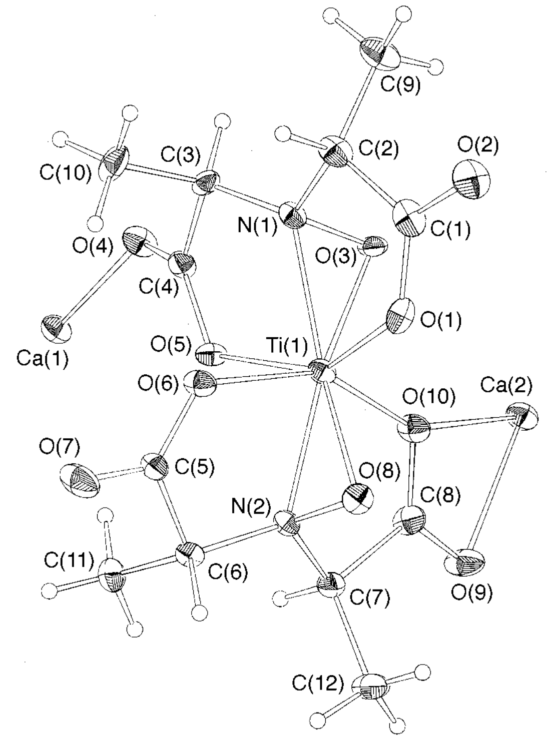

Fig. 1 An ORTEP[18] view showing the co-ordination around Ti(1) in $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4\cdot 2H_2O$ **3** (thermal ellipsoids 50% probability)

The dimensions of the four crystallographically independent Ti^{IV} centres are detailed in Table 2 and are similar in each case. The bond length ranges are: Ti–N (NO) 2.04(1)–2.10(1) Å; Ti–O (NO) 1.962(9)–2.001(9) Å; Ti–O (CO_2) 2.024(9)–2.100(9) Å; N–O 1.38(1)–1.44(1) Å; and the angles subtended by the η^2-NO groups at the Ti^{IV} range from 39.8(3) to 41.8(3)°. For each Ti^{IV} centre the two {TiNO} groups are essentially mutually perpendicular (dihedral angles, 91.0–94.6°) and perpendicular to the least-squares plane of the $\{TiO_4\}$ moiety involving the four carboxylato-oxygen atoms (dihedral angles 88.0–91.6°). Each of the carboxylato-oxygen atoms is displaced from this $\{TiO_4\}$ least-squares plane by a distance of between 0.35 and 0.50 Å, in an alternating up/down sequence. The anions possess no crystallographically imposed symmetry, however, the symmetry of each of these $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$ approximates to C_2; see Fig. 1, where the axis of rotation bisects the O(5)–Ti–O(6) and O(1)–Ti–O(10) interbond angles. All of these geometric and angular details are very similar to those observed for other Amavadin-style complexes, *e.g.* as documented in Table 2 for $[\Delta,\Lambda\text{-}Ti(hida)_2]^{2-}$ [12] and $[\Lambda\text{-}V(R,R\text{-hidpa})_2]^{2-}$.[5] A comparison with other titanium complexes[19–21] containing η^2-NO groups shows that both $[\Delta,\Lambda\text{-}Ti(hida)_2]^{2-}$ [12] and $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$ involve dimensions within the range previously reported for Ti–η^2-NO groups.

As we have already reported,[12] these Amavadin-style complexes show a considerable affinity for cations such as Ca^{II}, the binding occurring through the carboxylate oxygen atoms, and networks of the metal centres are formed. Figs. 2 and 3 show the formation of two strands composed of alternating Ti^{IV} and Ca^{II} centres, one involving Ti(1), Ca(1), Ti(2) and Ca(2) and the other Ti(3), Ca(3), Ti(4) and Ca(4). In each case $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$ binds to two Ca^{II} (see Fig. 1) with each $hidpa^{3-}$ ligand only binding to one Ca^{II}. Each of the Ca^{II} centres is seven-co-ordinate and, for three of them, this involves the ligation of five water molecules and the non-Ti-bonded O

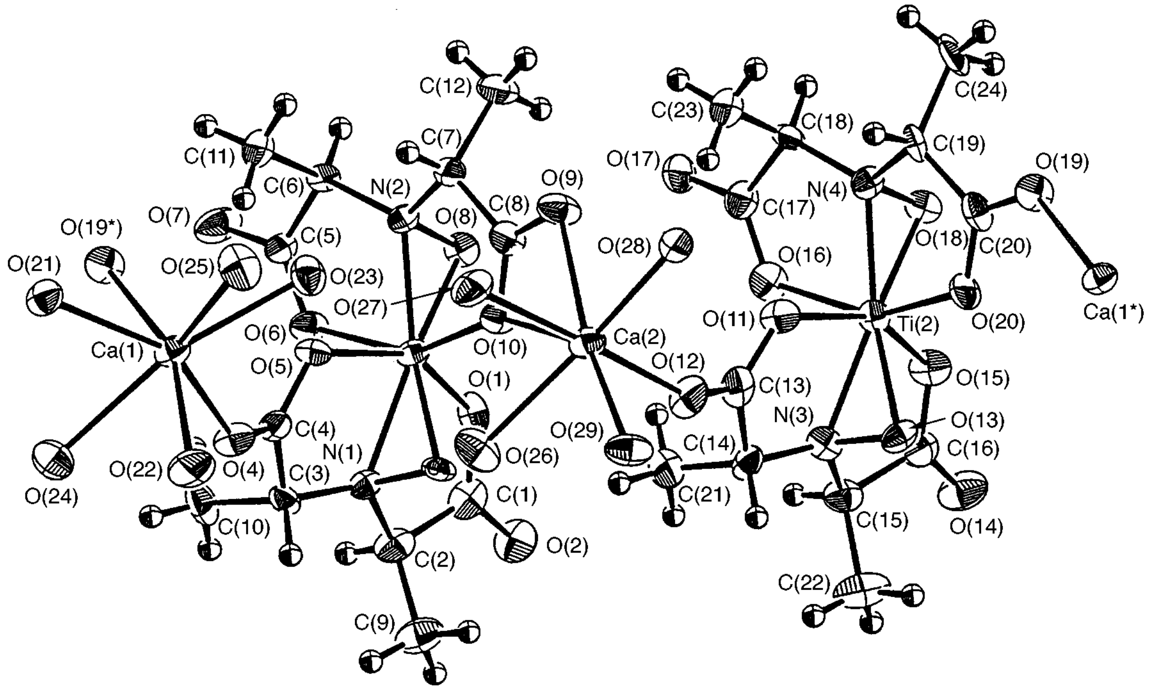

Fig. 2 An ORTEP view representing a portion of the infinite chain of $\{[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4{\cdot}2H_2O\}_n$, containing Ti(1), Ca(1), Ti(2), Ca(2) (thermal ellipsoids 30% probability)

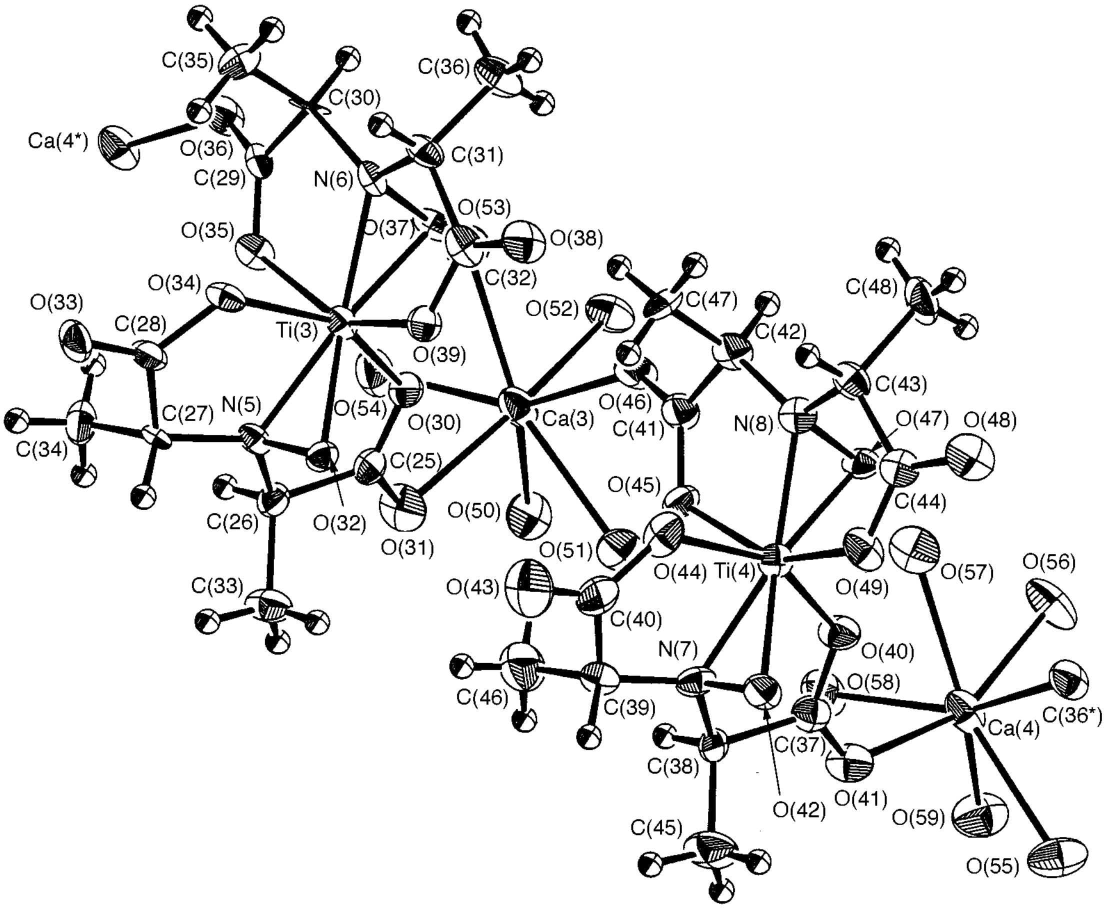

Fig. 3 An ORTEP view representing a portion of the infinite chain of $\{[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4{\cdot}2H_2O\}_n$, containing Ti(3), Ca(3), Ti(4), Ca(4) (thermal ellipsoids 30% probability)

atoms of the carboxylato groups of two different $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$ complexes. The exception is Ca(2) which is bonded to four H_2O molecules, the non-Ti-bonded carboxylato-oxygen atom [O(12)] of the Ti(2) complex and *both* oxygen atoms [O(9) and O(10)] of one carboxylato group of the Ti(1) complex. Therefore, the carboxylate group C(8)O(9)O(10) behaves simultaneously as a unidentate ligand to Ti(1), through O(10), and as a bidentate ligand to Ca(2), through O(9) and O(10) (Figs. 1 and 2). This distinctive mode of co-ordination of a carboxylato group has also been observed for $[Ca(H_2O)_2][\Delta,\Lambda\text{-}V(R,S\text{-hidba})_2]$ [H_3hidba = 2,2′-(hydroxyimino)dibutyric acid].[14] A search of the Cambridge Crystallographic Database using

Table 3 Proton and ^{13}C NMR resonances (ppm) of the anions of $[Ca(H_2O)_4][\Delta,\Lambda\text{-}Ti(hida)_2]\cdot 2H_2O$ **1**, $[NMe_4]_2[Ti(hida)_2]$ **2**, $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-}hidpa)_2]_4\cdot 2H_2O$ **3** and $[NMe_4]_2[\Delta,\Lambda\text{-}Ti(R,R\text{-}hidpa)_2]$ **4**

	^{1}H NMR resonances				^{13}C NMR resonances			
	CH	CH_2	CH_3	^{1}H couplings	CO_2^-	CH	CH_2	CH_3
1 in D_2O		4.35, doublet						
		4.21, doublet		4.35–4.09	178.21		61.65	
		4.09, doublet		4.21–4.03	178.01		61.40	
		4.03, doublet		*a*				
		$^2J_{H\text{-}H} = -16$ Hz						
2 in CD_3OD		4.28, doublet						
		4.13, doublet		4.28–3.91	177.40		62.34	
		3.91, doublet		4.13–3.89	177.15		61.96	
		3.89, doublet		*b*				
		$^2J_{H\text{-}H} = -16$ Hz						
3 freshly dissolved in D_2O	4.48, quartet		1.47, doublet		181.68	67.18		15.22
	4.00, quartet		1.43, doublet		180.77	64.09		12.51
	$^3J_{H\text{-}H} = 7.5$ Hz		$^3J_{H\text{-}H} = 7.5$ Hz					
3 after two weeks in D_2O	4.50, quartet		1.53, doublet		182.24	67.68		15.18
	4.38, quartet		1.49, doublet		181.73	67.16		14.91
	4.08, quartet		1.39, doublet		180.78	64.10		12.50
	4.00, quartet		1.35, doublet		180.73	63.41		12.46
	$^3J_{H\text{-}H} = 7.5$ Hz		$^3J_{H\text{-}H} = 7.5$ Hz					
4 in CD_3OD	4.38, quartet		1.64, doublet	4.38–1.43	181.30	68.11		15.28
	4.26, quartet		1.56, doublet	4.26–1.43	180.95	67.73		14.89
	3.95, quartet		1.43, doublet	3.95–1.64	179.57	64.01		12.46
	3.90, quartet			3.90–1.56	179.53	63.47		
	$^3J_{H\text{-}H} = 7.1$ Hz		$^3J_{H\text{-}H} = 7.1$ Hz	*c*				

[a] Coupling determined from spectrum simulation using the Bruker WIN-NMR simulation package.[25] [b] Coupling determined from ^{1}H–^{1}H decoupling experiment. [c] Couplings determined from ^{1}H–^{1}H correlation (COSY) experiment.

QUEST[22] showed that this form of co-ordination of Ca^{II} by a carboxylato group has also been reported for pentaaquacalcium(ethylenediaminedisuccinato)nickel(II) hydrate[23] and *catena*-[bis(calciumtartrato)tetraaquavanadium].[24] However, it should be noted that in **3**, the Ca(2)–O(10) bond [2.828(9) Å] is significantly longer than those observed for the other Ca–$O_{carboxylate}$ bonds in this compound [Ca–O 2.391(9)–2.448(10) Å]. A similar lengthening was also observed in the *catena*-[bis(calciumtartrato)tetraaquavanadium][24] system for the corresponding bridging oxygen bond: Ca–O bond lengths 2.745 *vs.* 2.485 Å[22] and to a lesser extent in $[Ca(H_2O)_2][\Delta,\Lambda\text{-}V\text{-}(R,S\text{-}hidba)_2]$,[14] 2.544(6) *vs.* 2.369(7), 2.381(7). The seven-fold co-ordination of Ca^{II} has been observed in the other related systems $[Ca(H_2O)_4][Ti(hida)_2]$,[12] $[Ca(H_2O)_5][Zr(hida)_2(H_2O)]$,[12] $[Ca(H_2O)_5][V(hida)_2]$[4] and $[Ca(H_2O)_5][\Lambda\text{-}V(S,S\text{-}hidpa)_2]$.[5] The crystal lattice is built up of zigzag strands of alternating $[\Delta\text{-}Ti(R,R\text{-}hidpa)_2]^{2-}$ and $[Ca(H_2O)_x]^{2+}$ ($x = 4$ or 5) linked inter-strand by Ca^{II} binding to carboxylato-oxygen atoms and intra- and inter-strand by hydrogen bonding from the H_2O molecules to the oxygen atoms of the anions, in addition the asymmetric unit contains two extra H_2O molecules [O(60) and O(61)] which are also observed to hydrogen bond to the carboxylate oxygen atoms.

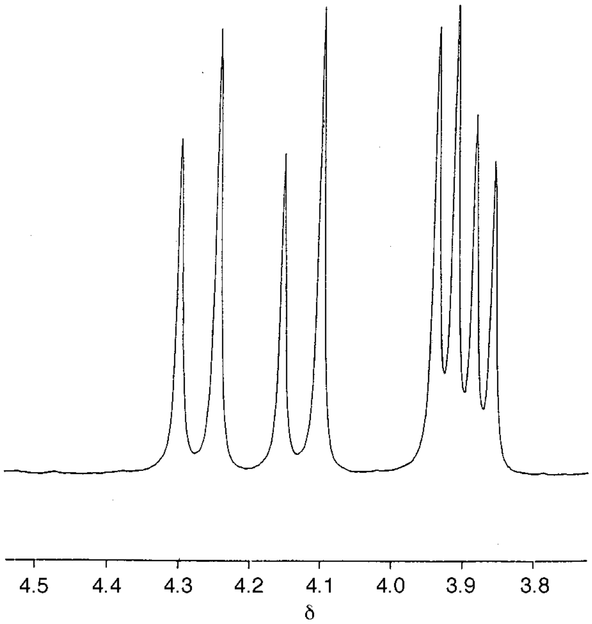

Fig. 4 The 300 MHz ^{1}H NMR spectrum of the methylene proton resonances of $[NMe_4]_2[Ti(hida)_2]$ **2** in CD_3OD at room temperature

Proton and ^{13}C NMR spectra

The use of $[NMe_4]^+$ counter ion has enabled ^{1}H and ^{13}C NMR spectroscopies to be undertaken in a variety of different deuteriated solvents.

$[Ti(hida)_2]^{2-}$. Single-crystal X-ray diffraction studies of **2** have shown the complex to contain both the Δ- and Λ-helical forms in the solid state.[12] The 300 MHz ^{1}H NMR spectrum of **2** in CD_3OD (Fig. 4, Table 3), involves four doublets at δ 4.28, 4.13, 3.91 and 3.89, arising from the inequivalence of the methylene protons, (coupling $^2J_{H\text{-}H} = -16$ Hz), consistent with idealised C_2 symmetry of each of the $[\Delta\text{-}Ti(hida)_2]^{2-}$ and $[\Lambda\text{-}Ti(hida)_2]^{2-}$ in solution. The Δ- and Λ-helical forms each give rise to 2 × 2 doublets, these complexes are enantiomers not diastereoisomers, so only four doublets are observed and not eight. This interpretation is consistent with the corresponding 75 MHz ^{13}C NMR spectrum, where two separate resonances were observed for both the carboxylate and methylene carbon atoms, (δ 177.40, 177.15) and (δ 62.34, 61.96), respectively (Table 3). The ^{1}H–^{1}H NMR decoupling experiments (irradiating at δ 4.28 or 4.13), showed that the proton resonance at δ 4.28 is coupled to that at δ 3.91 and that the proton reson-

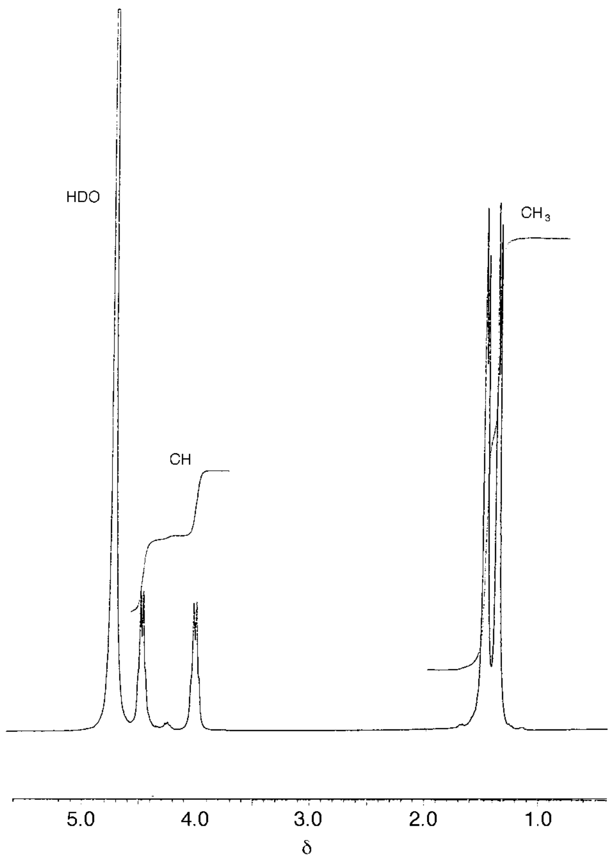

Fig. 5 The 300 MHz ^1H NMR spectrum of freshly dissolved crystalline $[Ca(H_2O)_4][Ca(H_2O)_5]_3[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4{\cdot}2H_2O$ **3** in D_2O at room temperature

ances at δ 4.13 and 3.89 are also coupled. This coupling was confirmed by a ^1H–^{13}C heteronuclear atom correlation NMR spectrum for **2** which showed that the proton resonances at δ 4.28 and 3.91 are coupled to that of the methylene carbon at δ 62.34 and that the proton resonances at δ 4.13 and 3.89 are coupled to the methylene carbon at δ 61.96.

The ^1H NMR spectrum for **1** in D_2O showed a similar splitting pattern to that observed for **2** in CD_3OD, although with slightly shifted resonances. Two doublets were observed centred at δ 4.35 and 4.21 ($^2J_{H-H} = -16$ Hz) with the second two doublets partially overlapping to give three peaks. Integration and the use of coupling, $^2J_{H-H} = -16$ Hz, calculated from the previous two doublets showed there to be two protons involved and gave centred values for these two doublets of δ 4.09 and 4.03. This was confirmed by a successful simulation of the spectrum[24] which additionally showed that the proton at δ 4.35 is coupled to that at δ 4.09 and the proton at δ 4.21 is coupled to that at δ 4.03. This pattern of coupling corresponds to that observed experimentally for **2** (see above). The ^{13}C NMR spectrum of **1** in D_2O showed two resonances for the carboxylate and two resonances for the methylene carbon atoms, at positions very similar to those observed for **2** in CD_3OD and consistent with the anions having C_2 symmetry in solution (Table 3).

$[Ti(R,R\text{-hidpa})_2]^{2-}$. The crystal structure of **3** showed the presence of only the Δ-helical form of $[Ti(R,R\text{-hidpa})_2]^{2-}$ with the anions having effective C_2 symmetry. The ^1H NMR spectrum of **3** freshly dissolved in D_2O, (Fig. 5, Table 3) showed two resonances at δ 4.48 and 4.00, assigned to the methine protons, and two doublets centred at δ 1.47 and 1.43 ($^3J_{H-H} = 7.5$ Hz), assigned to the methyl protons. Therefore, the ^1H NMR spectrum is consistent with the Ti^{IV} centres dissolving unchanged. This conclusion is corroborated by the ^{13}C NMR spectrum of **3** freshly dissolved in D_2O (Table 3) with only two resonances being observed in each of the methyl, methine and carboxylate regions of the spectrum. This solution of **3** in D_2O was allowed to stand for 2 weeks at room temperature and the ^1H (Fig. 6, Table 3) and ^{13}C (Table 3) NMR spectra were re-recorded. The ^1H NMR spectrum showed four quartets centred at δ 4.50, 4.38, 4.08 and 4.00 and four doublets centred at δ 1.53, 1.49, 1.39 and 1.35. Similarly, four peaks were now observed in each of the three regions of the ^{13}C NMR spectrum. Comparisons of the ^1H NMR spectra recorded for the freshly prepared and aged solutions of **3** in D_2O led to the assignment of the two outer quartets of the methine region to the Δ-helical form and the two inner quartets to the Λ-helical form of $[Ti(R,R\text{-hidpa})_2]^{2-}$. These ^1H and ^{13}C NMR studies showed that, on standing for 2 weeks in D_2O, $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$ epimerised to produce *ca.* 57% of the Δ- and 43% of the Λ-helical forms. Similar results have been observed for $[\Lambda\text{-}V(R,R\text{-hidpa})_2]^{2-}$, including the assignment of the pattern of the ^1H NMR resonances of the methine region of the Δ- and Λ-helical forms to the outer and inner quartets, respectively.[5] As further corroboration of the above interpretation of the ^1H and ^{13}C NMR spectra of $[\Delta\text{-}Ti(R,R\text{-hidpa})_2]^{2-}$, the 500 MHz ^1H NMR spectrum of **4** in CD_3OD (Table 3) is consistent with C_2 point symmetry for the eight-co-ordinate anion in solution and the presence of both Δ- and Λ-helical forms, in that four distinct resonances were observed for the methine protons. The methyl proton resonances were manifest as three doublets, with that at δ 1.43 corresponding to 6 H. A ^1H–^1H COSY experiment confirmed that the pattern of the resonances determined for **3** in D_2O (see above) was maintained for **4** in CD_3OD. This result, together with the integration of the ^1H resonances observed for **4**, indicated that *ca.* 55% of the Δ- and 45% of the Λ-helical form of $[Ti(R,R\text{-hidpa})_2]^{2-}$ are obtained on dissolution of **4** in CD_3OD; a similar situation to that observed after leaving a solution of **3** in D_2O for 2 weeks at room temperature. The ^{13}C NMR spectrum of **4** was also observed to be consistent with the presence

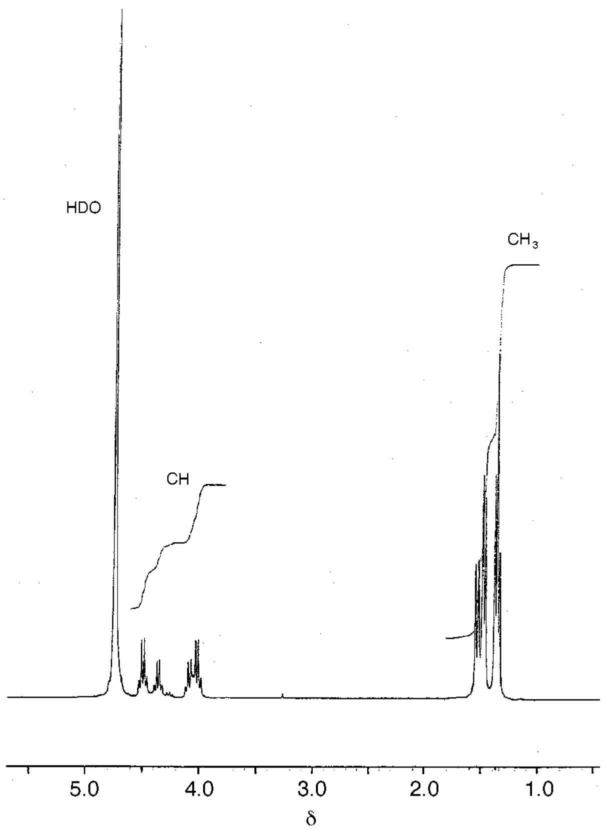

Fig. 6 The 300 MHz ^1H NMR spectrum of $[Ca(H_2O)_4][Ca(H_2O)_5]_3$-$[\Delta\text{-}Ti(R,R\text{-hidpa})_2]_4{\cdot}2H_2O$ recorded at room temperature in D_2O after standing at room temperature for two weeks in D_2O

Table 4 The 75 MHz ^{13}C NMR resonances (ppm) observed for the carboxylate carbon atoms of $[Ti(hida)_2]^{2-}$ in solution at room temperature

Compound	$(CD_3)_2SO$	CD_3OD	D_2O
2	173.36	177.40	179.82
	173.12	177.15	179.62
1			178.21
			178.01

of both helical forms of $[Ti(R,R\text{-hidpa})_2]^{2-}$. Both of the ^1H NMR spectra for **3** and **4** contained other resonances; in addition to those of $[NMe_4]^+$, HDO, $C(H/D)_3OD$, the observation of very weak resonances in the ^1H NMR spectrum in both the methine (quartets) and methyl (doublets) regions of the spectrum suggests the presence of small amounts of other isomers of $[Ti(R,R\text{-hidpa})_2]^{2-}$, probably involving *S*-chirality at one (or more) of the C atoms.

From these spectroscopic observations it is concluded that slow crystallisation allowed for the isolation of a single helical form of the metal $\{[\Delta\text{-Ti}(R,R\text{-hidpa})_2]^{2-}\}$ whereas rapid precipitation resulted in an approximately equimolar mixture of the two helical forms being obtained. Additionally, these experiments also show that on standing in solution at room temperature for *ca.* 2 weeks $[\Delta\text{-Ti}(R,R\text{-hidpa})_2]^{2-}$ epimerised to produce an equilibrium and approximately equimolar mixture of the two helical forms.

Carbon-13 NMR spectra of compound 2 in various solvents. The structural studies reported herein for $[\Delta\text{-Ti}(R,R\text{-hidpa})_2]^{2-}$ and previously[12] for $[Ti(hida)_2]^{2-}$ show the prevalence of the carboxylato-oxygen atoms to bind cations. This has also been observed for $[\Delta\text{-V}(S,S\text{-Hhidpa})_2]\cdot 4H_2O$, in which two of the non-V-bonded carboxylato-oxygen atoms each bind a proton.[5] These structural studies have also demonstrated that these anions become involved in considerable hydrogen bonding to H_2O molecules in the crystal lattices through the ‘hydrophilic’ equatorial region of the dianions (see Figs. 1–3). Interactions of solvent molecules with the carboxylato-oxygen atoms is considered[10,14] to be the reason for the marked solvent dependence of the V^V/V^{IV}[7,14] and Mo^{VI}/Mo^V, Mo^V/Mo^{IV}[9,10] redox couples of the ML_2 (L = $hida^{3-}$, $hidpa^{3-}$ or $hidba^{3-}$) complexes.

Carbon-13 NMR spectroscopy of (say) $[Ti(hida)_2]^{2-}$ affords another means of investigating the influence of solvents on anions of this type. We have observed the ^{13}C NMR spectrum of **2** in $(CD_3)_2SO$, CD_3OD and D_2O and the values observed for the carboxylato-carbon atoms are given in Table 4. A maximum downfield shift of *ca.* 6.5 ppm was observed in the position of the carboxylate ^{13}C resonance from $(CD_3)_2SO$ to D_2O. Thus, these ^{13}C NMR studies indicate a significant interaction of the carboxylato groups of $[Ti(hida)_2]^{2-}$ with solvent molecules.

The trend in the resonance positions observed, $D_2O > CD_3OD > (CD_3)_2SO$, is attributed to solvation and the significant hydrogen bonding, as observed in the solid-state structures. This trend in ^{13}C chemical shifts can be correlated with the variation in redox potentials observed for the V^V/V^{IV}, Mo^{VI}/Mo^V and Mo^V/Mo^{IV} couples of Amavadin-style complexes. Thus, the potential of each of these three couples varies as $H_2O < CH_3OH < Me_2SO$, corresponding to the stabilisation of the greater negative charge in water, though the dielectric properties of the solvents may also play a significant role in charge stabilisation. For Amavadin, the shift in the position of the V^V/V^{IV} redox couple is *ca.* 500 mV from Me_2SO to D_2O.[7]

Conclusion

These studies have extended the chemistry of Amavadin-style complexes for Ti^{IV}. The compound $[Ca(H_2O)_4][Ca(H_2O)_5]$-$[\Delta\text{-Ti}(R,R\text{-hidpa})_2]_4\cdot H_2O$ **3** crystallises stereospecifically as the Δ-helical form only as shown by single-crystal X-ray diffraction, ^1H and ^{13}C NMR spectroscopy. The isolation of $[Ti(R,R\text{-hidpa})_2]^{2-}$ in a single helical form, Δ, in **3** has enabled epimerisation of this anion to the Λ form to be followed by ^1H and ^{13}C NMR spectroscopy in D_2O. The crystal structure of **3** shows the formation of networks of Ti^{IV} and Ca^{II} centres linked by the interaction of the carboxylato-oxygen atoms of the anions with the cations. Carbon-13 NMR studies have provided clear evidence for a significant interaction of the solvent molecules with the hydrophilic equatorial surface of $[Ti(hida)_2]^{2-}$ with polar solvents.

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