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An X-ray crystallographic study on the molecular structures of seven-coordinate (ethylenediamine-*N*,*N*,*N'*-triacetato-*N'*-acetic acid)(aqua)-titanium(III) and -vanadium(III), $[Ti^{III}(H\text{-}edta)(H_2O)]\cdot H_2O$ and $[V^{III}(Hedta)(H_2O)]\cdot H_2O$

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Abstract

The molecular structures of the title complexes, $[Ti^{III}(Hedta)(H_2O)]\cdot H_2O$ (**I**) and $[V^{III}(Hedta)(H_2O)]\cdot H_2O$ (**II**) ($Hedta^{3-}$ = mono-protonated ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate) have been determined by single-crystal X-ray analyses. The crystal data are as follows: **I**: monoclinic, *Aa*, $a=13.401(1)$, $b=12.311(1)$, $c=8.552(1)$ Å, $\beta=97.35(1)°$, $V=1399.3(1)$ Å^3, $Z=4$, $R=0.018$ and $R_w=0.022$; **II**: monoclinic, *Aa*, $a=13.891(1)$, $b=8.558(1)$, $c=12.135(1)$ Å, $\beta=95.77(1)°$, $V=1435.4(1)$ Å^3, $Z=4$, $R=0.020$ and $R_w=0.028$. The former complex has a seven-coordinate and approximately pentagonal-bipyramidal structure in which $Hedta^{3-}$ acts as a hexadentate ligand, a proton is attached to the carbonyl oxygen atom on one of the equatorial glycine rings (G-rings), and a water molecule occupies one of the five basal coordination sites. The latter is also seven-coordinate but has a structure close to a mono-capped trigonal-prism in which $Hedta^{3-}$ is also hexadentate and a water molecule caps a quadrilateral face as a seventh ligand. A structural comparison of these and other Hedta complexes with the corresponding edta complexes revealed that $Hedta^{3-}$ serves well as a hexadentate ligand, for those metal ions which have a propensity to form seven-coordinate edta complexes, and that protonation takes place in most edta complexes on the carboxylate group of the more constrained equatorial glycine arm (G-ring).

Keywords: Crystal structures; Titanium complexes; Vanadium complexes; Polydentate ligand complexes; Seven-coordinate complexes

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1. Introduction

In our preceding papers [1–3], it has been demonstrated that Ti^{III} (d^1) and Fe^{II} (high-spin d^6) ions form a seven-coordinate edta complex $[M(edta)(H_2O)]^{n-}$ ($edta^{4-}$ = ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate), like V^{III} (d^2) [4], Co^{II} (high-spin d^7) [5a] (a six-coordinate but surprisingly distorted $[Co^{II}(edta)]^{2-}$ complex is also known [5b]) and Os^{IV} (low-spin d^4) [6] ions, though they do not have any of the spherically symmetric electron configurations [7]. These observations have been rationalized in terms of both sizes and d-electron configurations of the central metal ions; these metal ions may take a coordination number (CN) of 7 with edta, which have radii larger than the critical radii (e.g. 0.785 and 0.88 Å for ter- and bivalent ions, respectively [8,9] [2]) and yet have any of the spherically symmetric electron configurations (e.g. d^0, high-spin d^5, d^{10} and d^{10} s^2) or any of d^1, d^2, low-spin d^3 and d^4, and high-spin d^6 and d^7 configurations [1–3].

Fe^{III} (high-spin d^5) ion usually forms a seven-coordinate edta complex $[Fe(edta)(H_2O)]^-$ having a pentagonal-bipyramidal structure [10–13], but it is readily converted upon protonation to a six-coordinate and electrically neutral Hedta complex, $[Fe(Hedta)(H_2O)]$ ($Hedta^{3-}$ = mono-protonated edta), in which a proton is attached to the acetate group of the equatorial glycine arm forming otherwise a constrained G-ring, to free it from coordination [14]; Hedta serves as a pentadentate ligand and a water molecule completes the six-coordination. Many octahedral $[M^{III}(Hedta)(H_2O)]$ type

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[2] Ionic radii r_M are all those for a coordination number of 6, unless otherwise stated, throughout the present study [9].

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complexes are also known for other tervalent metal ions (M = Cr [15], Co [16], Ga [14a], Ru [17], Rh [18]), in which the protonated acetate group of the equatorial glycine arm is in all cases freed from coordination to dangle. Similar structural characteristics have been found in some other octahedral Hedta complexes, $[Ni^{II}(Hedta)(H_2O)]^-$ [19], $[Ge^{IV}(Hedta)(OH)]$ [8], $[Ru^{III}(Hedta)Cl]^-$ [20] and $[Ir^{III}(Hedta)Cl]^-$ [21], as well. Consequently, the above-mentioned tervalent Ti^{III} and V^{III} ions forming seven-coordinate edta complexes, might form such six-coordinate Hedta complexes, or they might retain seven-coordination even in their Hedta complexes, since some Hedta complexes are known for large metal ions in which Hedta acts as a hexadentate ligand, such as seven-coordinate $[Mn^{II}(Hedta)(H_2O)]^-$ [22], ten-coordinate $[La^{III}(Hedta)(H_2O)_4]$ [23], ψ-seven-coordinate $[Sb^{III}(Hedta)]$ [24] and ψ-nine-coordinate $[Bi^{III}(Hedta)]$ [25]. In the present study, X-ray crystallographic analyses have been performed on $[Ti^{III}(Hedta)(H_2O)]$ and $[V^{III}(Hedta)(H_2O)]$ to ascertain which situation actually emerges.

2. Experimental

2.1. Preparation of $[Ti(Hedta)(H_2O)]\cdot H_2O$ (I) and $[V(Hedta)(H_2O)]\cdot H_2O$ (II)

All the following procedures were carried out under an N_2 atmosphere. Equimolar amounts of $TiCl_3$ (2.31 g, 15 mmol) and H_4edta (4.38 g) were mixed in a small amount of water (10 ml) and ten times ethanol by volume was added. The resulting suspension was distilled until the steam coming out was almost neutral. An appropriate amount of water (~ 10 ml) was then added to dissolve all the deposited materials. The resulting solution was covered with an acetone vapor and stored at 0 °C. The green crystals of $[Ti(Hedta)(H_2O)]\cdot H_2O$ (formed in small quantities) were picked out by hand from the crystals (containing large amounts of undesired colorless crystals) deposited after three days and dried in an N_2 atmosphere. $[V(Hedta)(H_2O)]\cdot H_2O$ was prepared by passing a concentrated aqueous solution (~ 10 ml) containing $K[V(edta)(H_2O)]\cdot 2H_2O$ (5 g) [4] through cation-exchange resin of H^+ form. The red eluate was covered with an ethanol vapor and stored at 0 °C. Two kinds of crystals (~2 g), brown and reddish orange in color, deposited after a week were separated by hand-picking and were dried in an N_2 atmosphere. They were found to be $[V(Hedta)(H_2O)]\cdot H_2O$ and $[H_6edta][V(edta)(H_2O)]_2\cdot 4H_2O$, respectively, by subsequent X-ray structure analysis. The two Hedta complexes thus obtained exhibited the same properties as reported earlier [26].

2.2. Structure determination of Ti^{III}- and V^{III}-Hedta complexes

Suitable-size single crystals of $[Ti(Hedta)(H_2O)]\cdot H_2O$ (I) and $[V(Hedta)(H_2O)]\cdot H_2O$ (II) were mounted on a Mac Science MXC3 diffractometer and were irradiated with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell dimensions were obtained by least-squares from the angular settings of accurately centered 31 reflections with $30 < 2\theta < 34°$ and 31 reflections with $31 < 2\theta < 35°$ for **I** and **II**, respectively. The reflection intensities were collected in the usual manner; three check reflections measured after every 300 reflections showed no decrease in the intensity. The *Aa* space group was selected for both **I** and **II**, which led to successful refinements. The structures were solved by a direct method with the Monte Carlo-Multan program [27]. Most of the hydrogen atoms could be located in a difference Fourier map and refined isotropically. Absorption and extinction corrections were then applied [28,29] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final *R* values of 0.018 and 0.020 for **I** and **II**, respectively. All the calculations were carried out on a Titan 750 computer using the program system of Crystan-G [27]. The crystallographic data are summarized in Table 1. See also Section 4.

3. Results and discussion

Final positional and thermal parameters are given in Tables 2 and 3 for the non-hydrogen atoms and the proton attached to the C=O group in $[Ti(Hedta)(H_2O)]\cdot H_2O$ (**I**) and $[V(Hedta)(H_2O)]\cdot H_2O$ (**II**), respectively. Selected bond distances and angles in these complexes are listed in Tables 4–7.

3.1. Description of the molecular structure of $[Ti(Hedta)(H_2O)]\cdot H_2O$ (I)

Fig. 1 shows the molecular structure of $[Ti(Hedta)(H_2O)]\cdot H_2O$ determined in the present study. It can be seen there that the Ti^{III}–Hedta complex has a seven-coordinate and approximately pentagonal-bipyramidal (PB) structure with a water molecule as an additional ligand, and that $Hedta^{3-}$ acts as a hexadentate ligand; a proton is attached to the carbonyl oxygen atom (O7) of the equatorial glycine arm corresponding to the G-ring in the octahedral edta complexes, consistent with the much longer C6=O7 bond (1.286 Å), but the protonated acetate group of the glycine arm does not abandon the coordination to the Ti^{III} ion. Several octahedral complexes of the type $[M^{III}(Hedta)(H_2O)]$ have been found (M = Cr [15], Fe

Table 1
Crystal data, experimental conditions and refinement details

Chemical formula	$C_{10}H_{17}N_2O_{10}Ti$	$C_{10}H_{17}N_2O_{10}V$
Formula weight	373.12	376.18
Crystal size (mm)	$0.55\times0.37\times0.50$	$0.40\times0.40\times0.30$
a (Å)	13.401(2)	13.891(1)
b (Å)	12.311(2)	8.558(1)
c (Å)	8.552(1)	12.136(2)
β (°)	97.34(1)	95.77(1)
V (Å^3)	1399.3(4)	1435.4(4)
Crystal system	monoclinic	monoclinic
Space group	*Aa*	*Aa*
Z	4	4
D_{calc} (Mg m^{-3})	1.77	1.74
D_{obs} (Mg m^{-3})	1.68	1.74
λ (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
T (°C)	25	25
Monochromator	graphite	graphite
μ (mm^{-1})	0.602	0.683
Transmission factor	0.742–0.944	0.700–0.794
Diffractometer used	Mac Science MXC3	Mac Science MXC3
2θ Range (°)	$3<2\theta<55$	$3<2\theta<55$
Collected area	$h, +k, \pm l$	$\pm h, -k, +l$
No reflections		
collected	1607	1870
used ($\lvert F_o\rvert>3(\sigma(F_o))$)	1586	1630
Source of scattering factors	[a]	[a]
$\Delta\rho_{max}$–$\Delta\rho_{min}$ (e Å^{-3})	0.26 to −0.15	0.24 to −0.28
R [b]	0.018	0.020
R_w [b]	0.022	0.028
Weighting scheme, w	$1.0/(\sigma(F_o)^2+0.001\lvert F_o\rvert^2)$	$1.0/(\sigma(F_o)^2+0.004\lvert F_o\rvert^2)$

[a] Ref. [30].
[b] $R=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $R_w=[\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$; $w^{-1}=\sigma^2(F_o)$.

[14], Co [16], Ga [14a], Ru [17], Rh [18]), in which a proton is attached always to the carboxylate group of the equatorial glycine arm forming otherwise a G-ring; the protonated acetate group of the glycine arm leaves the coordination site to dangle and a water molecule instead occupies it. This suggests that the Ti^{III} ion as well as the V^{III} ion (vide infra) has a stronger tendency to take a coordination number (CN) of 7 even with Hedta, at least than does the Fe^{III} ion. The Fe^{III} ion has a critical radius [8,31] [3] ($r_M=0.785$ Å) between CN of 6 and 7, so that its edta complex abandons the seven-coordination when the G-ring is protonated, rearranging to the six-coordinate $[M(Hedta)(H_2O)]$ type complex [14]. On the other hand, the Ti^{III} ion is sufficiently large in size ($r_M=0.81$ Å) to retain seven-coordination with Hedta. Similarly, Mn^{II} (high-spin d^5) [22], La^{III} (f^0) [23], Sb^{III} ($d^{10}s^2$) [24] and Bi^{III} ($d^{10}s^2$) [25] ions form Hedta complexes in which $Hedta^{3-}$ survives as a hexadentate ligand, because their sizes are sufficiently large ($r_M=0.97$, 1.17, 0.90 and 1.17 Å, respectively) to accommodate a CN greater than six and because they have spherically symmetric electron configurations [1–3,7]. The former two ions actually take CN of 7 and 9, respectively [32,33], and the latter two ions probably maintain the ψ-PB and ψ-nine-coordinate structures [24,34] respectively, in their respective edta complexes. Consequently, it is proposed that those metal ions which form seven-coordinate edta complexes, i.e. Ti^{III}, V^{III} (vide infra), Mn^{II}, Fe^{II} (high-spin d^6 and $r_M=0.92$ Å), Co^{II} ($r_M=0.885$ Å), In^{III} (d^{10} and $r_M=0.94$ Å) [35], and Sb^{III} ions and probably the Sc^{III} ion (d^0 and $r_M=0.885$ Å), may form seven-coordinate Hedta complexes in which $H\text{-}edta^{3-}$ acts as a hexadentate ligand.

In contrast, Cr^{III}, Mn^{III} [36], Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, Ga^{III}, Ge^{IV}, Ru^{III}, Rh^{III} and Ir^{III} ions are not allowed to form such Hedta complexes on the steric and/or electronic grounds mentioned above. In other words, six-coordinate edta complexes [M(edta)] of these metal ions, if present, suffer considerable constraints on their equatorial glycine rings (G-rings), so that one acetate group of the glycine arm readily leaves the coordination site upon protonation to give the six-coordinate $[M(Hedta)(H_2O)]$ type complexes, resulting in the relaxation of the constraints [14b] and the preservation of their favored six-coordination. This explains why six-coordinate [M(Hedta)] type complexes are not known

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[3] The Fe^{III} ion has a critical size in that both six- and seven-coordinate edta complexes are known for it [10–13,31].

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) of $[Ti^{III}(Hedta)(H_2O)]\cdot H_2O$ (I)

N	Atom	x/a	y/b	z/c	B_{eq} [a] (Å^2)
1	Ti1	5033.4(0)	938.6(3)	9657.4(0)	1.32(1)
2	O1	4024(1)	2261(1)	9673(2)	2.33(4)
3	O2	4838(1)	1528(1)	7392(2)	2.35(4)
4	O3	4385(1)	897(1)	11874(2)	2.12(4)
5	O4	4205(1)	−431(1)	9206(2)	2.02(4)
6	O5	6263(1)	1889(1)	10342(2)	2.09(4)
7	O6	5455(2)	1842(2)	5137(2)	2.74(4)
8	O7	4137(1)	15(1)	14069(2)	2.29(4)
9	O8	3774(1)	−1732(1)	7448(2)	2.35(4)
10	O9	7666(1)	2241(1)	11940(2)	2.68(4)
11	N1	6038(1)	−69(1)	8250(2)	1.65(4)
12	N2	6038(1)	−113(1)	11518(2)	1.54(4)
13	C1	6939(2)	−484(2)	9269(3)	2.05(5)
14	C2	6612(2)	−948(2)	10740(3)	2.11(5)
15	C3	6353(2)	654(2)	7027(3)	2.26(5)
16	C4	5480(2)	1399(2)	6424(3)	1.99(5)
17	C5	5385(2)	−649(2)	12563(3)	1.92(5)
18	C6	4587(2)	156(2)	12843(3)	1.80(4)
19	C7	5399(2)	−967(2)	7503(3)	2.04(5)
20	C8	4379(2)	−1057(2)	8076(2)	1.72(4)
21	C9	6724(2)	668(2)	12450(3)	1.97(5)
22	C10	6921(2)	1667(2)	11508(2)	1.79(5)
23	H7	3750(28)	540(34)	14200(40)	2.03(0)
24	O10	8054(1)	3375(2)	9322(2)	2.72(4)

[a] $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij} a_i \cdot a_j$

in which Hedta is hexadentate. On the other hand, the chelate constraints are not so severe in the seven-coordinate $[M(edta)(H_2O)]$ complexes, because their central metal ions are sufficiently large. These compounds thus adopt seven-coordination even if they are protonated on the glycine arm. Therefore, these seven-coordinate Hedta complexes are expected to show stronger Brönsted acidity than the six-coordinate $[M(Hedta)(H_2O)]$ type complexes which rearrange upon deprotonation either to a six-coordinate $[M(edta)(H_2O)]$ type complex or eventually to a six-coordinate $[M(edta)]$ type complex, depending on the nature of the central metal ion M. If M has a larger radius than the critical radius (0.785 Å for M^{III}) and has a strong preference for six-coordination like Ru^{III}, Rh^{III} and Ir^{III} ions, deprotonation leaves the resulting carboxylate group uncoordinated, i.e. the $[M(edta)(H_2O)]$ type complex is formed in which edta is pentadentate; these six-coordinate $[M(Hedta)(H_2O)]$ complexes behave as a derivative of carboxylic acids. On the other hand, when M has a smaller radius than the critical radius like Cr^{III} and Co^{III} ions, deprotonation is followed by much slower anation with the resulting carboxylate group to give the six-coordinate $[M(edta)]$ type complex; these six-coordinate $[M(Hedta)(H_2O)]$ complexes exhibit ‘ time-dependent’ acid–base properties [16].

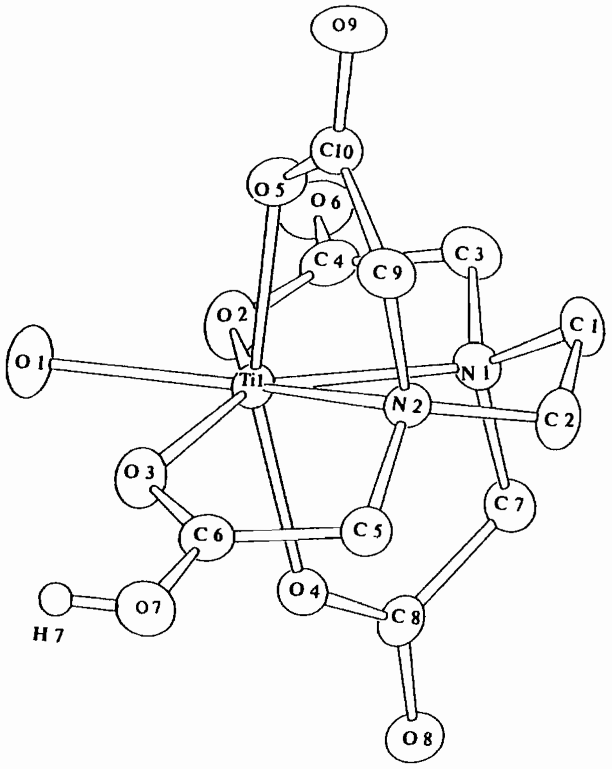

Fig. 1. Molecular structure of $[Ti(H_2O)(Hedta)]\cdot H_2O$ with atomic numbering. All hydrogen atoms except for the proton attached to the C=O group are omitted for clarity.

The H_2edta (= diprotonated edta) complexes are also known for large bivalent ions, Co^{II}, Sn^{II} ($d^{10}s^2$ and $r_M = 1.22$ Å for CN = 8) and Pb^{II} ($d^{10}s^2$ and $r_M = 1.33$ Å), in which H_2edta^{2-} serves as a hexadentate ligand; seven-coordinate $[Co(H_2edta)(H_2O)]$ [5a], ψ-seven-coordinate $[Sn(H_2edta)]$ [37] and ψ-eight-coordinate $[Pb(H_2edta)(H_2O)]$ [38][4]. On the other hand, $[Cu^{II}(H_2edta)(H_2O)]$ [39] and $[Ni^{II}(H_2edta)(H_2O)]$ [40] are six-coordinate with H_2edta^{2-} as a pentadentate ligand; one protonated G-ring remains coordinated, while the other leaves a coordination site, which is occupied by a water molecule. This is because the two metal ions have a preference for a CN of 6 with edta on steric ($r_M = 0.87$ and 0.83 Å, respectively) and/or electronic (d^9 and d^8 configurations, respectively) grounds, and probably because most of the constraints are relaxed on the liberation of one acetate group of the G-ring from the coordination sphere. In short, those large metal ions which form seven-coordinate edta complexes with $edta^{4-}$ as a hexadentate ligand, except the Fe^{III} ion [14], may form seven-coordinate Hedta or H_2edta complexes with $Hedta^{3-}$ or H_2edta^{2-} as a hexadentate ligand, unless these complexes are unstable to decomposition under acidic conditions like the Mg^{II} complex [41].

The ψ-seven-coordinate $[Sb^{III}(Hedta)]$ has a pseudo PB structure [24] like the present Ti^{III}–Hedta complex,

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[4] The exact composition is $Pb_2(H_2edta)_2\cdot 3H_2O$, which contains both dimeric eight-coordinate and monomeric ψ-eight-coordinate $[Pb(H_2edta)(H_2O)]$.

Table 3
Fractional atomic coordinates (×10^4) and equivalent isotropic temperature factors (B_{eq}) of [V^{III}(Hedta)(H$_2$O)]·H$_2$O (II)

N	Atom	x/a	y/b	z/c	B_{eq} [a] (Å^2)
1	V1	2236.0(0)	8510.7(4)	3371.0(0)	1.18(1)
2	O1	3100(1)	8024(2)	2116(2)	2.02(4)
3	O2	1899(1)	6262(2)	2892(2)	2.01(4)
4	O3	2757(1)	10684(2)	3063(2)	2.03(4)
5	O4	3532(2)	8375(2)	4381(2)	2.12(4)
6	O5	1038(2)	8874(2)	2306(2)	2.23(4)
7	O6	753(1)	4444(2)	2938(2)	2.57(5)
8	O7	3156(2)	13026(3)	3778(2)	3.67(6)
9	O8	4522(2)	6916(3)	5450(2)	2.95(5)
10	O9	−286(1)	10238(2)	1828(2)	2.32(4)
11	N1	1914(1)	7167(2)	4883(2)	1.49(4)
12	N2	1399(1)	10178(2)	4307(2)	1.53(4)
13	C1	1642(2)	8231(3)	5770(2)	2.02(5)
14	C2	960(2)	9458(3)	5259(2)	2.04(5)
15	C3	1128(2)	6049(3)	4526(2)	2.00(5)
16	C4	1262(2)	5513(3)	3361(2)	1.76(5)
17	C5	2115(2)	11394(3)	4717(2)	2.07(6)
18	C6	2731(2)	11774(3)	3783(2)	2.08(6)
19	C7	2806(2)	6301(3)	5278(2)	1.92(5)
20	C8	3661(2)	7262(3)	5034(2)	1.90(5)
21	C9	632(2)	10899(3)	3521(2)	1.94(5)
22	C10	450(2)	9930(3)	2492(2)	1.64(5)
23	H8	4570(40)	6150(60)	5900(50)	2.96(0)
24	O10	−1206(2)	4949(3)	2128(2)	3.53(6)

[a] $B_{eq}=\frac{4}{3}\sum_i\sum_j \beta_{ij}a_i\cdot a_j$

Table 4
Bond distances (Å) in [Ti^{III}(Hedta)(H$_2$O)]·H$_2$O (I)

Ti1–O1	2.118(2)	Ti1–O2	2.054(2)
Ti1–O3	2.184(2)	Ti1–O4	2.028(2)
Ti1–O5	2.044(2)	Ti1–N1	2.283(2)
Ti1–N2	2.339(2)	O7–H7	0.84(4)
C4–O2	1.278(3)	C4–O6	1.225(3)
C4–C3	1.524(3)	C6–O7	1.286(3)
C6–O3	1.239(3)	C6–C5	1.500(3)
C8–O8	1.235(3)	C8–O4	1.280(3)
C8–C7	1.514(3)	C10–O9	1.241(3)
C10–O5	1.273(3)	C10–C9	1.512(3)
N1–C1	1.486(3)	N2–C2	1.492(3)
N1–C3	1.476(3)	N1–C7	1.491(3)
N2–C5	1.483(3)	N2–C9	1.489(3)
C1–C2	1.498(3)		

Table 5
Bond distances in (Å) [V^{III}(Hedta)(H$_2$O)]·H$_2$O (II)

V1–O1	2.074(2)	V1–O2	2.051(2)
V1–O3	2.044(2)	V1–O4	2.077(2)
V1–O5	2.026(2)	V1–N1	2.248(2)
V1–N2	2.224(2)	O8–H8	0.85(5)
C4–O2	1.273(3)	C4–O6	1.236(3)
C4–C3	1.516(4)	C6–O7	1.223(4)
C6–O3	1.282(3)	C6–C5	1.522(4)
C8–O8	1.285(3)	C8–O4	1.241(3)
C8–C7	1.498(4)	C10–O9	1.264(3)
C10–O5	1.253(3)	C10–C9	1.500(3)
N1–C1	1.487(3)	N2–C2	1.492(3)
N1–C3	1.483(3)	N1–C7	1.482(3)
N2–C5	1.490(3)	N2–C9	1.491(3)
C1–C2	1.505(4)		

Table 6
Bond angles (°) in [Ti^{III}(Hedta)(H$_2$O)]·H$_2$O (I)

O1–Ti1–O2	74.31(7)	O1–Ti1–O3	71.78(6)
O1–Ti1–O4	107.80(7)	O1–Ti1–O5	92.88(7)
O1–Ti1–N1	147.24(6)	O1–Ti1–N2	137.19(6)
O2–Ti1–O3	144.07(6)	O2–Ti1–O4	96.53(7)
O2–Ti1–O5	93.95(7)	O2–Ti1–N1	73.00(7)
O2–Ti1–N2	146.11(7)	O3–Ti1–O4	82.93(6)
O3–Ti1–O5	99.22(6)	O3–Ti1–N1	140.48(6)
O3–Ti1–N2	69.81(6)	O4–Ti1–O5	158.68(6)
O4–Ti1–N1	78.07(7)	O4–Ti1–N2	85.57(6)
O5–Ti1–N1	87.37(7)	O5–Ti1–N2	75.48(6)
N1–Ti1–N2	74.41(6)	C6–O7–H7	111.4(26)
Ti1–O2–C4	123.5(1)	Ti1–O3–C6	121.4(2)
Ti1–O4–C8	119.8(2)	Ti1–O5–C10	123.6(1)
Ti1–N1–C1	111.5(1)	Ti1–N1–C3	106.7(1)
Ti1–N1–C7	106.5(1)	Ti1–N2–C2	111.3(1)
Ti1–N2–C5	108.9(1)	Ti1–N2–C9	105.6(1)
C1–N1–C3	109.7(2)	C1–N1–C7	112.1(2)
C3–N1–C7	110.2(2)	C2–N2–C5	109.9(2)
C2–N2–C9	111.4(2)	C5–N2–C9	109.7(2)
O2–C4–O6	125.7(2)	O3–C6–O7	124.0(2)
O2–C4–C3	114.0(2)	O3–C6–C5	118.6(2)
O6–C4–C3	120.2(2)	O7–C6–C5	117.3(2)
O4–C8–O8	124.1(2)	O5–C10–O9	124.2(2)
O4–C8–C7	117.3(2)	O5–C10–C9	116.2(2)
O8–C8–C7	118.6(2)	O9–C10–C9	119.5(2)
N1–C3–C4	109.0(2)	N1–C7–C8	114.1(2)
N2–C5–C6	106.8(2)	N2–C9–C10	112.2(2)
N1–C1–C2	108.7(2)	N2–C2–C1	109.5(2)

so that its equatorial G-rings are readily identified and a proton is evidently on one of the G-rings. On the other hand, the [Mn^{II}(Hedta)(H$_2$O)]$^-$ [22] has a structure close to a mono-capped trigonal-prism (C_{2v}-CTP) [5] and the [La^{III}(Hedta)(H$_2$O)$_4$] [23] is ten-coordinate, so that distinction between R- and G-rings is inappropriate for both complexes. However, if the two ligating O atoms which make the widest bite angle with the central metal ion, are tentatively regarded as being axial (i.e. O$_2$ and O$_4$ atoms in Ref. [22]) [3], a proton is shared between the two G-rings for the Mn^{II}–Hedta complex. Even if the usual convention that one glycine arm on one N atom of edta, making a smaller angle with the mean plane of the E-ring, is denoted as the G-ring, and the other, the R-ring [7], is applied, the same result is obtained. Furthermore, most of the above-mentioned Hedta and H$_2$edta complexes [7,25] as well as [Ir(H$_2$edta)Cl$_2$]$^-$ [21], [V(H$_2$edta)(O)$_2$]$^-$ [42], [Co(H$_2$edta)(en)]$^+$ [43] and [Tc$_2$(H$_2$edta)$_2$(μ-O)$_2$] [44] have their G-rings or glycine arms (forming otherwise

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[5] It seems more appropriate to regard this complex as having a pseudo PB structure, as opposed to the earlier assertion [7].

Table 7
Bond angles (°) in $[V^{III}(Hedta)(H_2O)]\cdot H_2O$ (II)

O1–V1–O2	74.66(8)	O1–V1–O3	78.87(8)
O1–V1–O4	83.76(8)	O1–V1–O5	93.49(8)
O1–V1–N1	132.39(8)	O1–V1–N2	151.05(8)
O2–V1–O3	151.28(7)	O2–V1–O4	105.94(8)
O2–V1–O5	79.26(8)	O2–V1–N1	72.12(7)
O2–V1–N2	129.12(8)	O3–V1–O4	81.77(7)
O3–V1–O5	91.54(8)	O3–V1–N1	135.88(7)
O3–V1–N2	73.88(7)	O4–V1–O5	173.14(8)
O4–V1–N1	73.84(8)	O4–V1–N2	101.59(8)
O5–V1–N1	112.39(8)	O5–V1–N2	77.83(8)
N2–V1–N1	75.75(7)	C8–O8–H8	116.4(36)
V1–O2–C4	119.6(2)	V1–O3–C6	120.2(2)
V1–O4–C8	118.7(2)	V1–O5–C10	120.3(2)
V1–N1–C1	111.3(1)	V1–N1–C3	107.0(1)
V1–N1–C7	106.9(1)	V1–N2–C2	113.9(1)
V1–N2–C5	104.6(1)	V1–N2–C9	108.4(1)
C1–N1–C3	111.9(2)	C1–N1–C7	109.7(2)
C3–N1–C7	109.8(2)	C2–N2–C5	109.9(2)
C2–N2–C9	110.2(2)	C5–N2–C9	109.6(2)
O2–C4–O6	125.5(2)	O3–C6–O7	126.0(3)
O2–C4–C3	114.9(2)	O3–C6–C5	114.1(2)
O6–C4–C3	119.5(2)	O7–C6–C5	119.9(2)
O4–C8–O8	119.8(2)	O5–C10–O9	122.4(2)
O4–C8–C7	118.8(2)	O5–C10–C9	119.4(2)
O8–C8–C7	121.4(2)	O9–C10–C9	118.2(2)
N1–C3–C4	108.1(2)	N1–C7–C8	108.4(2)
N2–C5–C6	107.9(2)	N2–C9–C10	110.7(2)
N1–C1–C2	108.9(2)	N2–C2–C1	108.6(2)

G-rings) protonated preferentially, when the distinction between the G- and R-rings is possible; the distinction is difficult for ten-coordinate $[La(Hedta)(H_2O)_4]$ [23] and ψ-seven-coordinate $[Sn(H_2edta)]$ [37].

In this way, protonation seems to take place exclusively on the G-ring(s) in edta complexes. In general, the G-rings have narrower O–M–N bite angles than do the R-rings in octahedral six-coordinate and PB seven-coordinate edta complexes, which reflects the larger constraints imposed on the G-rings and leads to the weaker (and usually longer) equatorial M–O bonds than the axial ones. Therefore, the carbonyl O atoms of the G-rings should be protonated preferentially. Thus, octahedral Hedta and H_2edta complexes naturally have their equatorial glycine arms (forming otherwise the G-rings) protonated [7]. In the seven-coordinate $[Ti(edta)(H_2O)]^-$ with a pseudo PB structure [1,3], the O–Ti–N bite angles are 71.3 and 71.5° for the equatorial G-rings, while they are both 77.1° for the axial R-rings, and the equatorial M–O bond distances are 2.101 and 2.113 Å, but the axial ones are 2.026 and 2.028 Å. The narrower O–Ti–N bite angles are also found for the G-rings in $[Ti(edta)(H_2O)]^-$ with a pseudo C_{2v}-CTP structure [3]. As a result, protonation is expected to take place on the C=O group of one of the G-rings in the Ti^{III}–edta complex, as is the case, and similar structural characteristics are preserved in the resulting seven-coordinate $[Ti(Hedta)(H_2O)]$ and are observed in some seven-coordinate edta complexes, at least on average, in the solid state, such as $[Mg^{II}(edta)(H_2O)]^{2-}$ [45], $[Ti^{IV}(edta)(H_2O)]$ [46], $[Mn^{II}(edta)(H_2O)]^{2-}$ [32], $[Fe^{III}(edta)(H_2O)]^-$ [10–13], $[Co^{II}(edta)(H_2O)]^{2-}$ [5a], $[Cd^{II}(edta)(H_2O)]^{2-}$ [47], $[Sn^{IV}(edta)(H_2O)]$ [48], $[Sn^{II}(edta)]^{2-}$ [49], and probably $[In^{III}(edta)(OSO_2)]^{3-}$ [35] and $[Os^{IV}(edta)(H_2O)]$ [6].

3.2. Description of the molecular structure of $[V(Hedta)(H_2O)]\cdot H_2O$ (II)

Fig. 2 shows the molecular structure of $[V^{III}(Hedta)(H_2O)]$ (II), which is also seven-coordinate but has an approximate C_{2v}-CTP structure like the parent edta complex, $[V^{III}(edta)(H_2O)]^-$ [4]. $Hedta^{3-}$ also acts as a hexadenate ligand and a water molecule caps a quadrilateral face; the V^{III} ion also prefers a CN of 7 with Hedta, though its radius ($r_M = 0.78$ Å) is marginally comparable with the critical radius (0.785 Å), i.e. the radius of the Fe^{III} ion forming a six-coordinate Hedta complex [14]. This is probably because seven-coordination is electronically stable for the V^{III} ion (d^2) (and for the Ti^{III} ion (d^1) as well), as compared with

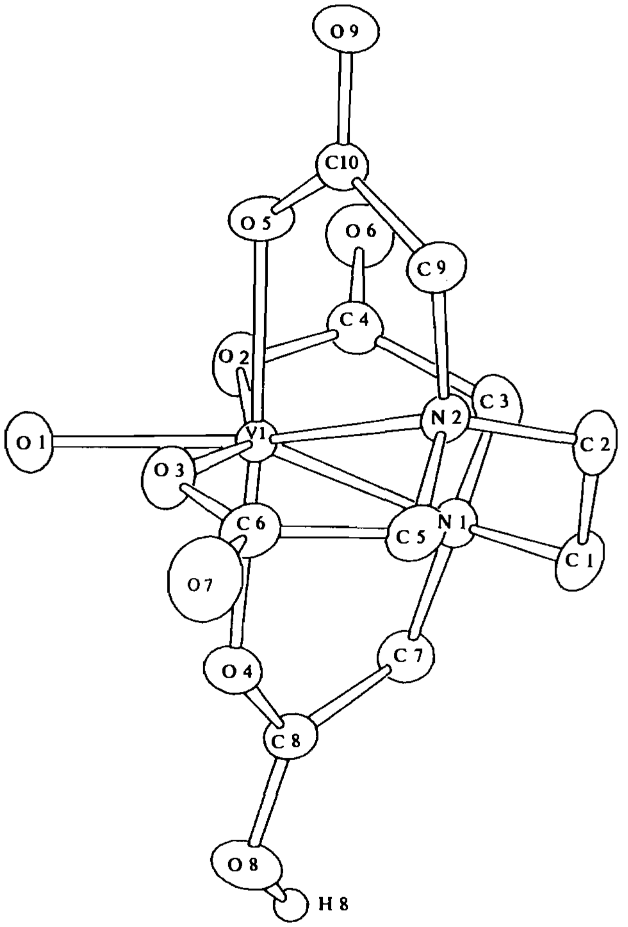

Fig. 2. Molecular structure of $[V(H_2O)(Hedta)]\cdot H_2O$ with atomic numbering. All hydrogen atoms except for the proton attached to the C=O group are omitted for clarity.

octahedral six-coordination, as confirmed previously on the basis of angular-overlap calculations [1–3].

It is also inappropriate to define R- or G-rings in this V^{III}–Hedta complex because it has a pseudo C_{2v}-CTP structure. However, if we regard as being axial the two ligating O atoms making the widest bite angle O–V–O, as above [3,7], it follows that a proton is attached to the R-ring, i.e. to the O8 atom of its C=O group, consistent with the longer C8=O8 bond. The C10=O9 bond in another R-ring is also long, which is, however, due to the weak hydrogen-bonding interaction of the O9 atom to the H8 atom on the O8 atom in the neighboring complex and to its coordinated water molecule (see Section 4).

The parent V^{III}–edta complex has a pseudo C_{2v}-CTP structure in the solid state [4], which is asymmetrically distorted; the O–V–N bite angle (O3–V–N1 in Ref. [4]) of one R-ring is relatively narrow and is comparable with that (O5–V–N2) of one G-ring, suggesting that one (V–O3 bond) of the axial V–O bonds is relatively weak. In fact, it is fairly long for the axial V–O bond, particularly in the sodium salt. This may explain why a proton is attached exceptionally to the C=O group on one of the axial R-rings in $[V^{III}(Hedta)(H_2O)]$.

However, it might be plausible that the V^{III}–edta complex assumes a more symmetric C_{2v}-CTP structure in solution such that no distinction is possible between the G- and R-rings like in the highly symmetric $[Fe^{II}(edta)(H_2O)]^{2-}$ [2]. If so, it is meaningless to assign which ring (G or R) is to be protonated in this complex on the basis of the solid state structure. In our attempt to prepare $[V^{III}(Hedta)(H_2O)]$, the complex salt having a composition of $[H_6edta][V^{III}(edta)(H_2O)]_2 \cdot 4H_2O$ was accidentally obtained. The structure analysis [50] revealed that the complex anion has an approximate C_{2v}-CTP structure and that the intermolecular interactions are relatively weak. The relevant structure parameters obtained are as follows; the O–V–N bite angles are 72.0(1) and 72.2(1)°, and 75.4(1) and 77.3(1)°, respectively, for the G- and R-rings defined in the same manner as above, the equatorial V–O bond distances are 2.108(3) and 2.087(3) Å, and the axial V–O bond distances are 2.034(3) and 2.044(3) Å. As a result, protonation should take place on one of the more constrained G-rings in the V^{III}–edta complex. Consequently, it is not clear at present why a proton is attached exceptionally to the R-ring in $[V^{III}(Hedta)(H_2O)]$. The steric demand of the crystal packing might explain this finding, because the difference between the R- and G-rings is inherently small for the V^{III}–Hedta complex having a structure close to a C_{2v}-CTP. To our knowledge, $[V^{III}(Hedta)(H_2O)]$ is the only Hedta complex that has its R-ring protonated. [6]

3.3. Structural comparison of Ti^{III}– and V^{III}–Hedta complexes with the parent edta complexes

It has been found in our preceding studies [1,3] that the Ti^{III} ion forms a seven-coordinate edta complex, but its structure is either pseudo PB or C_{2v}-CTP, depending on the counterions with which the complex anion forms salts. In contrast, seven-coordinate Fe^{III}– and V^{III}–edta complexes seem to adopt, respectively, approximate PB and C_{2v}-CTP structures exclusively, for any counterion examined so far [4,10–13]. The present study confirms that the V^{III}–edta complex persists in adopting an approximate C_{2v}-CTP structure even when its 'counterion' is H^+ (and H_6edta^{2+}).

The molecular structures are comparatively similar between the edta and Hedta complexes for both Ti^{III} and V^{III} ions, provided that the Ti^{III}–edta complex with a pseudo PB structure (i.e. the Na^+ salt [1]) is considered for comparison. Notable and common differences are found only in the carboxylate group, as expected, to which a proton is attached in the Hedta complexes. That is, the M–O and C=O bonds in the M–O–C=O moiety are lengthened, while the O–C bond in it is shortened, upon protonation to the C=O group. Similar long and short bonds are noted in other Hedta and H_2edta complexes mentioned above. In addition, the bond angles around the C=O carbon atom are also changed. In particular, the O–C(O)–C angle increases, because the C=O bond bears a single-bond character to some extent upon protonation to its oxygen atom. Other relevant angles are also affected, but these differences in bond distances and angles are localized to the carboxylato group only. It is thus concluded that the overall structures of the Ti^{III}– and V^{III}–edta complexes are little affected when a proton is attached to the C=O group of the glycine moiety. This may explain the earlier observation that redox rate constants between Ti^{III}–edta and some Co(III) complexes are insensitive to $[H^+]$ down to 0.01 M, resulting in 50% monoprotonation of the Ti^{III}–edta complex [51].

4. Supplementary material

Tables are available from the authors giving anisotropic thermal parameters, H atom coordinates, all bond distances and angles, and observed and calculated structure factors.

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