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Short Communication

The molecular structure of sodium (aqua)(ethylenediaminetetraacetato)titanate(III) dihydrate, $Na[Ti(H_2O)(edta)]\cdot 2H_2O$, as determined by X-ray crystal analysis

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Abstract

A single-crystal X-ray analysis revealed that the Ti(III)-edta complex formulated as $[Ti(H_2O)(edta)]^-$ has a seven-coordinate and distorted pentagonal-bipyramidal structure in which edta serves as a hexadentate ligand and a water molecule occupies one of the five basal sites. The complex anion as a whole is very similar in structure to the corresponding seven-coordinate Ti(IV)–edta complex reported earlier, and is one of a few examples of seven-coordinate transition-metal edta complexes in which the metal ion has a non-symmetrical electronic configuration.

Introduction

Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate ($edta^{4-}$) forms stable complexes with various metal ions and their structures have been extensively studied [1]. Since edta serves potentially as a hexadentate ligand, most of the transition-metal complexes with it have a six-coordinate, octahedral (Oh) structure. However, seven- or eight-coordinate edta complexes with water molecules as additional ligand(s), have sometimes been established at least in the solid state, particularly for large metal ions with d^0, high-spin d^5, and d^{10} configurations to which no crystal field stabilization contributes [2]. Notable ones are Mg(II), Ti(IV), Mn(II), Fe(III), Cd(II) and Sn(IV) complexes (seven-coordinate), and Ca(II) and Zr(IV) complexes (eight-coordinate), all of which may adopt any geometrical structures as far as the crystal field stabilization energy is concerned. V(III) and Os(IV) ions exceptionally form a seven-coordinate edta complex [3, 4], in spite of their non-symmetrical d^2 and d^4 (low-spin) configurations, respectively. Here, we report another example of seven-coordinate edta complexes in which the central metal ion has a configuration other than d^0, high-spin d^5, and d^{10}.

Experimental

Preparation of $Na[Ti(H_2O)(edta)]\cdot 2H_2O$

This complex salt was prepared under nitrogen atmosphere following the procedures applied to prepare $K_3[Ti(H_2O)(ox)_3]\cdot 4H_2O$ (ox = oxalate dianion) [5], using $Na_2H_2edta\cdot 2H_2O$ and Na_2CO_3 in place of $K_2ox\cdot H_2O$. The blue product precipitated upon addition of ethanol exhibited the same qualitative properties as described previously [6], but the number of water of crystallization proved to be two but not four, consistent with the previous observation that two water molecules are lost at 105 °C.

X-ray diffraction

A single crystal of suitable size (0.53 × 0.40 × 0.40 mm) was mounted on a Mac Science MXC3 diffractometer and was irradiated with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Determination of cell constants and collection of reflection intensities were carried out in the usual manner. Out of 1826 unique reflections measured by the ω-scan technique at 25 °C, 1804 reflections with $|F_o| > 3\sigma(F_o)$ were included in the structure analysis.

Crystal data for $C_{10}H_{18}N_2NaO_{11}Ti$

Monoclinic, space group *A*a, $a = 15.097(4)$, $b = 11.921(2)$, $c = 8.937(2)$ Å, $\beta = 99.64(2)°$, $V = 1585.7$ Å^3, $\rho_{calc} = 1.73$ g/cm^3, $Z = 4$ and $MW = 413.13$.

Determination and refinement of the structure

The structure was solved by direct methods and standard difference map techniques on a Titan 750 computer with a Monte Carlo-Multan [7]. All H atoms were located in a difference map after all non-H atoms had been located and refined anisotropically. Absorption correction [8] was then applied and several cycles of refinement led to a final *R* value of 0.022 ($R_w = 0.028$ with $w = \{\sigma(F_o)^2 + 0.0001|F_o|^2\}^{-1}$).

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Results and discussion

Description of the molecular structure

Final positional and thermal parameters are given in Table 1. Figure 1 shows the molecular structure of the complex anion, $[Ti(III)(H_2O)(edta)]^-$ with atomic numbering, and selected bond distances and angles within the complex are listed in Tables 2 and 3, respectively.

It is evident from Fig. 1 that the complex anion has a seven-coordinate and approximately pentagonal-bipyramidal (PB) structure in which $edta^{4-}$ serves as a hexadentate ligand and a water molecule occupies one of the five basal coordination sites; a nearly planar pentagon is formed by O5, O11, O13, N14, N15 and Ti atoms, their average deviation from the plane is 0.20 Å, and the axial O7–Ti–O9 angle is 161.6° (cf. 0.15 Å and 156.4°, respectively, for the isostructural $[Ti(IV)(H_2O)(edta)]$ [9]). These structural characteristics are common to all the PB metal–edta complexes reported so far, such as $[Mg(II)(H_2O)(edta)]^{2-}$ [10], $[Ti(IV)(H_2O)(edta)]$ [9] and $[Fe(III)(H_2O)(edta)]^-$ [11]. In contrast, one of the axial sites is occupied by a water molecule in the corresponding tri-oxalato complex, $[Ti(III)(H_2O)(ox)_3]^{3-}$ which also has approximate PB structure with two ox ligands in the equatorial plane [5]. Since a similar seven-coordinate PB structure is also adopted by two other Ti(III)–ox complexes, $[Ti(H_2O)_3(ox)_2]^-$ [12]* and $[Ti_2(H_2O)_6(ox)_3]$ [13]*, the Ti(III) ion seems to have a strong tendency to take a seven-coordinate structure [14].

TABLE 1. Fractional coordinates (× 10^4) and thermal parameters ($Å^2$)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} [a]
Ti	796.1(1)	858.0(3)	1302.8(1)	1.33(2)
Na2	2195.7(8)	306.6(9)	−2594(1)	2.15(3)
O3	−1770(2)	−2488(2)	884(4)	4.14(8)
O4	−2150(2)	202(3)	−4719(4)	3.97(7)
O5	1674(2)	−520(2)	1258(2)	2.19(5)
O6	−1483(1)	−632(2)	−901(3)	2.47(5)
O7	−281(1)	−170(2)	779(2)	2.15(5)
O8	1936(1)	3585(2)	3653(2)	2.24(5)
O9	1563(1)	2216(2)	1993(3)	2.70(6)
O10	736(2)	30(2)	5860(2)	2.52(5)
O11	1101(1)	268(2)	3560(2)	2.09(5)
O12	1590(2)	2232(2)	−2525(3)	2.84(6)
O13	1310(1)	1042(2)	−729(2)	1.97(4)
N14	−79(2)	1835(2)	2769(2)	1.79(5)
N15	−196(2)	1929(2)	−360(3)	1.72(5)
C16	−950(2)	2181(3)	1842(4)	2.15(6)
C17	−768(2)	2702(3)	384(4)	2.40(7)
C18	−752(2)	1074(2)	−1292(3)	2.22(6)
C19	−868(2)	12(2)	−404(3)	1.80(6)
C20	460(2)	2815(3)	3431(4)	2.45(7)
C21	1400(2)	2882(2)	3025(3)	1.73(6)
C22	−243(2)	1075(3)	4004(3)	2.28(7)
C23	592(2)	413(2)	4561(3)	1.76(6)
C24	327(2)	2590(2)	−1309(3)	2.16(7)
C25	1130(2)	1916(2)	−1563(3)	1.94(6)

[a] $B_{eq} = 8/3\pi^2(U_{11} + U_{22} + U_{33})$.

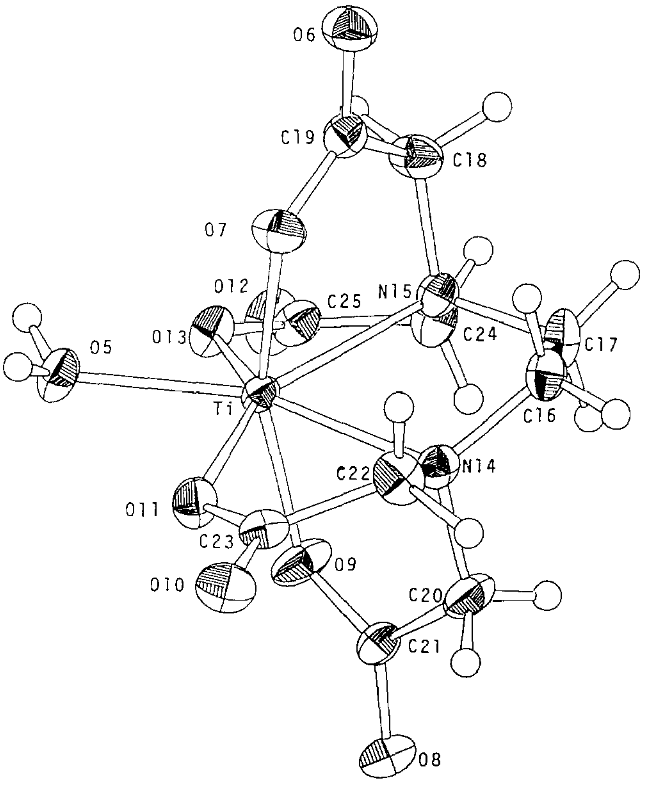

Fig. 1. Molecular structure of the anion $[Ti(H_2O)(edta)]^-$ with atomic numbering.

TABLE 2. Comparison of bond distances (Å) between Ti(III)– and Ti(IV)–$edta^{4-}$ complexes

$[Ti(III)(H_2O)(edta)]^-$		$[Ti(IV)(H_2O)(edta)]$ [a]	
To O (axial carboxylate)			
Ti−O9	2.026(2)	Ti−O4	1.922(2)
Ti−O7	2.028(2)	Ti−O3	1.926(2)
To O (equatorial carboxylate)			
Ti−O13	2.102(2)	Ti−O2	1.985(2)
Ti−O11	2.113(2)	Ti−O1	1.979(2)
To O (water)			
Ti−O5	2.115(2)	Ti−O5	2.084(2)
To N			
Ti−N15	2.310(2)	Ti−N1	2.293(2)
Ti−N14	2.323(2)	Ti−N2	2.312(2)

[a] Ref. 9.

If a transition-metal (ion) is surrounded by seven equivalent ligand atoms at equi-distances in a PB or mono-capped trigonal prismatic (C_{2v}-CTP) structure,

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*It is interesting to note that two ox ligands reside in the equatorial plane for the three Ti(III)–ox complexes.

TABLE 3. Comparison of bond angles (°) between Ti(III)- and Ti(IV)–edta^{4-} complexes

$[Ti(III)(H_2O)(edta)]^-$		$[Ti(IV)(H_2O)(edta)]$[a]	
O9–Ti–O7	161.59(9)	O3–Ti–O4	156.4(1)
O9–Ti–O13	84.56(9)	O4–Ti–O2	86.3(1)
O9–Ti–O11	87.29(8)	O4–Ti–O1	98.5(1)
O7–Ti–O13	105.14(8)	O3–Ti–O2	101.5(1)
O7–Ti–O11	93.30(8)	O3–Ti–O1	88.8(1)
O9–Ti–O5	107.39(8)	O4–Ti–O5	102.2(1)
O7–Ti–O5	90.39(8)	O3–Ti–O5	101.5(1)
O9–Ti–N15	91.74(8)	O4–Ti–N1	84.1(1)
O9–Ti–N14	77.12(8)	O4–Ti–N2	76.4(1)
O7–Ti–N15	77.10(8)	O3–Ti–N1	77.1(1)
O7–Ti–N14	85.62(8)	O3–Ti–N2	86.4(1)
O13–Ti–O11	143.75(8)	O1–Ti–O2	142.7(1)
O13–Ti–O5	75.02(8)	O2–Ti–O5	71.4(1)
O11–Ti–O5	73.91(8)	O1–Ti–O5	71.4(1)
O13–Ti–N15	71.34(8)	O2–Ti–N1	73.0(1)
O13–Ti–N14	139.62(8)	O2–Ti–N2	143.9(1)
O11–Ti–N15	144.31(8)	O1–Ti–N1	144.2(1)
O11–Ti–N14	71.45(8)	O1–Ti–N2	72.1(1)
O5–Ti–N15	139.25(8)	O5–Ti–N1	143.3(1)
O5–Ti–N14	144.82(8)	O5–Ti–N2	142.8(1)
N15–Ti–N14	73.57(8)	N1–Ti–N2	73.9(1)

[a] Ref. 9.

it has two lower-lying d-orbitals which are completely or almost σ non-bonding, respectively [15]; the d_{xz} and d_{yz} orbitals in PB have an anti-bonding energy of $4.5e_\pi$, and the $d_{x^2-y^2}$ and d_{yz} orbitals in C_{2v}-CTP have an anti-bonding energy of $0.13e_\sigma-4.5e_\pi$ and $0.22e_\sigma-4.3e_\pi$, respectively, on the basis of angular overlap calculations [16]. As a result, not only d^1 but d^2 and low-spin d^3 and d^4 ions, as well as high-spin d^6 and d^7 ions (corresponding to d^1 and d^2 ions, respectively, to both of which a symmetrical high-spin d^5 configuration is added) may well form seven-coordinate complexes, provided that requirements for their size and/or electric charge are met [2], as exemplified by the edta complexes of V(III) (d^2), Os(IV) (low-spin d^4) and Co(II) (high-spin d^7) [17] ions. (A six-coordinate Co(II)–edta complex is also known [17c].) Furthermore, we recently obtained direct evidence that the Fe(II) ion (high-spin d^6) also forms a seven-coordinate edta complex in the solid state [18]. In this way, it is not unusual from the electronic point of view that the Ti(III) ion forms a seven-coordinate complex with edta. In addition, the Ti(III) ion has a radius of 0.81 Å somewhat larger than the 'critical radius' of the Fe(III) ion (0.785 Å) which takes both six- and seven-coordinate structures [2]. Therefore, the Ti(III) ion is large enough in size to tolerate a seven-coordinate structure.

Structural comparison between Ti(III)- and Ti(IV)–edta complexes

Tables 2 and 3 compare some structural parameters of the present Ti(III)–edta complex with those of the isostructural $[Ti(IV)(H_2O)(edta)]$ complex reported earlier [9]. The axial Ti–O7 and Ti–O9 bonds are shorter than the equitorial Ti–O11 and Ti–O13 ones in both complexes, as is always the case in seven-coordinate PB complexes [5, 10–12, 14], and all the Ti–L bonds in the Ti(III) complex are, as expected, longer than the corresponding bonds in the Ti(IV) complex. Detailed comparison of these Ti–L bond distances reveals that Ti–O (carboxylato) bonds, particularly equatorial ones (Ti–O11 and Ti–O13) are more lengthened than anticipated when the Ti(IV) ion (0.745 Å) is substituted for the larger Ti(III) ion, whereas the Ti–N bonds undergo much smaller changes in length. These observations indicate that the Ti(IV) ion (d^0) has a stronger affinity for the carboxylato ligand but has a weaker affinity for the amine ligand than the Ti(III) ion (d^1) does, consistent with our earlier assertion [19]. The Ti(III)–O5 bond distance of 2.115 Å compares well with the equatorial Ti(III)–OH_2 bond distance of 2.130 Å in $[Ti(III)(H_2O)_3(ox)_2]^-$ [12].

On the other hand, all the L–Ti–L′ angles are almost comparable between the two Ti–edta complexes, and the overall chelate ring strain is also comparable, as judged from the angle sums of respective chelate rings: E ring, 517.5° (515.3° for Ti(IV)); R rings, 529.8° and 538.2° (533.9° and 534.3° for Ti(IV)); G rings, 525.5° and 526.2° (525.8° and 528.3° for Ti(IV)). Other detailed discussions will be presented elsewhere together with the crystal structure of the violet $Ba[Ti(H_2O)(edta)]Cl\cdot 6H_2O$ [6].*

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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*The Ba salt has been erroneously reported to have eight waters of crystallization, but it actually proved to have six, consistent with its thermal behavior at 105 °C. [6].

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