X-Ray Crystallographic Studies on the Molecular Structures of Some Salts of Titanium(III) Complexes with Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate, Ba[Ti(edta)(H_2O)]Cl·6H_2O, Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O, and K[Ti(edta)(H_2O)]·2.5H_2O

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The crystal and molecular structures of three Ti^{III}-edta complex salts (edta=ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate), violet Ba[Ti(edta)(H_2O)]Cl·6H_2O (**I**), reddish violet Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O (**II**), and purple K[Ti(edta)(H_2O)]·2.5H_2O (**III**), were determined by a single crystal X-ray diffraction method. The crystal data are as follows: I: Monoclinic, $P2_1/a$, a=14.480(2), b=19.760(3), c=7.517(1) Å, β=94.21(1)°, Z=4; II: Monoclinic, $P2_1$, a=18.176(3), b=12.688(3), c=8.045(2) Å, β=93.05(2)°, Z=2; III: Orthorhombic, *Fdd*2, a=15.453(3), b=60.247(8), c=7.237(2) Å, Z=16. It was found that all of these complexes have seven-coordinate and distorted mono-capped trigonal-prismatic (C_{2v}-CTP) structures, in contrast to the corresponding dark-blue sodium salt, Na[Ti(edta)(H_2O)]·2H_2O, which was previously confirmed to be also seven-coordinated, but to have an approximately pentagonal-bipyramidal(PB) structure. The delicate color changes of the Ti^{III}-edta complex salts observed in the solid state when the counterion is varied are due to an accompanying subtle modification in the coordination geometry around the Ti^{III} ion. The kinetic lability and acid-base behavior of the Ti^{III}-edta complex in solution reported earlier are accounted for by the presence of a labile water molecule in the first coordination sphere.

Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (edta) forms complexes with almost any metal ions; their structures have been extensively studied, particularly using a single-crystal X-ray diffraction method.[1] Of considerable interest are their coordination numbers (*CN*) and geometries, because they sometimes take *CN*'s greater than six for large metal ions, though edta is potentially a hexadentate ligand. For example, seven-coordinate structures have been established in the solid state for edta complexes with Mg^{II},[2,3] Ti^{IV},[4] V^{III},[5] Mn^{II},[6,7] Fe^{III},[8] Cd^{II},[9] In^{III},[10] Sn^{IV},[11] and Os^{IV}[12] ions. They adopt structures close to either a pentagonal bipyramid (PB) or a mono-capped trigonal prism (C_{2V}-CTP), usually with one water molecule as an additional ligand. These metal ions have a common characteristic in their electronic configurations: all, except for the V^{III} and Os^{IV} ions, assume any of the spherically symmetric, or non-directional, d^0, d^5 (high-spin), and d^{10} cofigurations, which allow adopting any geometrical structure as far as the crystal field stabilization is concerned.[1,2,4] It is then apparently exceptional that the V^{III} (d^2) and Os^{IV} (low-spin d^4) ions form seven-coordinate edta complexes.

In our previous communication,[13] it was reported that the Ti^{III} (d^1) ion also forms a seven-coordinate edta complex which has an approximate PB structure in the dark-blue sodium salt, Na[Ti(edta)(H_2O)]·2H_2O, and that this complex provides another example of such exceptional seven-coordinate edta complexes. On the other hand, many other salts of this complex anion have been isolated,[14] most of which are purple to violet in color. They are therefore expected to have structures different from a PB adopted by the dark-blue sodium salt. With this expectation in mind, single-crystal X-ray analyses were performed on the three Ti^{III}-edta complex salts: violet Ba[Ti(edta)(H_2O)]Cl·6H_2O, reddish violet Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O, and purple K[Ti(edta)(H_2O)]·2.5H_2O.

Experimental

Preparation of Ti(III)-edta Complex Salts. Violet Ba[Ti(edta)(H_2O)]Cl·6H_2O and purple K[Ti(edta)(H_2O)]·2.5H_2O were prepared as described in the literature.[14] Although they had been supposed to hold eight and six molecules of water, respectively, their exact compositions were determined as above through the present study. Reddish violet Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O was accidentally isolated in an attempt to convert the dark-blue sodium salt, Na[Ti(edta)(H_2O)]·2H_2O into the H[Ti(edta)(H_2O)], by adding HCl. It is definitely different in color from the starting sodium salt, to which it is gradually restored when kept in contact with the solution. All operations were carried out under an N_2 atmosphere.

Structure Determination. Single crystals of Ba[Ti(edta)(H_2O)]Cl·6H_2O (**I**), Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O (**II**), and K[Ti(edta)(H_2O)]·2.5H_2O (**III**) were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The unit-cell dimensions were obtained by least squares from the angular settings of accurately centered 32 reflections with $30° < 2\theta < 35°$, 25 reflections with $28° < 2\theta < 35°$, and 31 reflections with $26° < 2\theta < 35°$ for **I**, **II**, and **III**, respectively. The reflection intensities were collected in the usual manner; three check reflections measured after every 100 reflections showed no decrease in the intensity. The $P2_1/a$ (variant of No. 14), $P2_1$, and *Fdd*2 were selected as space groups for **I**, **II**, and **III**, respectively, which led to successful refinements, though systematic absences of the reflections suggested $P2_1/m$ as another possible space group for **II**.

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

	I	II	III
Chemical formula	$C_{10}H_{26}N_2O_{15}BaClTi$	$C_{20}H_{42}N_4O_{25}ClNa_3Ti_2$	$C_{10}H_{19}N_2O_{11.5}KTi$
Formula weight	634.98	938.75	438.25
Crystal size/mm^3	0.51×0.17×0.05	0.78×0.13×0.19	0.58×0.60×0.13
a/Å	14.480 (2)	18.176 (3)	15.453 (3)
b/Å	19.760 (3)	12.688 (3)	60.247 (8)
c/Å	7.517 (1)	8.045 (2)	7.237 (2)
β/°	94.21 (1)	93.05 (2)	
V/Å^3	2144.9 (6)	1842.5 (6)	6737 (2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$ (variant of No. 14)	$P2_1$	$Fdd2$
Z	4	2	16
D_{calcd}/Mg m^{-3}	2.00	1.69	1.73
λ/Å	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)
T/°C	25	25	25
Monochromator	Graphite	Graphite	Graphite
μ/mm^{-1}	2.235	0.572	0.746
Transmission factor	0.714—1.079	0.860—0.920	0.732—1.261
Diffractometer used	Mac Science MXC3	Mac Science MXC3	Mac Science MXC3
2θ range/°	3 <2θ<55	3<2θ<55	3<2θ<55
Collected area	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$	$+h$, $+k$, $+l$
No. of reflections			
collected	5622	5127	2210
used ($\|F_o\|>3\sigma(F_o)$)	4331	3949	2015
Source of scattering factors	a)	a)	a)
$\Delta\rho_{max}-\Delta\rho_{min}$/e Å^{-3}	0.78—−0.79	0.65—−0.31	1.93—−2.03
R[b)]	0.026	0.039	0.078
R_w[b)]	0.024	0.059	0.127
Weighting scheme	$w=1/\sigma(F_o)^2$	$w=1/(\sigma(F_o)^2+0.0039\|F_o\|^2)$	$w=1/\sigma(F_o)^2$

a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," ed by J. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, England (1974), Vol. IV. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The structures were solved by a direct method with the Monte Carlo–Multan program.[15] Most of the hydrogen atoms could be located in a difference Fourier map and refined isotropically; the remaining hydrogen atoms (of water molecules) were neglected for **I** and **II**, whereas only those on the methylene groups were located for **III** at their ideal geometries and were fixed at their positions; the hydrogen atoms of water molecules in **III** were not included in the refinement of the structure. Absorption and extinction corrections were then applied,[16,17] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R values of 0.026, 0.039, and 0.078 for **I**, **II**, and **III**, respectively. The inverted chirality for **II** and **III** gave larger R values. All of the calculations were performed on a Titan 750 computer using the program system of Crystan-G.[15] The crystallographic data and crystal analyses are summarized in Table 1. Full listings of the data-collection information, bond distances, bond angles, hydrogen atom positional parameters, and structure factors for **I**, **II**, and **III** are deposited as Document No. 66053 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

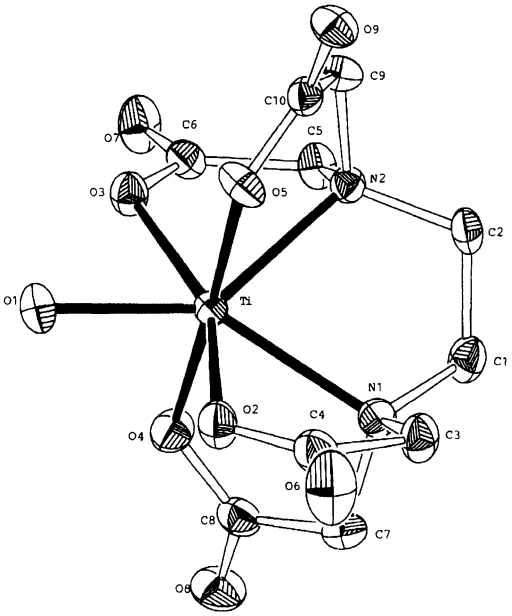

Fig. 1. Molecular structure of the complex anion in $Ba[Ti(edta)(H_2O)]Cl\cdot 6H_2O$ (**I**).

Results and Discussion

Molecular Structures of $Ba[Ti(edta)(H_2O)]Cl\cdot 6H_2O$ (I), $Na_2[Ti(edta)(H_2O)]_2\cdot NaCl\cdot 7H_2O$ (II), and $K[Ti(edta)(H_2O)]\cdot 2.5H_2O$ (III). The final positional and thermal parameters for non-hydro-

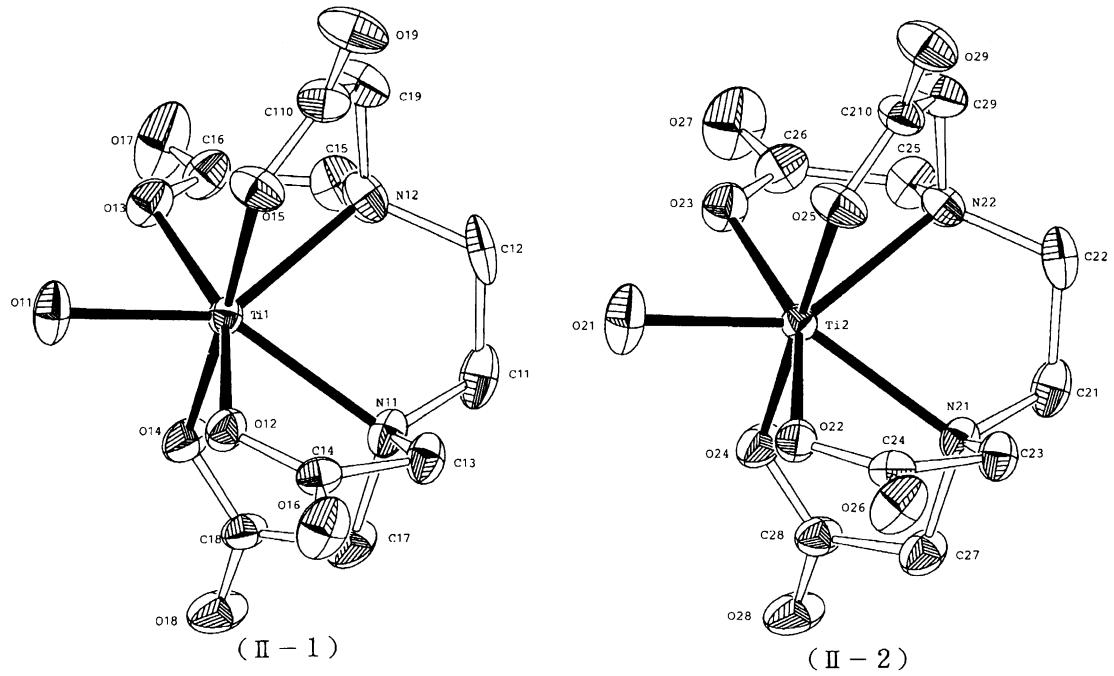

Fig. 2. Molecular structures of the two independent complex anions (**II**-1 and **II**-2) in $Na_2[Ti(edta)(H_2O)]_2 \cdot NaCl \cdot 7H_2O$ (**II**). The inverted structure is shown for **II**-1 for a comparison.

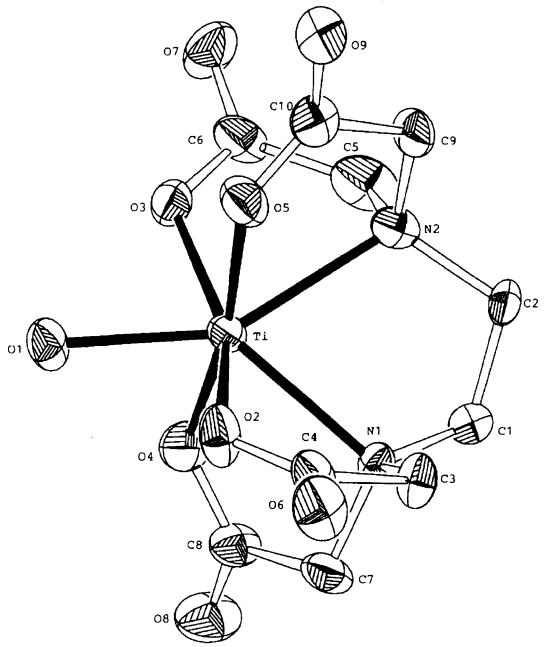

Fig. 3. Molecular structure of the complex anion in $K[Ti(edta)(H_2O)] \cdot 2.5H_2O$ (**III**).

gen atoms are given in Tables 2, 3, and 4 for crystals **I**—**III**, respectively. Figures 1, 2, and 3 show the molecular structures of the complex anion, $[Ti(edta)(H_2O)]^-$, found in the three crystals, along with the atomic numbering. In crystal **II**, two independent complex anions (**II**-1 and **II**-2) were found which are very similar in structure to each other; they are depicted together in Fig. 2. Selected bond distances and angles within each complex anion are listed in Tables 5 and 6, respectively, together with those of the blue sodium salt, $Na[Ti(edta)(H_2O)] \cdot 2H_2O$ (IV).[13]

It is evident in Figs. 1, 2, and 3 that all of the complex anions have seven-coordinate structures close to a mono-capped trigonal prism (C_{2v}-CTP) in which edta serves as a hexadentate ligand with its two N atoms at a unique edge and four O atoms at corners of a slightly distorted quadrilateral face; a water molecule caps the face. The three crystals may therefore well be similar in color (violet to purple) and the chloride ion coordination presumed in the Ba salt[14] is denied.

On the other hand, the dark-blue sodium salt, $Na[Ti(edta)(H_2O)] \cdot 2H_2O$, previously subjected to an X-ray structure analysis,[13] contains the corresponding seven-coordinate complex anion, which has an approximately pentagonal-bipyramidal (PB) structure with a water molecule at one of the five basal coordination sites. It is therefore attributed to the different coordination geometry (PB) around the Ti^{III} ion that the dark blue sodium salt is distinctly different in color from the present three salts (**I**—**III**), all with approximate C_{2v}-CTP structures. In other words, the two seven-coordinate structures, PB and C_{2v}-CTP, are facilely interconverted[18,19] for the Ti^{III}-edta complex anion when the counterion is appropriately varied. Actually, the main difference between the two structures is a conformational difference in the diamine chelate ring (E-ring). Since the complex anion in an aqueous solution is purple, but not blue in color, it probably has a structure close to a C_{2v}-CTP structure. Similarly, seven-coordinate Mg^{II}- and

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}) of Ba[Ti(edta)(H_2O)]Cl·6H_2O (**I**)

Atom	x	y	z	$B_{eq}^{a)}$/Å^2
Ti	665.0 (3)	−2498.1 (2)	−1405.4 (6)	1.32 (1)
O1	1676 (1)	−2807 (1)	549 (3)	1.94 (5)
O2	844 (1)	−3497 (1)	−2146 (3)	2.22 (5)
O3	935 (1)	−1608 (1)	132 (2)	1.85 (4)
O4	1679 (1)	−2103 (1)	−2876 (2)	2.22 (5)
O5	−318 (1)	−2906 (1)	166 (3)	2.12 (5)
O6	107 (2)	−4392 (1)	−3356 (4)	3.82 (7)
O7	917 (1)	−486 (1)	26 (3)	2.59 (6)
O8	2256 (1)	−1895 (1)	−5482 (3)	2.70 (6)
O9	−1713 (1)	−2864 (1)	1215 (3)	2.07 (5)
N1	99 (2)	−2618 (1)	−4330 (3)	1.65 (5)
N2	−594 (1)	−1784 (1)	−1767 (3)	1.41 (5)
C1	−588 (2)	−2085 (2)	−4909 (4)	2.02 (7)
C2	−1191 (2)	−1941 (2)	−3406 (4)	1.86 (7)
C3	−322 (2)	−3298 (2)	−4466 (4)	2.19 (7)
C4	245 (2)	−3780 (2)	−3248 (4)	2.30 (7)
C5	−236 (2)	−1086 (1)	−1782 (4)	1.78 (6)
C6	596 (2)	−1040 (1)	−436 (4)	1.74 (6)
C7	901 (2)	−2582 (2)	−5457 (4)	2.32 (8)
C8	1668 (2)	−2148 (2)	−4588 (4)	1.92 (7)
C9	−1147 (2)	−1881 (2)	−196 (4)	1.87 (7)
C10	−1075 (2)	−2611 (1)	424 (4)	1.63 (6)
O10	4417 (2)	−679 (2)	1711 (5)	4.49 (9)
O11	3337 (2)	−302 (1)	5166 (4)	3.10 (6)
O12	2717 (2)	483 (1)	1105 (4)	4.03 (8)
O13	2777 (2)	−996 (2)	−1598 (3)	4.38 (8)
O14	−779 (2)	−409 (2)	2839 (4)	4.17 (8)
O15	1082 (2)	−533 (2)	4182 (4)	4.48 (9)
Ba	2552.8 (1)	−880.4 (1)	2046.5 (2)	1.691 (8)
Cl	2736.0 (7)	1016.4 (4)	−3005 (1)	3.93 (3)

a) $B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}) of Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O (**II**)

Atom	x	y	z	$B_{eq}^{a)}$/Å^2
Ti1	−4729.9 (4)	2774.4	3209.5 (8)	1.43 (3)
Ti2	−389.3 (4)	2739.3 (9)	−1977.6 (8)	1.46 (3)
O11	−5219 (2)	4054 (3)	1919 (5)	2.7 (1)
O12	−4004 (2)	3052 (3)	1372 (4)	2.08 (8)
O13	−5693 (2)	3013 (3)	4476 (4)	2.39 (8)
O14	−5410 (2)	1721 (3)	1834 (5)	2.52 (9)
O15	−4101 (2)	3867 (3)	4578 (4)	2.46 (8)
O16	−2896 (2)	2837 (4)	380 (5)	3.3 (1)
O17	−6537 (3)	2169 (4)	5888 (7)	4.7 (1)
O18	−5525 (2)	334 (4)	183 (5)	3.2 (1)
O19	−3525 (3)	4365 (4)	6964 (5)	3.6 (1)
N11	−4027 (2)	1270 (3)	2893 (5)	2.01 (9)
N12	−4574 (2)	2085 (4)	5836 (5)	2.4 (1)
C11	−4001 (3)	620 (4)	4417 (8)	2.9 (1)
C12	−3954 (3)	1315 (5)	5906 (8)	3.2 (1)
C13	−3286 (2)	1626 (4)	2449 (7)	2.1 (1)
C14	−3380 (2)	2566 (4)	1287 (6)	1.9 (1)
C15	−5288 (3)	1605 (4)	6210 (7)	2.7 (1)
C16	−5893 (3)	2312 (4)	5488 (7)	2.4 (1)
C17	−4360 (3)	668 (4)	1460 (8)	2.8 (1)
C18	−5162 (3)	911 (4)	1140 (6)	2.0 (1)
C19	−4396 (3)	2956 (5)	7004 (6)	2.9 (1)
C110	−3956 (3)	3788 (4)	6159 (6)	2.4 (1)
O21	156 (2)	3929 (5)	−3261 (8)	3.4 (1)
O22	−1025 (2)	2894 (3)	−4162 (4)	2.13 (8)
O23	511 (2)	3061 (3)	−377 (4)	2.38 (8)
O24	299 (2)	1604 (3)	−2912 (5)	2.50 (9)
O25	−1100 (2)	3869 (3)	−1130 (4)	2.56 (9)
O26	−2180 (2)	2871 (4)	−5181 (5)	3.13 (9)
O27	1266 (2)	2493 (4)	1663 (6)	4.3 (1)
O28	466 (2)	67 (3)	−4179 (5)	3.1 (1)
O29	−1710 (2)	4583 (4)	905 (5)	3.2 (1)
N21	−1107 (2)	1253 (3)	−2344 (5)	1.87 (9)
N22	−662 (2)	2203 (3)	665 (5)	1.94 (9)
C21	−1164 (3)	645 (4)	−774 (7)	2.5 (1)
C22	−1263 (3)	1412 (5)	659 (7)	2.6 (1)
C23	−1828 (3)	1652 (4)	−3030 (7)	2.1 (1)
C24	−1692 (3)	2530 (4)	−4230 (6)	2.1 (1)
C25	36 (3)	1803 (5)	1460 (7)	2.6 (1)
C26	656 (3)	2495 (4)	909 (7)	2.6 (1)
C27	−765 (3)	575 (4)	−3591 (7)	2.5 (1)
C28	66 (2)	748 (4)	−3555 (6)	2.1 (1)
C29	−892 (3)	3156 (5)	1562 (6)	2.7 (1)
C210	−1282 (3)	3935 (4)	386 (6)	2.2 (1)
O30	3016 (2)	1525 (4)	1245 (6)	3.3 (1)
O31	2045 (2)	47 (3)	3386 (5)	2.66 (9)
O32	1795 (2)	1699 (3)	−3725 (5)	2.8 (1)
O33	3109 (2)	126 (3)	−2868 (5)	2.47 (9)
O34	−1615 (3)	−626 (4)	3335 (6)	3.7 (1)
O35	−2246 (3)	−1974 (5)	882 (6)	4.3 (1)
O36	−2540 (3)	−1355 (4)	−4250 (7)	4.0 (1)
Cl	−3126.3 (7)	−356 (2)	−1108 (2)	3.52 (4)
Na1	3171 (1)	−267 (2)	69 (2)	2.75 (6)
Na2	1849 (1)	−253 (2)	−3789 (2)	2.57 (5)
Na3	2169 (1)	1863 (2)	3486 (3)	2.88 (6)

a) $B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Mn^{II}-edta complexes have been reported to adopt both the PB and C_{2v}-CTP structures in the solid state, depending on the counterions which form salts with them.[2,3,6,7] In contrast, seven-coordinate Fe^{III}- and V^{III}-edta complexes[1,5,8] seem at present to adopt one structure exclusively, i.e., PB and C_{2v}-CTP structures, respectively, for any counterion examined so far. Judging from the earlier observations that Ca[Fe(cydta)(H_2O)]$_2$·8H_2O,[20] Na[V(cydta)(H_2O)]·5H_2O,[21] and [V(hedtra)(H_2O)][22] all have approximate C_{2v}-CTP structures (cydta=*trans*-1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetate and hedtra=*N*′-(2-hydroxyethyl)-ethylenediamine-*N*,*N*,*N*′-triacetate), it seems hopelessly difficult to predict which structure, PB or C_{2v}-CTP, a particular seven-coordinate edta complex takes.[18,19]

Electronic and Steric Requirements for a Seven-Coordinate Ti^{III}-edta Complex. It is now established here that the Ti^{III} ion (d^1) forms a seven-coordinate edta complex anion in four different salts, though it does not have any of spherically symmetric d-electron configurations. However, the apparently exceptional seven-coordination is rationalized for

Table 4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}) of K[Ti(edta)(H_2O)]·2.5H_2O (**III**)

Atom	x	y	z	$B_{eq}^{a)}$/Å^2
Ti	540.2 (9)	−733.9 (3)	−5286.3	1.74 (6)
O1	1244 (4)	−970 (1)	−6807 (9)	2.5 (2)
O2	1389 (5)	−871 (1)	−3350 (11)	3.0 (2)
O3	−241 (4)	−741 (1)	−7571 (12)	2.5 (2)
O4	1300 (5)	−512 (1)	−6686 (11)	3.0 (2)
O5	−264 (4)	−986 (1)	−4288 (13)	3.2 (2)
O6	1685 (5)	−913 (2)	−380 (11)	3.5 (2)
O7	−1486 (6)	−658 (2)	−8960 (14)	4.0 (2)
O8	2274 (5)	−238 (2)	−6674 (13)	3.7 (2)
O9	−1550 (4)	−1113.9 (9)	−3432 (13)	2.8 (2)
N1	904 (5)	−464 (1)	−3182 (11)	1.9 (2)
N2	−770 (5)	−558 (1)	−4415 (12)	2.1 (2)
C1	242 (6)	−279 (2)	−3196 (16)	2.5 (2)
C2	−645 (6)	−372 (2)	−3020 (15)	2.6 (2)
C3	1000 (6)	−581 (2)	−1340 (14)	2.3 (2)
C4	1394 (6)	−804 (2)	−1662 (13)	2.4 (2)
C5	−1074 (7)	−462 (2)	−6189 (17)	3.5 (3)
C6	−951 (6)	−630 (2)	−7714 (15)	3.2 (2)
C7	1749 (6)	−370 (2)	−3790 (15)	3.1 (2)
C8	1778 (6)	−366 (2)	−5876 (16)	2.3 (2)
C9	−1378 (6)	−722 (1)	−3723 (17)	2.4 (2)
C10	−1028 (6)	−968 (2)	−3848 (14)	2.4 (2)
O10	412 (5)	1163 (1)	680 (14)	3.8 (2)
O11	1565 (6)	−42 (2)	174 (16)	5.1 (3)
O12	0	0	2285 (27)	6.1 (5)
K	−2204 (1)	−1125.6 (5)	−9886 (4)	3.21 (7)

a) $B_{eq}=4/3\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 5. Bond Distances around the Ti^{III} Ion in Å

	I	**II**-1	**II**-2	**III**	**IV**[a)]
Ti-O1	2.087 (2)	2.097 (4)	2.104 (6)	2.100 (8)	2.115 (2)
Ti-O2	2.073 (2)	2.058 (3)	2.057 (3)	2.090 (8)	2.102 (2)
Ti-O3	2.125 (2)	2.085 (4)	2.062 (3)	2.048 (8)	2.113 (2)
Ti-O4	2.056 (2)	2.092 (4)	2.071 (4)	2.047 (8)	2.028 (2)
Ti-O5	2.078 (2)	2.072 (4)	2.066 (4)	2.091 (8)	2.026 (2)
Ti-N1	2.301 (2)	2.315 (4)	2.299 (4)	2.297 (8)	2.310 (2)
Ti-N2	2.305 (2)	2.290 (4)	2.310 (4)	2.372 (8)	2.323 (2)

a) **IV**: Na[Ti(edta)(H_2O)]·2H_2O (Ref. 13).

this complex as follows. Suppose a transition-metal ion surrounded by seven equivalent ligand atoms at equi-distances in a PB or C_{2v}-CTP environment. It then has two low-lying d-orbitals which are completely and almost completely σ-nonbonding, respectively, but are both π-antibonding for π-donors.[13,18,23] Consequently, those metal ions in which all d-electrons occupy these two d-orbitals only may well form seven-coordinate complexes, because they are electronically as stable as the corresponding six-coordiate, octahedral complexes, if the steric requirements[1,2,4,24] are fulfilled. They include not only d^1 and d^2, but also low-spin d^3 and d^4 ions. In fact, several seven-coordinate complexes are known for $Ti^{III}(d^1)$, $V^{III}(d^2)$, Nb^{I}(low-spin d^4), Nb^{III}-Nb^{IV}(d^2-d^1), Ta^{I} (low-spin d^4), Ta^{III}-Ta^{IV}(d^2-d^1), Cr^{II}(low-spin d^4), Mo^{II}-Mo^{IV}(low-spin d^4-d^2), W^{II}-W^{IV}(low-spin d^4-d^2), Re^{III}(low-spin d^4), and Os^{IV}(low-spin d^4) ions,[19,25] and seven-coordinate edta complexes have actually been described for V^{III} and Os^{IV} ions.[5,12] If the ligands are strong π-acceptors, such as CN^-, CNR, and CO, the two low-lying d-orbitals become strongly π-bonding,[13,18] so that seven-coordinate structures are favored over six-coordinate ones. Such examples of homoleptic seven-coordinate complexes are $[V^{III}(CN)_7]^{4-}$,[26] $[Cr^{II}(CNR)_7]^{2+}$,[27] $[Mo^{II}(CNR)_7]^{2+}$,[28] $[Mo^{II}(CN)_7]^{5-}$,[29] $[Mo^{III}(CN)_7]^{4-}$,[30] $[W^{II}(CNR)_7]^{2+}$,[28c,31] $[W^{II}(CN)_7]^{5-}$,[32] and $[Re^{III}(CN)_7]^{4-}$.[33]

For the Ti^{III} ion with the d^1 configuration in question, at least four seven-coordinate complexes are known to date: $[Ti(ox)_3(H_2O)]^{3-}$,[34] $[Ti(ox)_2(H_2O)_3]^-$,[35] $[Ti_2(ox)_3(H_2O)_6]$,[36] and $[Ti(CN)_7]^{4-}$,[37] all of which adopt either a PB or a C_{2v}-CTP structure. In this way, the Ti^{III} ions is more or less apt to take a seven-coordinate structure. In addition, it has a radius of 0.81 Å,[38] somewhat larger than the "critical radius" of 0.785 Å between coordination numbers 6 and 7 for the edta complexes of tervalent metal ions,[24] i. e., an ionic radius of Fe^{III} ion whose edta complex takes both six- and seven-coordinate structures.[1,8,39] It is therefore not unusual from both electronic and steric points of view that the Ti^{III}-edta complex is seven-coordinate with a water molecule in the first coordination sphere, which accounts for the kinetic lability[40] and acid-base behavior[14] of the complex anion in solution.

It should be added to the above discussion that the critical radii are safely used to predict the coordination numbers (CN) of metal-edta complexes only when the electronic requirements for the seven-coordination mentioned above are fulfilled.[24] For example, Ru^{III} (low-spin d^5),[41] Rh^{III} (low-spin d^6),[42] and Ir^{III} (low-spin d^6)[43] ions which are greatly stabilized in an octahedral (Oh) environment, form six-coordinate edta complexes exclusively, though their ionic radii (0.82, 0.805, and 0.82 Å,[38] respectively) are larger than the critical radius of 0.785 Å for tervalent ions and are comparable with the radius of the Ti^{III} ion (0.81 Å), which forms a seven-coordinate edta complex, as confirmed by the present study. Since these ions are too large to be encircled octahedrally by edta alone, they form unique and octahedral edta complexes in which edta serves as a pentadentate ligand with the sixth coordination site occupied by another ligand, such as water or a halogen.[24,44]

Comparison of the Molecular Structures of [Ti(edta)(H_2O)]$^-$ Anions in I—III. Some selected bond distances and angles are compared among the four C_{2v}-CTP complex anions in Tables 5 and 6, respectively; the corresponding data for the dark-blue PB complex (**IV**) are also listed there for a comparison.[13] As can be seen in Figs. 1, 2, and 3, although the four

Table 6. Selected Bond Angles in Degree

	I	II-1	II-2	III	IV[a)]
O1–Ti–O2	79.36 (8)	77.3 (1)	76.5 (2)	76.0 (3)	75.02 (8)
O1–Ti–O3	76.56 (8)	77.8 (1)	77.8 (2)	82.4 (3)	73.91 (8)
O1–Ti–O4	89.88 (8)	90.7 (2)	90.8 (2)	83.4 (3)	90.39 (8)
O1–Ti–O5	87.74 (8)	87.1 (1)	88.8 (2)	89.8 (3)	107.39 (8)
O2–Ti–N1	71.84 (8)	71.8 (1)	71.5 (1)	71.4 (3)	71.34 (8)
O3–Ti–N2	70.74 (7)	70.7 (1)	71.5 (1)	73.7 (3)	71.45 (8)
O4–Ti–N1	75.14 (8)	74.1 (1)	74.2 (1)	74.1 (3)	77.10 (8)
O5–Ti–N2	74.67 (8)	74.2 (2)	74.6 (1)	74.1 (3)	77.12 (8)
O4–Ti–O5	177.61 (8)	177.1 (1)	177.8 (1)	170.4 (3)	161.59 (8)
N1–Ti–N2	74.17 (8)	75.2 (2)	74.3 (1)	73.5 (3)	73.57 (8)
Ti–O2–C4	119.7 (2)	123.2 (3)	118.7 (3)	121.1 (7)	120.9 (2)
Ti–O3–C6	119.4 (2)	119.0 (3)	121.1 (3)	123.8 (7)	124.1 (2)
Ti–O4–C8	123.6 (2)	122.7 (3)	123.5 (3)	123.2 (7)	120.4 (2)
Ti–O5–C10	123.0 (2)	123.4 (3)	123.7 (3)	126.6 (7)	123.3 (2)
Ti–N1–C1	112.9 (2)	111.2 (3)	112.3 (3)	110.6 (6)	114.6 (2)
Ti–N1–C3	106.0 (2)	106.6 (3)	104.3 (3)	106.1 (5)	108.2 (2)
Ti–N1–C7	107.5 (2)	107.8 (3)	108.1 (3)	106.8 (6)	103.1 (2)
C1–N1–C3	111.1 (2)	112.6 (4)	113.2 (4)	114.4 (8)	109.3 (2)
C1–N1–C7	109.4 (2)	110.6 (4)	108.9 (4)	108.0 (8)	111.0 (2)
C3–N1–C7	109.8 (2)	107.8 (4)	109.7 (4)	110.6 (7)	110.5 (2)
Ti–N2–C2	112.2 (2)	110.0 (3)	112.9 (3)	113.4 (5)	111.0 (2)
Ti–N2–C5	107.4 (2)	106.3 (3)	106.3 (3)	102.4 (6)	107.2 (2)
Ti–N2–C9	107.2 (2)	108.3 (3)	106.7 (3)	109.7 (6)	108.8 (2)
C2–N2–C5	111.8 (2)	112.8 (4)	112.3 (4)	109.2 (8)	110.0 (2)
C2–N2–C9	108.5 (2)	109.3 (4)	109.4 (4)	110.8 (8)	112.1 (2)
C5–N2–C9	109.6 (2)	110.1 (4)	109.0 (4)	111.0 (8)	109.4 (2)
N1–C1–C2	109.0 (2)	109.6 (4)	109.1 (4)	110.2 (8)	109.4 (2)
N2–C2–C1	109.2 (2)	110.4 (5)	108.7 (4)	109.7 (8)	108.8 (2)
N1–C3–C4	109.1 (2)	108.4 (4)	108.8 (4)	108.7 (8)	108.7 (2)
O2–C4–C3	115.2 (3)	114.4 (4)	115.0 (4)	115.4 (9)	116.3 (2)
N2–C5–C6	108.2 (2)	107.4 (4)	107.7 (4)	109 (1)	109.4 (2)
O3–C6–C5	115.8 (2)	116.0 (4)	116.3 (4)	113.3 (9)	114.0 (2)
N1–C7–C8	111.1 (2)	112.3 (4)	110.6 (4)	109.1 (8)	112.5 (2)
O4–C8–C7	115.1 (2)	117.2 (4)	116.1 (4)	115.4 (9)	116.7 (2)
N2–C9–C10	109.7 (2)	109.9 (4)	111.3 (4)	113.5 (8)	114.5 (2)
O5–C10–C9	115.5 (2)	114.5 (4)	114.6 (4)	115.3 (9)	116.2 (2)

a) **IV**: Na[Ti(edta)(H_2O)]·2H_2O (Ref. 13).

complex anions in **I**—**III** are fairly similar in structure to each other, a close inspection of these figures and the structural data given in Tables 5 and 6 reveals that the complex anion in the purple K salt (**III**) is distinctly different concerning some structural details from other three complex anions in **I** and **II**, as shown below.

First of all, the four Ti–O (carboxylato) bonds on the quadrilateral face (Ti–O2, Ti–O3, Ti–O4, and Ti–O5) are almost similar in length to each other, as are the Ti–N bonds for the four complex anions, as required by the C_{2v}-CTP structure; they are also comparable on the average with those of the PB complex in the dark-blue sodium salt (**IV**). A notable exception is the Ti–N2 bond in the purple K salt (**III**), which is even longer than the "equatorial" Ti–N bonds in the dark-blue PB complex (**IV**). Similarly, the O5–C10 and C9–C10 bonds associated with the same glycine chelate ring (R2 defined latter) in the K salt (**III**) are somewhat shorter and longer, respectively, than the corresponding bonds in other salts including the dark-blue sodium salt (**IV**) (see Table S-2 in supplementary material). Furthermore, some of the L–Ti–L′ bond angles in the purple K salt (**III**) are fairly different from the corresponding angles in other three C_{2v}-CTP complexes (Table 6). In short, the complex anion in the purple K salt (**III**) differs dedicately in coordination geometry around the Ti ion from those in the violet Ba (**I**) and reddish-violet Na (**II**) salts, while the latter three complex anions (in **I**, **II**-1, and **II**-2) have comparatively similar structure parameters, consistent with their similar colors.

In Table 7 are given deviations of respective atoms from the least-squares plane defined by Ti, O1, O2, and O3 atoms and from the least-squares quadrilateral plane defined by O2, O3, O4, and O5 atoms for the four C_{2v}-CTP complex anions. It is evident there that the planarity of the former plane is fairly high, except for the K salt, and that the K salt differs from the other salts in the deviation pattern of the two N atoms. In contrast, the planarity of the quadrilateral plane is higher for the K salt. These observations also point to the structural

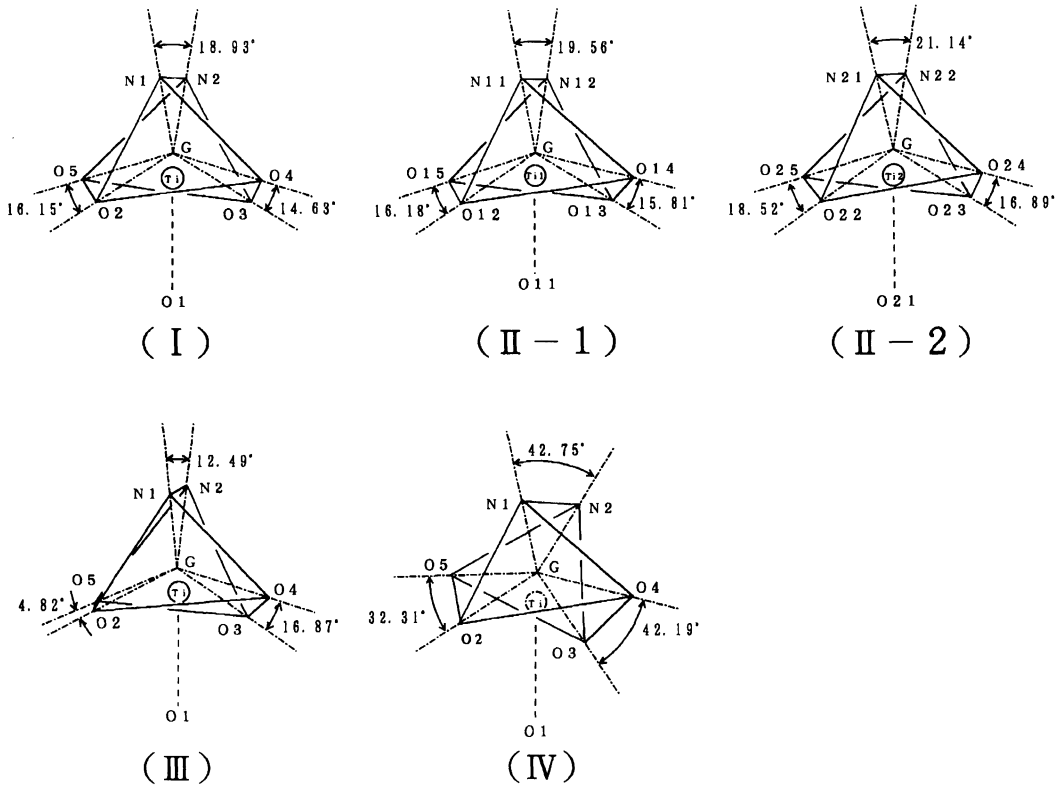

Fig. 4. Projections of the coordination spheres for Ba[Ti(edta)(H_2O)]Cl·6H_2O (**I**), Na_2[Ti(edta)(H_2O)]$_2$·NaCl·7H_2O (**II**-1 and **II**-2), and K[Ti(edta)(H_2O)]·2.5H_2O (**III**), along the axis passing through the centers of gravity (G) of the triangular faces. A mirror image is projected in **II**-1 for a comparison.

Table 7. Deviations from the Least-Squares Planes in Å

	I	II-1	II-2	III
Plane defined by Ti, O1, O2, and O3				
Ti	−0.017	−0.019	−0.025	0.163
O1	−0.004	−0.005	−0.007	0.035
O2	0.011	0.012	0.016	−0.099
O3	0.010	0.012	0.016	−0.099
N1	0.705	0.728	0.667	1.289
N2	−0.858	−0.853	−0.850	−0.394
Plane defined by O2, O3, O4, and O5				
O2	0.200	0.202	0.230	0.127
O3	0.196	0.206	0.221	0.143
O4	−0.200	−0.205	−0.228	−0.123
O5	−0.195	−0.203	−0.223	−0.147

difference of the K salt from other salts.

Figure 4 shows the coordination spheres of all the relevant complex anions projected along the axis passing through the centers of gravity (G) of the two triangular faces comprising O2, O4, and N1 atoms, and O3, O5, and N2 atoms. The dihedral angles of the two faces are 0.99° (**I**), 0.85° (**II**-1), 0.94° (**II**-2), 0.78° (**III**), and 10.5° (PB complex **IV**), indicating that the two faces are almost parallel to each other for the four C_{2v}-CTP complexes, as is often the case.[5] The twist angles of the two faces, (θ_1(O2–G–O5), θ_2(O3–G–O4), and θ_3(N1–G–N2)) are, respectively, 16.2, 14.6, and 18.9° (**I**), 16.2, 15.8, and 19.6° (**II**-1), 18.5, 16.9, and 21.1° (**II**-2), and 4.8, 16.9, and 12.5° (**III**). These values are roughly comparable with those reported earlier for other C_{2v}-CTP complexes with edta and edta-like ligands.[5] Here again, θ_1 of the K salt is much smaller in magnitude than those of other C_{2v}-CTP complex anions, which leads to a higher planarity of the quadrilateral plane in the K salt. In this respect, the K salt bears a structural resemblance to the Na and NH_4 salts of the V(III)-edta complex, θ_1 to θ_3 values of which are respectively 3.5, 21.1, and 14.8° (for Na salt), and 2.0 (2.1), 18.1 (18.1), and 12.1° (11.8°) (for NH_4 salt);[5] it might be better described as a 4 : 3 piano stool[28d] or trigonal base-tetragonal base.[18,45] The dark-blue PB complex naturally has much greater θ values (32.3, 42.2, and 42.8°, respectively).

Finally, attention has been paid to the chelate ring strains of all the relevant complex anions, which are deduced from the bond-angle sums of the respective chelate rings given in Table 8. Since the O4–Ti–O5 bite angle is closer to 180° than is the O2–Ti–O3 angle for all of the C_{2v}-CTP complex anions, the O4 and O5 ligand atoms are regarded as being axial after the notations employed for the Oh or PB edta complex. It then follows that the Ti–O4–C8–C7–N1–Ti and Ti–O5–C10–C9–N2–Ti chelates are R-rings (R1 and R2, respectively) and that the Ti–O2–C4–C3–N1–Ti and Ti–O3–C6–C5–N2–Ti chelates are G-rings (G1 and G2, respectively). It is evident in Table 8 that the R-rings

Table 8. Bond Angle Sums of Chelate Rings in Degree

Ring[a)]	I	II-1	II-2	III	IV[b)]
R1	532.4	534.1	532.5	528.6	529.8
R2	530.1	530.3	530.9	539.2	538.2
G1	521.8	524.4	518.3	522.7	525.6
G2	521.5	519.4	522.9	522.2	526.2
E	517.5	516.4	517.3	517.4	517.4

a) R1: Ti–O4–C8–C7–N1–Ti, R2: Ti–O5–C10–C9–N2–Ti, G1: Ti–O2–C4–C3–N1–Ti, G2: Ti–O3–C6–C5–N2–Ti, E: Ti–N1–C1–C2–N2–Ti. b) **IV**: Na[Ti(edta)-(H_2O)]·2H_2O (Ref. 13).

have bond-angle sums closer to an ideal sum of 538.4° for the glycine chelate ring than do the G-rings for all the Ti(III)-edta complex anions, indicating that the G-rings are more strained than the R-rings like in the usual six-coordinate octahedral edta complexes.[46,47] In addition, the G-rings have slightly smaller bond-angle sums in the four C_{2v}-CTP complexes (**I**—**III**) than in the PB complex (**IV**), implying that the four C_{2v}-CTP complexes suffer a slightly greater strain in the G-rings than does the PB complex. On the other hand, the R- and E-rings have comparable bond-angle sums between the two structures (an ideal sum for the E-ring is 527.9°).[47] The same trends in the bond-angle sums as above are also noted in the seven-coordinate Mg^{II}- and V^{III}-edta complexes.[2,3,5]

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