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Syntheses and Crystal Structures of Seven-Coordinate (Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetato)aquavanadate(III) Complexes

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K[V(edta)(H_2O)]·$2H_2O$ (**1a**) was prepared by the reaction of VCl_3 with K_4 edta. The compound was converted to its sodium and ammonium salts by use of a cation exchange resin. Crystal structure analyses of Na[V(edta)(H_2O)]·$3H_2O$ (**1b**) and NH_4[V(edta)(H_2O)]·$2.5H_2O$ (**1c**) revealed that in both compounds the vanadium atom adopts a capped trigonal-prismatic structures with a hexadentate ethylenediaminetetraacetato ligand and an aqua ligand. Crystal data are as follows: **1b**: Monoclinic, $P2_1/a$, a=17.831 (3), b=8.408 (1), c=11.595 (2) Å, β=109.39 (1)°, Z=4, R=0.045 for 6321 reflections; **1c**: Monoclinic, Aa, a=8.552 (1), b=59.948 (6), c=7.226 (1) Å, β=114.95 (1)°, Z=8, R=0.050 for 6087 reflections.

The coordination chemistry of vanadium(III) is attracting attention in connection with its biological importance in tunichromes1) and vanadium-containing nitrogenase.2) Vanadium(III) usually forms complexes with coordination number six,3) but its chemistry has been poorly investigated.

In the course of our research in electron transfer reactions, we found that the kinetics of the electron transfer reactions between [V^{III}(hedra)(H_2O)]4) and halogenopentaamminecobalt(III) complexes obey the zeroth-order rate law when excess V(III) is used.5) To elucidate the mechanism of this reaction, we analyzed the crystal structures of the reactant [V^{III}(hedra)(H_2O)]·$2H_2O$ and the final product K[V^{IV}O(hedra)]·H_2O. To our surprise, V(III) adopts a capped trigonal-prismatic seven-coordinate structure: The coordinated hedtra ligand is hexadentate and one water molecule occupies the seventh coordination position of vanadium(III).6) This prompted us to study the structures of vanadium(III) complexes containing edta-related aminopolycarboxylate ligands. Some preliminary results for Na[V(edta)(H_2O)]·$3H_2O$ have already been reported.7,8) It was apparent that the edta complex also forms a capped trigonal-prismatic seven-coodinate structure. The geometry of [V(edta)(H_2O)]$^-$ is quite deformed: The coordination sphere was shown to lack an approximate two-fold axis along the V–H_2O bond in contrast to the [V(hedtra)(H_2O)] complex. Many edta complexes with an aqua ligand have also been reported to adopt seven coordination as capped trigonal prisms or pentagonal bipyramids. However, they usually have an exact or approximate two-fold axis along the M–H_2O bond. Furthermore, coordination structures of some seven-coordinate edta complex anions depend on the nature of cation. Thus [Mg(edta)(H_2O)]$^{2-}$ adopts a capped trigonal prismatic structure in the sodium salt,9) while in the magnesium salt it is pentagonal bipyramidal.10) The iron(III)–edta complex forms six-coordinate structure in the lithium11) and guanidinium salts,12) and pentagonal bipyramidal seven-coodinate structure in many other salts.13–18) Therefore it would be important to elucidate whether the large deformation observed in the coordination sphere of the [V(edta)(H_2O)]$^-$ anion is intrinsic to a single ion or is due to steric hindrance related to ion packing. In this paper, the crystal structure of the ammonium salt of vanadium(III)–edta complex is analyzed and compared it with those of [V^{III}(hedtra)(H_2O)]·$2H_2O$6) and Na[V(edta)(H_2O)]·$3H_2O$.

Experimental

General Procedure. The complexes were prepared and handled under a nitrogen or argon atmosphere. A column (10 mmϕ) of Dowex 50W-X8(50—100 mesh) was used for exchanging cations in the vanadium(III)–edta complex.

Synthesis of K[V(edta)(H_2O)]·$2H_2O$ (1a). H_4edta (11.69 g, 40 mmol) was added to 100 cm^3 of water and neutralized with 11.20 g (80 mmol) of potassium carbonate. To the solution was added 6.30 g (40 mmol) of VCl_3 and the solution was stirred for 15 min. Evaporation of the solvent using a rotary evaporator followed by addition of ethanol gave pale brown flocculent crystals, which were collected by filtration and washed with ethanol and ether, successively. Yield 15.5 g (90%). Found: C, 27.55; H, 4.36; N, 6.61%. Calcd for $C_{10}H_{18}KN_2O_{11}V$: C, 27.78; H, 4.20; N, 6.48%.

Synthesis of Na[V(edta)(H_2O)]·$3H_2O$ (1b). An aqueous solution (6 cm^3) containing 1.0 g (2.3 mmol) of K[V(edta)-(H_2O)]·$2H_2O$ was passed through a column packed with 2.5 cm^3 of Na-type cation exchange resin. The sodium salt was obtained as pale purple crystals almost quantitatively by evaporation of the eluate using a rotary evaporator followed by addition of ethanol. Found: C, 28.43; H, 4.44; N, 6.18%. Calcd for $C_{10}H_2ON_2NaO_{12}V$: C, 27.66; H, 4.64; N, 6.45%. Parallel-piped crystals suitable for X-ray diffractometry were obtained by standing a saturated aqueous solution in a desiccator over phosphorus pentoxide under an argon atmosphere.

Synthesis of NH_4[V(edta)(H_2O)]·$2.5H_2O$ (1c). The title compound was prepared by the same procedure as the preparation of **1b**, using a requisite amount of NH_4-type cation exchange resin instead of the Na-type one. Yield 88%. Found: C, 28.45; H, 5.78; N, 9.94%. Calcd for $C_{10}H_{23}N_3O_{11.5}V$: C, 28.58; H, 5.52; N, 10.00%. Columnar crystals suitable for X-ray diffractometry were also obtained by the same procedure as for the sodium salt.

X-Ray Crystal Structure Determination of 1b and 1c. Diffraction data were collected on a Rigaku AFC-6A four-

Table 1. Crystal Data for $Na[V(edta)(H_2O)]\cdot 3H_2O$ (**1b**) and $NH_4[V(edta)(H_2O)]\cdot 2.5H_2O$ (**1c**)

	1b	**1c**
Formula	$C_{10}H_{20}N_2NaO_{12}V$	$C_{10}H_{23}N_3O_{11.5}V$
Fw	534.20	430.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	Aa
a/Å	17.831(3)	8.552(1)
b/Å	8.408(1)	59.948(6)
c/Å	11.595(2)	7.226(1)
β/deg	109.39(1)	114.95(1)
U/Å^3	1639.8(5)	3358.9(8)
Z	4	8
d_{calcd}/g cm^{-3}	1.76	1.70
d_{measd}/g cm^{-3}	1.74	1.69
μ/cm^{-1}	7.44	6.99
Cryst size/mm	0.5×0.3×0.3	0.40×0.12×0.26
Temp/°C	20	20
2θ range/deg	3—65	3—70
Scan mode	ω-2θ	ω
ω-Scan width/deg	$1.1+0.35\tan\theta$	1.2
No. of unique data	6321	7484
No. of data used with $\lvert F_o\rvert>3\sigma(F_o)$	4216	6087
No. of parameters refined	284	565
R[a)]	0.045	0.050
R_w[b)]	0.085	0.062

a) $R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$. b) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=[\sigma^2(|F_o|)+aF_o^2]^{-1}$, where a is 0.015 for **1a** and 0.003 for **1c**.

circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ=0.71073 Å). Crystallographic and experimental data for the complexes are listed in Table 1. The reflection data were corrected for Lorentz and polarization factors. No correction was applied for absorption or extinction. All the structures were solved by the conventional heavy-atom method and the parameters were refined by the block-diagonal least-squares method. Anisotropic tempeprature factors were applied for the non-hydrogen atoms. Positions of hydrogen atoms, except for those of water molecules, were deduced from difference Fourier syntheses and refined with isotropic temperature factors. Two hydrogen atom positions for **1b** were fixed at the calculated coordinates. There is ambiguity in the identification of nitrogen atoms of ammonium ions, and oxygen atoms of water of crystallization for **1c**. The atoms with maximum number of hydrogen bonds were assigned as the ammonium nitrogen atoms. This assignment gave a reasonable arrangement of anions and cations in the crystal. The inverse chirality for **1c** gave a larger R value (0.052). Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from Refs. 19 and 20, respectively. The calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Computer Center of Tohoku University using the Universal Computation Program System UNICS III.[21)]

Results and Discussion

Syntheses and Properties of the Vanadium(III) Complexes. The complex was prepared by direct reaction of the potassium salt of edta with vanadium(III) chloride. This method is more convenient than the reduction of the $[VO(edta)]^{2-}$ complex using sodium amalgam.[22)] The complexes are reasonably air-stable in

Table 2. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for $Na[V(edta)(H_2O)]\cdot 3H_2O$ (**1b**)

Atom	x	y	z	B_{eq}/Å^2 [a)]
V	8416.7(2)	8079.8(5)	3011.8(4)	1.2
O(1)	7260(1)	8782(2)	2083(2)	1.9
O(2)	6088(1)	8195(3)	703(2)	2.5
O(3)	8569(1)	7391(3)	4793(2)	2.1
O(4)	8002(1)	6407(4)	6077(2)	2.8
O(5)	9606(1)	8567(2)	3842(2)	1.7
O(6)	10813(1)	7523(3)	4689(2)	2.8
O(7)	8575(1)	9057(2)	1520(2)	1.9
O(8)	9377(1)	9168(3)	413(2)	2.2
O(W1)	8344(1)	10351(3)	3649(2)	2.1
N(1)	7633(1)	5976(3)	2861(2)	1.5
N(2)	9050(1)	6139(3)	2422(2)	1.3
C(1)	8081(2)	4482(3)	2911(3)	1.7
C(2)	8575(2)	4645(3)	2085(2)	1.8
C(3)	6947(2)	6074(3)	1722(2)	1.7
C(4)	6732(1)	7798(3)	1466(2)	1.6
C(5)	7352(2)	6057(4)	3931(2)	1.9
C(6)	8020(2)	6639(4)	5036(2)	1.8
C(7)	9759(2)	5852(3)	3506(3)	1.9
C(8)	10103(2)	7430(3)	4070(2)	1.7
C(9)	9304(2)	6737(3)	1407(3)	1.8
C(10)	9075(2)	8455(3)	1085(2)	1.5
Na	−88.9(7)	1769(1)	841(1)	1.9
O(W2)	229(2)	1308(4)	2976(2)	4.4
O(W3)	802(2)	3823(3)	1596(2)	3.6
O(W4)	2477(2)	3314(4)	737(3)	3.9

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{\text{eq}}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$. B_{ij} is defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

the solid state, though prolonged exposure of aqueous solutions to air results in oxidation to vanadium(IV) complexes. The crystals of $Na[V(edta)(H_2O)]\cdot3H_2O$ and $NH_4[V(edta)H_2O)]\cdot2.5H_2O$ exhibit dichroism and look purple or grayish green depending on the direction.

Structures of $Na[V(edta)(H_2O)]\cdot3H_2O$ (1b) and $NH_4[V(edta)(H_2O)]\cdot2.5H_2O$ (1c). Final atomic coordinates and equivalent isotropic temperature factors for $Na[V(edta)(H_2O)]\cdot3H_2O$ (**1b**) and $NH_4[V(edta)(H_2O)]\cdot2.5H_2O$ (**1c**) are listed in Tables 2 and 3, respectively. Bond lengths and angles for **1b** and **1c** are given in Table 4.[23] ORTEP drawings of the $[V(edta)(H_2O)]^-$ ions are shown in Fig. 1. Crystals of the ammonium salt are composed of two crystallographically independent complex anions, but the structures of both complexes are almost the same and are also quite similar to that of the sodium salt.

In the complexes, edta acts as a hexadentate ligand forming a twisted trigonal prism, and one water molecule is also coordinated to the vanadium atom in a capping position. Thus the geometry around the vanadium atom is a capped trigonal-prism. The structure of

Table 3. Final Atomic Coordinates ($\times10^4$ for x and z and $\times10^5$ for y) and Equivalent Isotropic Temperature Factors for $NH_4[V(edta)(H_2O)]\cdot2.5H_2O$ (**1c**)

Atom	x	y	z	$B_{eq}/Å^{2\,a)}$	Atom	x	y	z	$B_{eq}/Å^{2\,a)}$
V(1)	5000	44756(1)	5000	1.4	O(24)	−636(5)	35116(6)	708(5)	3.5
V(2)	2821.3(7)	30243(1)	3912.4(9)	1.3	O(25)	4272(3)	30166(4)	2277(4)	2.1
O(11)	6613(4)	46245(4)	7741(4)	2.3	O(26)	6711(4)	31044(6)	2055(5)	3.4
O(12)	7350(4)	46535(5)	11069(4)	2.8	O(27)	4300(4)	27623(4)	5478(5)	2.6
O(13)	6383(4)	42456(4)	4206(4)	2.3	O(28)	6878(4)	26248(5)	7511(5)	2.9
O(14)	8458(5)	39900(6)	5245(5)	3.4	O(2W1)	1322(4)	28052(4)	1626(4)	2.1
O(15)	3555(3)	44819(5)	1921(4)	2.2	N(21)	2093(3)	32824(4)	5573(4)	1.6
O(16)	1102(5)	43968(6)	−738(5)	3.5	N(22)	5355(3)	31898(4)	5993(4)	1.6
O(17)	3520(3)	47379(4)	5085(5)	2.5	C(21)	3373(4)	34668(5)	6228(5)	1.9
O(18)	953(4)	48737(5)	4550(6)	2.9	C(22)	5157(4)	33711(6)	7293(5)	2.0
O(1W1)	6493(3)	46942(4)	4204(4)	2.0	C(23)	1906(5)	31755(6)	7324(5)	2.1
N(11)	5738(3)	42172(4)	7397(4)	1.6	C(24)	1127(4)	29484(6)	6644(5)	1.9
N(12)	2468(4)	43084(4)	4538(4)	1.7	C(25)	400(4)	33720(6)	4104(5)	2.0
C(11)	4445(4)	40333(5)	6756(5)	1.9	C(26)	387(4)	33838(5)	2014(5)	2.1
C(12)	2665(4)	41308(6)	6046(6)	2.0	C(27)	5999(5)	32890(6)	4549(6)	2.4
C(13)	5907(5)	43233(6)	9321(5)	2.1	C(28)	5693(4)	31254(6)	2846(5)	2.0
C(14)	6703(4)	45512(5)	9432(5)	1.9	C(29)	6571(5)	30155(6)	7261(6)	2.4
C(15)	7417(4)	41294(6)	7619(5)	2.1	C(210)	5895(5)	27839(5)	6701(5)	1.9
C(16)	7424(5)	41163(6)	5522(6)	2.1	N(3)	8144(5)	26196(6)	2009(6)	2.7
C(17)	1841(5)	42127(6)	2467(5)	2.3	N(4)	9675(5)	48789(6)	7769(6)	2.7
C(18)	2135(4)	43770(6)	1061(5)	2.1	O(W1)	4549(5)	25879(6)	874(6)	3.4
C(19)	1249(5)	44827(6)	4592(7)	2.6	O(W2)	3922(8)	37540(9)	1964(8)	5.1
C(110)	1944(4)	47179(5)	4722(5)	1.9	O(W3)	817(6)	37128(9)	8271(7)	5.1
O(21)	1208(4)	28753(4)	5035(4)	2.4	O(W4)	7019(6)	37895(8)	1380(7)	4.7
O(22)	478(4)	28448(5)	7626(4)	2.7	O(W5)	3276(5)	49129(6)	235(6)	3.4
O(23)	1448(4)	32534(4)	1740(4)	2.2					

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$. B_{ij} is defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

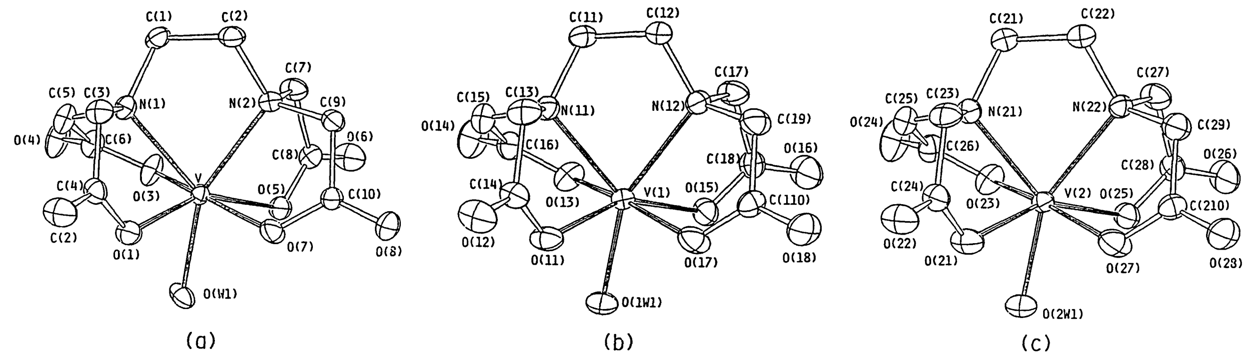

Fig. 1. Molecular structures of $[V(edta)(H_2O)]^-$ with atomic numbering scheme. Hydrogen atoms are omitted for clarity. (a) $Na[V(edta)(H_2O)]\cdot3H_2O$ (**1b**), (b) complex 1 of $NH_4[V(edta)(H_2O)]\cdot2.5H_2O$ (**1c**), and (c) complex 2 of **1c**.

$[V(edta)(H_2O)]^-$ is quite similar to that of $[V(hedtra)(H_2O)]\cdot 2H_2O$ (**2**).6) The averaged V–O(carboxylato) bond lengths are 2.052 (23) Å for **1b** and 2.051 (16) for **1c**, these values being almost equal to that in **2** (2.048(13) Å).6) However, the bond lengths in $[V(edta)(H_2O)]^-$ range more widely than those in $[V(hedtra)(H_2O)]$. This difference is reflected in the difference of configurations of both complexes. Figure 2 shows the projections of coordination spheres for $[V(edta)(H_2O)]^-$ and $[V(hedtra)(H_2O)]$ along the axis passing through the centers of gravity, CE1 and CE2, of the N(*n*1)–O(*n*1)–O(*n*3) and N(*n*2)–O(*n*5)–O(*n*7) triangular faces, where *n* is zero for **1b** and **2**, respectively, and is the first digit of atomic numbering, 1 or 2, for **1c**. In each complex these triangles are almost parallel to each other (dihedral angles between the planes are 4.90 for **1b**, 3.28 and 3.11 for **1c**, and 2.20° for **2**, respectively), but they are twisted with respect to each other. As parameters for the degree of twist between the two trianglular surfaces, we can define the twist angles as θ_1: N(*n*1)–CE1–CE2–N(*n*2), θ_2: O(*n*1)–CE1–CE2–O(*n*5), and θ_3: O(*n*3)–CE1–CE2–O(*n*7). These angles are also given in Fig. 2. Although $[V(hedtra)(H_2O)]$ has an approximate C_2 axis along the V–H_2O bond, $[V(edta)(H_2O)]^-$ has no such symmetry. On the other hand, the O(*n*1), O(*n*7), N(*n*1), and N(*n*2) atoms for $[V(edta)(H_2O)]^-$ are almost coplanar; they deviate from the least-squares plane by only −0.028, +0.026, +0.029, and −0.027 Å for **1b**, +0.013, −0.012, −0.013, and +0.013 Å for the complex 1 of **1c**, and +0.12, −0.12, −0.12, and +0.12 Å for the complex 2 of **1c**, respectively. These planes are almost parallel to the O(*n*3)–O(*n*5)–O(*n*W) plane. The dihedral angles between the planes are 4.96° for **1b** and 4.93° for complexes 1 and 2 of **1c**, respectively. Thus the geometry of $[V(edta)(H_2O)]^-$ may also be described as a 4:3 piano stool24) or tetragonal base-trigonal base.25) It is of interest to note that the edta ligand, which has higher symmetry than the hedtra ligand, adopts a coordination structure of lower symmetry than the latter ligand. In the previous communication we mentioned that this low symmetry for $[V(edta)(H_2O)]^-$ is peculiar among the various seven coordinate structures with edta and aqua ligands. Table 5 shows the twist angles, θ_1, θ_2, and θ_3, of the capped trigonal-prismatic complexes with edta-like ligands. All complexes except for $[V(edta)(H_2O)]^-$ have an approximate or crystallographic two-fold axis along the M–H_2O bond as is shown by the equivalence of θ_2 with θ_3. The lack of symmetry in $[V(edta)(H_2O)]^-$ is also reflected in the large difference in the angles, O(*n*1)–N(*n*1)–O(*n*3) and O(*n*5)–N(*n*2)–O(*n*7): 84.1 (1) vs. 62.31 (7)° for **1b**, 81.9(1) vs. 62.2(1) and 81.7(1) vs. 61.5(2) for **1c**. The corresponding angles for **2** are much less different: 75.41 (6) vs. 70.67 (6)°.

Table 4. Interatomic Distances and Angles for $Na[V(edta)(H_2O)]\cdot 3H_2O$ (**1b**) and $NH_4[V(edta)(H_2O)]\cdot 2.5H_2O$ (**1c**)

Bond length	*l*/Å		
	1b	**1c**	
	n=0	*n*=1	*n*=2
V(*n*)–N(*n*1)	2.225(2)	2.208(3)	2.203(3)
V(*n*)–N(*n*2)	2.218(3)	2.279(3)	2.278(2)
V(*n*)–O(*n*1)	2.071(2)	2.078(2)	2.075(4)
V(*n*)–O(*n*3)	2.074(2)	2.050(3)	2.043(2)
V(*n*)–O(*n*5)	2.058(2)	2.039(2)	2.043(3)
V(*n*)–O(*n*7)	2.017(2)	2.036(3)	2.034(2)
V(*n*)–O(*n*W1)	2.067(2)	2.073(3)	2.076(2)
C(*n*4)–O(*n*1)	1.279(3)	1.271(5)	1.271(5)
C(*n*4)–O(*n*2)	1.241(3)	1.237(4)	1.237(6)
C(*n*6)–O(*n*3)	1.273(4)	1.258(4)	1.275(5)
C(*n*6)–O(*n*4)	1.235(4)	1.243(6)	1.244(4)
C(*n*8)–O(*n*5)	1.271(3)	1.273(4)	1.285(4)
C(*n*8)–O(*n*6)	1.233(3)	1.231(4)	1.233(6)
C(*n*10)–O(*n*7)	1.267(4)	1.265(5)	1.281(4)
C(*n*10)–O(*n*8)	1.239(4)	1.232(5)	1.242(4)
N(*n*1)–C(*n*1)	1.480(3)	1.490(4)	1.486(4)
N(*n*1)–C(*n*3)	1.474(3)	1.479(5)	1.486(5)
N(*n*1)–C(*n*5)	1.486(4)	1.473(5)	1.488(4)
N(*n*2)–C(*n*2)	1.493(3)	1.481(5)	1.492(5)
N(*n*2)–C(*n*7)	1.476(3)	1.476(4)	1.494(6)
N(*n*2)–C(*n*9)	1.483(4)	1.488(5)	1.486(4)
C(*n*1)–C(*n*2)	1.508(5)	1.505(5)	1.502(5)
C(*n*3)–C(*n*4)	1.504(4)	1.513(5)	1.504(5)
C(*n*5)–C(*n*6)	1.512(3)	1.520(6)	1.507(6)
C(*n*7)–C(*n*8)	1.516(4)	1.510(6)	1.507(6)
C(*n*9)–C(*n*10)	1.514(4)	1.518(5)	1.493(5)
Bond angle	ϕ/deg		
O(*n*1)–V(*n*)–O(*n*W1)	75.65(8)	75.74(10)	75.47(12)
O(*n*3)–V(*n*)–O(*n*W1)	84.56(9)	81.50(12)	81.49(9)
O(*n*5)–V(*n*)–O(*n*W1)	80.00(8)	81.17(11)	81.23(12)
O(*n*7)–V(*n*)–O(*n*W1)	88.47(9)	89.06(12)	89.11(9)
O(*n*W1)–V(*n*)–N(*n*1)	130.56(9)	130.94(11)	130.99(10)
O(*n*W1)–V(*n*)–N(*n*2)	152.72(8)	153.59(11)	153.73(9)
O(*n*1)–V(*n*)–O(*n*3)	112.09(8)	109.05(11)	109.16(12)
O(*n*1)–V(*n*)–O(*n*7)	80.61(8)	79.09(10)	79.06(12)
O(*n*3)–V(*n*)–O(*n*5)	79.39(8)	82.10(11)	82.15(12)
O(*n*5)–V(*n*)–O(*n*7)	84.50(8)	85.43(10)	85.27(12)
O(*n*1)–V(*n*)–N(*n*1)	72.21(8)	72.45(9)	72.66(13)
O(*n*3)–V(*n*)–N(*n*1)	74.21(8)	74.93(11)	75.12(10)
O(*n*5)–V(*n*)–N(*n*2)	74.90(8)	75.36(10)	75.58(11)
O(*n*7)–V(*n*)–N(*n*2)	78.75(9)	77.27(11)	76.95(9)
N(*n*1)–V(*n*)–N(*n*2)	76.21(8)	75.29(10)	75.13(10)
V(*n*)–N(*n*1)–C(*n*1)	110.8(2)	110.2(2)	110.9(2)
V(*n*)–N(*n*1)–C(*n*3)	109.8(2)	108.5(2)	108.5(2)
V(*n*)–N(*n*1)–C(*n*5)	105.9(2)	106.2(2)	106.2(2)
V(*n*)–N(*n*2)–C(*n*2)	113.4(2)	113.7(2)	113.8(2)
V(*n*)–N(*n*2)–C(*n*7)	103.7(1)	103.6(2)	103.9(2)
V(*n*)–N(*n*2)–C(*n*9)	108.4(2)	108.7(2)	108.9(2)
V(*n*)–O(*n*1)–C(*n*4)	121.8(2)	121.0(2)	120.7(3)
V(*n*)–O(*n*3)–C(*n*6)	120.2(2)	120.7(3)	120.6(3)
V(*n*)–O(*n*5)–C(*n*8)	119.1(2)	122.6(2)	121.8(3)
V(*n*)–O(*n*7)–C(*n*10)	119.8(2)	122.8(2)	122.5(2)

Figure 3 shows the packing diagram of $Na[V(edta)(H_2O)]\cdot 3H_2O$. Two O(8) atoms of neighboring anions bridge two sodium ions around the center of symmetry (Na···Na=3.628 (3) Å), and the sodium ions are coordinated tetrahedrally with crystal water molecules (O(W2) and O(W3)) and two O(8) atoms, with bond distances ranging from 2.312(3) to 2.381 (3) Å. In

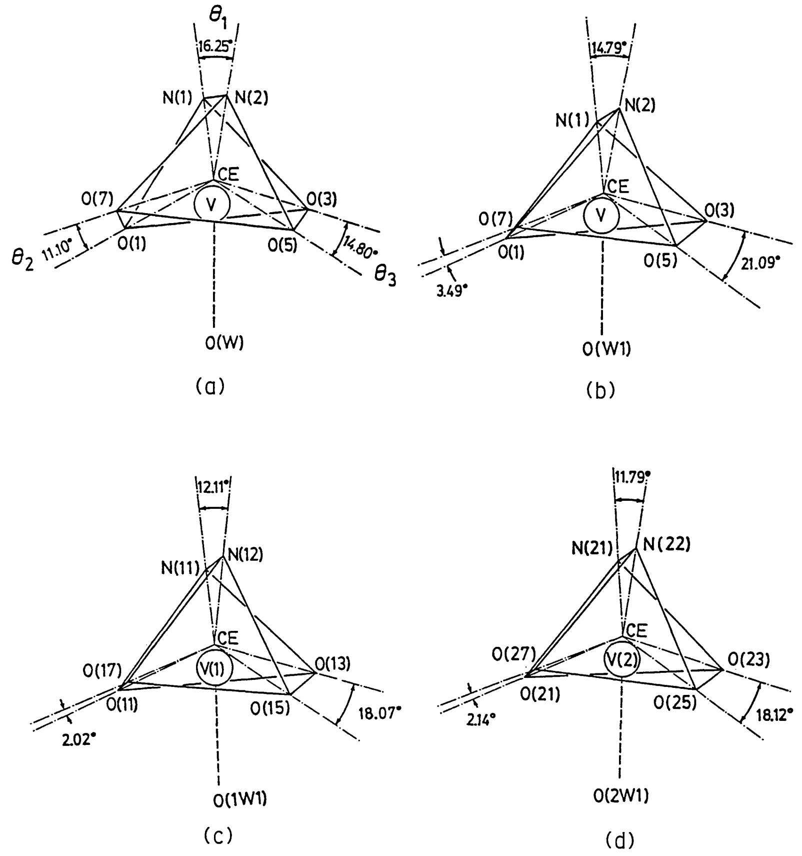

Fig. 2. Projections of the coordination spheres for (a) $[V(hedtra)(H_2O)]$, (b) $[V(edta)(H_2O)]^-$ of the sodium salt, (c) and (d) $[V(edta)(H_2O)]^-$ of the ammonium salt, along the axis passing through the centers of gravity (CE) of the trianguler faces. Twist angles between the triangular faces, θ_1, θ_2, and θ_3, are also depicted.

Table 5. Comparison of Twist Angles, θ_1, θ_2, and θ_3,[a] of Capped Trigonal-Prismatic Seven-Coordinate Complexes with Edta-Like Ligands

Complex	θ_1/deg	θ_2/deg	θ_3/deg
$[V(hedtra)(H_2O)]$[b]	16.25	11.10	14.80
$Na[V(edta)(H_2O)]\cdot 3H_2O$[c]	14.79	3.49	21.09
$NH_4[V(edtra)(H_2O)]\cdot 2.5H_2O$[c]	12.11	2.02	18.07
	11.79	2.14	18.12
$Na_2[Mg(edta)(H_2O)]\cdot 5H_2O$[d]	8.67	8.32	8.32
$MnH_2[Mn(edta)(H_2O)]_2\cdot 10H_2O$[e]	27.21	23.98	26.03
$[Os(edta)(H_2O)]\cdot H_2O$[f]	22.25	18.36	12.30
$Ca[Fe(cydta)(H_2O)]\cdot 8H_2O$[g]	26.86	26.26	23.44

a) See text and Fig. 2(a). b) Ref. 6. c) This work. d) Ref. 26. e) Ref. 27. f) Ref. 28. g) Ref. 29.

the ammonium salt (Fig. 4), the cations are hydrogen-bonded to O(*n*8) atoms: $N(3)\cdots O(28^{i})=2.961$ (4), $N(4)\cdots O(18^{ii})=2.958$ (7) Å, where i and ii denote the symmetry operations *x*, *y*, 1+*z*, and 1+*x*, *y*, *z*, respectively. However, these hydrogen bonds are weak compared to the other hydrogen bonds found between the ammonium cations and water molecules (the hydrogen bond distances range from 2.822 (5) to 2.898 (5) Å). Thus the distortion of the complex anions found in the sodium and ammonium salts may be due to the interaction between

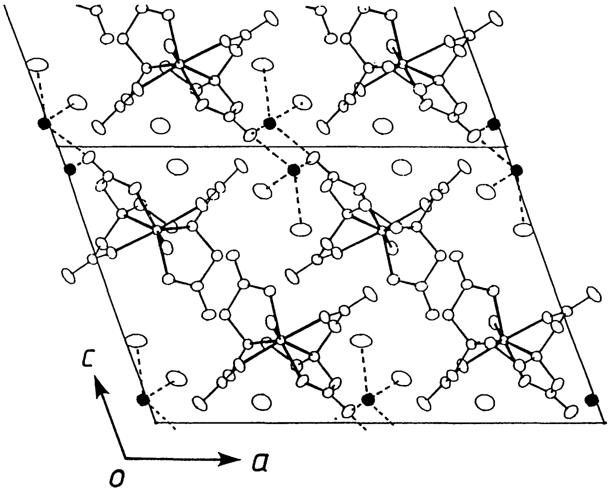

Fig. 3. Cell projection for $Na[V(edta)(H_2O)]\cdot 3H_2O$ (**1b**) along *b*. Sodium ions are depicted by solid elipsoids. Coordination bonds between sodium and oxygen atoms are shown with dotted lines.

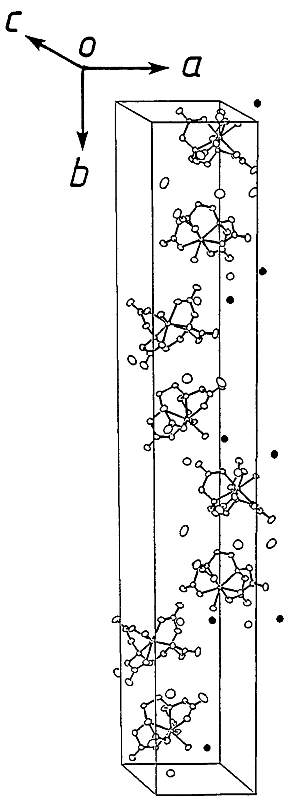

Fig. 4. Perspective of the unit cell for $NH_4[V(edta)(H_2O)]\cdot 2.5H_2O$ (**1c**). Ammonium nitrogen atoms are depicted by solid elipsoids.

the O(n8) atom and the cation; rather, the large deformation may be intrinsic to the $[V(edta)(H_2O)]^-$ anion and due to the d^2 configuration of vanadium(III) ion. For $[V(hedtra)(H_2O)]$, this distortion may be compensated by the rather weak bond between vanadium and the hydroxyethyl group.

The capped trigonal-prismatic structure of $[V^{III}(edta)(H_2O)]^-$ is in contrast to the pentagonal-bipyramidal structure of $[Fe^{III}(edta)(H_2O)]^-$,[13-18] although the ionic radii of Fe(III) and V(III) are almost the same ($r_{Fe^{3+}}$=0.645 vs. $r_{V^{3+}}$=0.640 Å).[30] This may be due to the difference of electronic configurations between iron(III) and vanadium(III): d^5 and d^2, respectively.

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