© 2001 The Chemical Society of Japan

Syntheses, Structures, and Properties of Vanadium(III) Complexes with the Hexadentate Ligand, Tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate, *N*,*N*′-Bis(2-pyridylmethyl)-1,2-ethanediamine-*N*,*N*′-diacetate, and *N*,*N*′-Bis(2-pyridylmethyl)-1,3-propanediamine-*N*,*N*′-diacetate

Kan Kanamori,* **Ayako Kyotoh, Kazuya Fujimoto, Kiyonori Nagata, Honoh Suzuki, and Ken-ichi Okamoto**†

Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930-8555

†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

(Received May 23, 2001)

Vanadium(III) complexes with the hexadentate ligand, tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (tmdta), *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine-*N*,*N*′-diacetate (bpedda), and *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine-*N*,*N*′-diacetate (bppdda), have been prepared. The structures of the tmdta (**1**) and bpedda (**3**) complexes have been determined by X-ray crystallography. The stereochemical property of complex **1** was compared with that of the corresponding Cr(III) complex (**2**), whose structure was also determined by X-ray crystallography. The tmdta complexes adopt a distorted octahedral structure, including a seven-membered chelate ring formed by the tetramethylenediamine moiety of the tmdta ligand. The bpedda complex has been determined to be a heptacoordinate complex with a distorted pentagonal bipyramidal geometry. The isolated bppdda complex has been characterized to be a μ-oxo dinuclear vanadium(III) complex on the basis of its spectral features. The tmdta and bpedda complexes do not yield a corresponding μ-oxo dinuclear vanadium(III) complex on base hydrolysis.

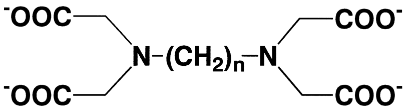
Current interest revolves around the coordination chemistry of vanadium(III) with regard to the role of vanadium(III) in certain sea animals, ascidian[1] and fan warm.[2] In most cases the functions of metal compounds in biological systems are regulated by their coordination geometries. Thus, the development of the coordination stereochemistry of vanadium(III) compounds should be of importance in order to reveal the puzzling role of vanadium(III) species in life, though neither the structure nor the chemical formula of vanadium(III) species in the above animals has been clarified at present.

The coordination stereochemistry of the vanadium(III) ion is flexibly changed by the chelate-ring size and the class of the coordination group of the ligands. For example, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (edta), which forms only five-membered chelate rings, yields the heptacoordinate vanadium(III) complex,[3] while 1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate (trdta),[4] forming one six-membered chelate ring and 1,2-diaminoethane-*N*,*N*′-diacetate-*N*,*N*′-dipropionate (eddda),[5,6] forming two six-membered chelate rings, yield the hexacoordinate vanadium(III) complexes. On the other hand, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen), which forms only five-membered chelate rings as edta, coordinates to the vanadium(III) center in the quiquedentate fashion and yields the heptacoordinate or hexacoordinate vanadium(III) complex, depending on the kind of coexisting anion.[7] This ligand also acts as a bridging ligand.[7] As for the tripodal tetradentate ligands, nitrilotriacetate (nta) yields the heptacoordinate vanadium(III) complex, but *N*-(2-pyridylmethyl)iminodiaceate (pda) yields the hexacoordinate one, though both ligands form only five membered chelate rings.[8] It is, therefore, of importance to determine the coordination geometry of the vanadium(III) complexes with various types of ligands, since the properties and functions of vanadium(III) complexes are greatly influenced by their structures. Here, we report on the syntheses and structures of vanadium(III) complexes with tetramethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (tmdta), *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine-*N*,*N*′-diacetate (bpedda), and *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine-*N*,*N*′-diacetate (bppdda), which are shown in Scheme 1. The present ligands are interesting, because tmdta forms a seven-membered chelate ring that is rarely found, and because bpedda and bppdda have structures intermediate between edta and tpen, and trdta and tptn (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,3-propanediamine), respectively.

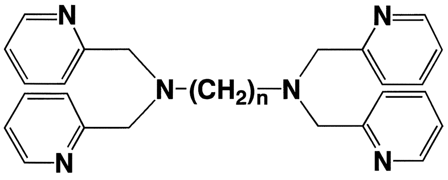
Experimental

Preparation of Ligands. H_4tmdta was prepared according to a literature method.[9]

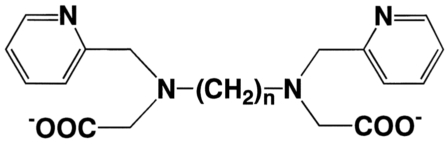
Ba(bpedda)·2LiClO$_4$·H$_2$O. A solution (20 cm^3) of monochloroacetic acid (7.56 g; 0.08 mol) was neutralized by adding solid LiOH·H$_2$O (3.36 g; 0.08 mol) in small portions below 10 °C. To this solution was added 9.69 g (0.04 mol) of *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen).[10] After the mixture was homogenized by adding 20 cm^3 of ethanol, 3.36 g (0.08 mol) of LiOH·H$_2$O was added in small portions while keeping the pH of the solution below 11 at room temperature. After the addition



n=2: edta; n=3: trdta; n=4: tmdta



n=2: tpen; n=3: tptn



n=2: bpedda; n=3: bppdda

Scheme 1.

of lithium hydroxide was completed, stirring was continued for one day. The resulting solution was evaporated until syrupy, and 60 cm^3 of methanol was added to it. The precipitate was filtered off. A methanolic solution (20 cm^3) of $BaClO_4 \cdot 3H_2O$ (15.61 g; 0.04 mol) was added to the filtrate, resulting in the precipitation of a light-yellow powder. The powder was collected by filtration and recrystallized from 800 cm^3 of methanol. The yield was 24 g (83%). Found: C, 29.99; H, 3.18; N, 7.54%. Calcd for $C_{18}H_{22}N_4O_{13}BaCl_2Li_2$: C, 29.84; H, 3.06; N, 7.73%. Selected IR data (KBr disk): 1571, 1432, 1406, 1326, 1143, 1116, 1087 cm^{-1}.

H_2bppdda·2HClO$_4$·1.5H$_2$O. *N*,*N′*-Bis(2-pyridylmethyl)-1,3-propanediamine (bispictn)[11] was allowed to react with monochloroacetic acid in a similar manner as mentioned above. The reaction mixture was concentrated until syrupy, and 100 cm^3 of water was then added to it. To this solution was added 25.1 g (0.15 mol) of 60% $HClO_4$. The solution was stored in a refrigerator to complete the precipitation of a light-yellow powder. The powder was filtered, washed with ethanol, and air-dried. The yield was 7.2 g (40%). Found: C, 37.83; H, 4.89; N, 9.29%. Calcd for $C_{19}H_{29}N_4O_{13.5}Cl_2$: C, 38.01; H, 4.87; N, 9.33%. Selected IR data (KBr disk): 1731, 1613, 1537, 1464, 1399, 1236, 1121, 1094, 894, 778, 626 cm^{-1}.

Preparation of Complexes. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or in a nitrogen-filled grove box. K[Cr(tmdta)]·H_2O (**2**) was prepared according to a literature method with some modifications.[12]

Cs[V^{III}(tmdta)]·H$_2$O (1). A suspension containing $V_2(SO_4)_3$ (1.95 g; 5 mmol), H$_4$tmdta (3.2 g; 10 mmol), $BaCO_3$ (2.96 g; 15 mmol), and Cs_2CO_3 (1.6 g; 5 mmol) in 50 cm^3 of water was stirred at 60 °C for 24 h. The precipitated barium sulfate was filtered out. The filtrate was evaporated to dryness. After the residual was dissolved in 4 cm^3 of water, 2 cm^3 of ethanol was added. Reddish-brown plate-like crystals were deposited. The yield was 2.2 g (86%). Found: C,27.72; H,3.49; N, 5.31%. Calcd for $C_{12}H_{18}N_2O_9VCs$: C,27.72; H,3.49; N, 5.39%. Selected IR data (KBr disk): 1663, 1459, 1341, 1252, 1089, 1005, 917, 780, 553 cm^{-1}. The corresponding potassium salt was also obtained as reddish-brown needle-like crystals in 43% yield by using K_2CO_3 in the place of Cs_2CO_3. Found: C, 32.64; H, 4.66; N, 6.41%. Calcd for $C_{12}H_{20}N_2O_{10}VK$: C, 32.64; H, 4.57; N, 6.35%. Selected IR data (KBr disk): 1634, 1626, 1459, 1340, 1253, 1089, 1005, 919, 780, 553 cm^{-1}.

[V^{III}(bpedda)(H$_2$O)]ClO$_4$ (3). A mixture of $V_2(SO_4)_3$ (0.98 g; 2.5 mmol), Ba(bpedda)·2LiClO$_4$·H$_2$O (3.6 g; 5.0 mmol), and Li_2SO_4 (0.32 g; 2.5 mmol) in 50 cm^3 of water was stirred at 60 °C for one day. The precipitated barium sulfate was filtered out. The resulting brown solution was kept standing at room temperature overnight. The deposited brown crystals were filtered, washed with cold water, and air-dried. The yield was 1.8 g (70%). Found: C, 41.33; H, 4.45; N, 10.75%. Calcd for $C_{18}H_{22}N_4O_9ClV$: C, 41.20; H, 4.23; N, 10.68%. Selected IR data (KBr disk): 1637, 1437, 1368, 1085, 861, 759, 715, 617 cm^{-1}.

[V$^{III}_2$(μ-O)(bppdda)$_2$]·5H$_2$O (4). Vanadium(III) sulfate (1.95 g; 5 mmol) was dissolved in 30 cm^3 of water by stirring the mixture at 60 °C for one day. To the solution was added a methanolic solution (30 cm^3) of H$_2$bppnda·2HClO$_4$·1.5H$_2$O (3.72 g; 10 mmol). Barium carbonate (2.96 g; 15 mmol) was added to the solution. The precipitated barium sulfate was filtered out. The filtrate was concentrated to ca. 30 cm^3 and kept standing at room temperature overnight. The deposited reddish-purple fine needles were collected by filtration. The yield was 2.37 g (50%). Found: C, 47.72; H, 5.64; N, 11.52%. Calcd for $C_{38}H_{54}N_8O_{14}V_2$: C, 48.01; H, 5.74; N, 11.81%. Selected IR data (KBr disk): 1635, 1434, 1374, 1345, 1291, 973, 771, 643, 568 cm^{-1}.

Measurements. UV-vis spectra were measured using a JASCO Ubest 50 spectrophotometer. Diffuse reflectance spectra were obtained for complexes diluted with MgO. Infrared spectra were recorded using a JASCO FT/IR-8000S spectrophotometer.

X-ray Structure Determination. Crystal structures of Cs[V^{III}(tmdta)]·H$_2$O (**1**), K[Cr^{III}(tmdta)]·H$_2$O (**2**), and [V^{III}(bpedda)(H$_2$O)]ClO$_4$ (**3**) were determined by X-ray crystallography. The crystallographic data are summarized in Table 1. Each single crystal was mounted on a glass fiber, coated with epoxy, and centered on a Rigaku AFC7R (**1** and **2**) or a Rigaku AFC7S (**3**) diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares refinement, using the setting angle of 25 reflections in the range $28.4° < 2\theta < 30.0°$ (**1**), $29.4° < 2\theta < 30.0°$ (**2**), and $29.6° < 2\theta < 30.0°$ (**3**). Data reduction and the application of Lorentz, polarization, linear decay correction, and empirical absorption corrections based on a series of psi scans were carried out using AFC7R (**1** and **2**) or AFC7S (**3**) software (RIGAKU).

The structure was solved by a direct method (SHELXS-97 (**1** and **2**) and SIR92 in TEXAN (**3**)) and conventional Fourier techniques. The structure was refined by full-matrix least-squares on *F* using an anisotropic thermal parameter for non-hydrogen atoms. The hydrogen atoms were fixed by geometrical constrains. The calculations for **1** and **2** were done with SHELXS/2 97.[13] The calculation for **3** was done on an INDIGO II computer using the crystallographic package TEXAN.[14] A list of the final atomic coordinates, full bond distances and angles, and anisotropic thermal parameters were deposited as Document No. 74504 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 168398–168400.

Table 1. Crystallographic Data

	$Cs[V(tmdta)]\cdot H_2O$	$K[Cr(tmdta)]\cdot H_2O$	$[V(bpedda)(H_2O)]ClO_4$
Formula	$C_{12}H_{18}CsN_2O_9V$	$C_{12}H_{18}CrKN_2O_9$	$C_{18}H_{22}ClN_4O_9V$
Formula wt	518.13	425.38	524.79
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$ (No. 14)	$P1$ (No. 1)	I_{bca} (No. 73)
a/Å	7.059(6)	9.674(2)	23.876(2)
b/Å	27.548(5)	12.942(3)	15.469(2)
c/Å	9.535(8)	6.994(1)	11.706(1)
α/°		99.26(2)	
β/°	108.48(6)	108.92(2)	
γ/°		87.40(2)	
V/Å^3	1759(2)	817.6(3)	4323.5(6)
Z	4	2	8
D_{calcd}/g cm^{-3}	1.957	1.728	1.612
Crystal size/mm	0.2 × 0.2 × 0.15	0.4 × 0.2 × 0.2	0.45 × 0.25 × 0.25
λ(Mo $K\alpha$)/Å	0.71073	0.71073	0.71069
Temp/K	296(2)	296(2)	296(2)
Reflections			
Total	5107	5019	2758
$F_o > 2\sigma(F_o)$	3588	4339	1723[c)]
F(000)	1016	438	2160
No. of variables	226	463	165
R[a)] (R_w)[b)]	0.037(0.090)	0.026(0.073)	0.045(0.052)

a) $R = (\Sigma|(F_o| - |(F_c|)/\Sigma(|F_o|)$, b) $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)^{1/2}$, c) $F_o > 3\sigma(F_o)$.

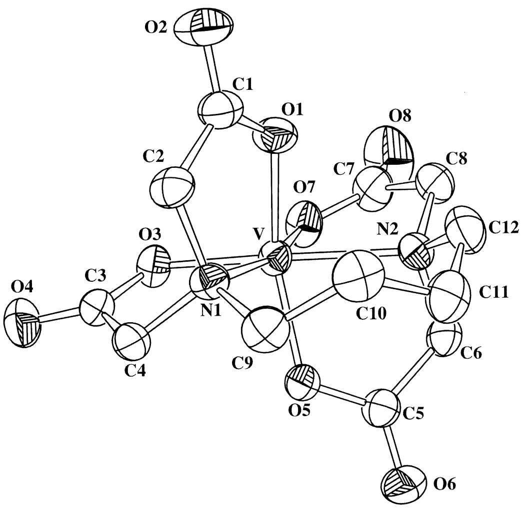


Fig. 1. Perspective view of $[V^{III}(tmdta)]^-$.

Table 2. Selected Bond Distances (Å) and Angles (°) for $Cs[V(tmdta)]\cdot H_2O$ (**1**) and $K[Cr(tmdta)]\cdot H_2O$ (**2**)

$Cs[V(tmdta)]\cdot H_2O$ (**1**)		$K[Cr(tmdta)]\cdot H_2O$ (**2**)		
Bond Distances				
V–O1	1.966(3)	Cr–O1	1.956(5)	1.968(5)
V–O3	1.983(3)	Cr–O3	1.959(5)	1.967(4)
V–O5	1.953(2)	Cr–O5	1.961(5)	1.958(5)
V–O7	1.995(3)	Cr–O7	1.964(5)	1.991(5)
V–N1	2.171(3)	Cr–N1	2.144(5)	2.085(6)
V–N2	2.180(3)	Cr–N2	2.122(5)	2.104(5)
Bond Angles				
O1–V–O3	98.96(12)	O1–Cr–O3	94.0(2)	95.4(2)
O1–V–O5	153.52(12)	O1–Cr–O5	166.7(2)	165.8(2)
O1–V–O7	94.64(12)	O1–Cr–O7	91.1(2)	92.1(2)
O1–V–N1	79.93(11)	O1–Cr–N1	83.6(2)	82.4(2)
O1–V–N2	86.35(12)	O1–Cr–N2	90.3(2)	89.6(2)
O3–V–O5	98.97(11)	O3–Cr–O5	94.2(2)	94.7(2)
O3–V–O7	90.00(12)	O3–Cr–O7	88.4(2)	88.9(2)
O3–V–N1	78.76(12)	O3–Cr–N1	80.2(2)	80.1(2)
O3–V–N2	167.84(11)	O3–Cr–N2	168.5(2)	167.6(2)
O5–V–O7	104.68(12)	O5–Cr–O7	99.6(2)	98.0(2)
O5–V–N1	84.64(11)	O5–Cr–N1	87.6(2)	89.6(2)
O5–V–N2	80.05(11)	O5–Cr–N2	83.6(2)	82.5(2)
O7–V–N1	166.50(11)	O7–Cr–N1	166.9(2)	167.1(2)
O7–V–N2	78.62(13)	O7–Cr–N2	80.9(2)	79.6(2)
N1–V–N2	113.07(12)	N1–Cr–N2	111.0(2)	111.9(2)

Results and Discussion

Structural Characteristics of $Cs[V^{III}(tmdta)]\cdot H_2O$ (1) and $K[Cr^{III}(tmdta)]\cdot H_2O$ (2). Chelation of metal ions by tmdta includes a seven-membered chelate ring, which is far less common than five- and six-membered chelate rings. A perspective view of $[V^{III}(tmdta)]^-$ is shown in Fig. 1, with its numbering scheme. The selected bond distances and angles are summarized in Table 2. To our knowledge, this is the first example of a vanadium(III) complex containing a seven-membered diamine chelate ring as far as we know. A chromium(III) complex with tmdta has been prepared,[12] but the crystal structure of the complex has not been reported. We, thus determined the crystal structure of $K[Cr^{III}(tmdta)]\cdot H_2O$. The selected bond distances and angles are also listed in Table 2. Comparisons of the bond distances and angles of $[V^{III}(tmdta)]^-$ with those of $[Cr^{III}(tmdta)]^-$ complex would be useful in order to make the structural characteristics of vanadium(III) complexes clearer.

The vanadium(III) center of $[\mathrm{V^{III}(tmdta)}]^-$ adopts a distorted octahedral structure. The V–O distances of the in-plane acetate arms (V–O3 and V–O7) are slightly longer than those of the out-of-plane acetate arms (V–O1 and V–O5). This tendency is also found for $[\mathrm{V^{III}(trdta)}]^-$,[4] while the corresponding difference in $[\mathrm{Cr^{III}(tmdta)}]^-$ is negligibly small. The average V–O distance of $[\mathrm{V^{III}(tmdta)}]^-$ (1.974 Å) is very close to that of $[\mathrm{V^{III}(trdta)}]^-$ (1.978 Å), but the average V–N distance of the tmdta complex (2.176 Å) is slightly longer than that of the trdta complex (2.143 Å). The V–O and V–N distances of $[\mathrm{V^{III}(tmdta)}]^-$ are longer than the corresponding ones of $[\mathrm{Cr^{III}(tmdta)}]^-$ (1.966 and 2.114 Å, respectively). The observed elongation of the coordination bond distances of $[\mathrm{V^{III}(tmdta)}]^-$ is consistent with a larger ionic radius of vanadium(III) (0.780 Å) than that of chromium(III) (0.765 Å).[15]

The bite angle of the seven-membered diamine chelate ring in $[\mathrm{V^{III}(tmdta)}]^-$ is 113.07(12)°, which is much larger than that of the six-membered diamine chelate ring in $[\mathrm{V^{III}(trdta)}]^-$ (96.67(8) Å).[4] The expansion in the bite angle of the diamine chelate ring is compensated by a reduction of the bond angle in the opposite site (90.00(12) for $[\mathrm{V^{III}(tmdta)}]^-$ vs 102.44(8) for $[\mathrm{V^{III}(trdta)}]^-$). The deviations of V, N1, N2, O3, and O7 atoms from the least-squares plane are 0.026(1), −0.090(1), 0.076(1), 0.101(2), and −0.113(2) Å, respectively, suggesting planarity of this plane. The sum of the deviations from the ideal octahedral cis angle (90°) is 111.95° in $[\mathrm{V^{III}(tmdta)}]^-$, while the corresponding ones in $[\mathrm{Cr^{III}(tmdta)}]^-$ are 75.9° and 79.4°. The sums of the trans angle deviations from 180° are 52.14° for the vanadium(III) complex, and 37.9° and 39.5° for the chromium(III) complex. This fact suggests that the coordination structure of $[\mathrm{V^{III}(tmdta)}]^-$ is distorted to a larger extent from the regular octahedron than that of $[\mathrm{Cr^{III}(tmdta)}]^-$.

The tetramethylenediamine chelate ring adopts a twist-chair conformation. A similar conformation has been found in *cis*-$[\mathrm{Co(NO_2)_2(tmd)_2}]\mathrm{NO_3}$. (tmd = tetramethylenediamine).[16]

Structures of bpedda and bppdda Complexes. Figure 2 displays a perspective view of complex cation $[\mathrm{V^{III}(bpedda)(H_2O)}]^+$ with its numbering scheme. The selected bond distances and angles are listed in Table 3. The vanadium(III) center adopts a heptacoordination, which is completed by a hexadentate bpedda and an additional aqua ligand. The ideal geometrical structures of hepta-coordination include the pentagonal bipyramid, a capped octahedron, and a capped trigonal prism. All geometrical structures have been realized for vanadium(III) complexes: $[\mathrm{V(SO_4)(tpen)}]^+$,[7] $[\mathrm{V_2(dpot)_2}]^{2-}$,[4,17] (dpot: 2-oxo-1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate) and $[\mathrm{V_2(hpnbpda)_2}]$[18] (hpnbpda: *N*,*N*′-bis(2-pyridylmethyl)-2-oxo-1,3-propanediamine-*N*,*N*′-diacetate) for the pentagonal bipyramidal structure; $[\mathrm{V(nta)(H_2O)_3}]$[19] for the capped octahedral structure; $[\mathrm{V(edta)(H_2O)}]^-$,[3] $[\mathrm{V(cydta)(H_2O)}]^-$,[20] and $[\mathrm{V(hedtra)(H_2O)}]$[21] (hedtra: *N*′-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetate) for the capped trigonal prismatic structure.

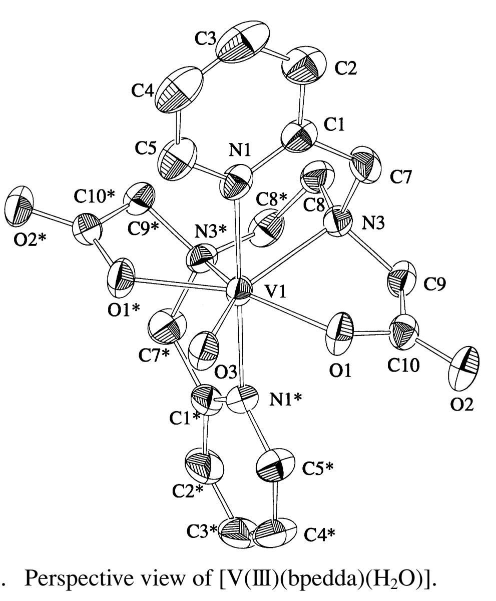


Fig. 2. Perspective view of $[\mathrm{V(III)(bpedda)(H_2O)}]$.

Table 3. Selected Bond Distances (Å) and Angles (°) for $[\mathrm{V(bpedda)(H_2O)}]\mathrm{ClO_4}$

Bond Distances			
V1–O1	2.044(2)	V1–O3	2.067(3)
V1–N1	2.164(3)	V1–N3	2.225(3)
Bond Angles			
O1–V1–O3	75.30(7)	O1–V1–N1	96.9(1)
O1–V1–N1*	83.1(1)	O1–V1–N3	72.4(1)
O3–V1–N1	89.93(8)	N1–V1–N1*	179.9(2)
N1–V1–N3	75.2(1)	N1–V1–N3*	104.9(1)
N3–V1–N3*	75.5(1)		

The coordination geometry of $[\mathrm{V^{III}(bpedda)(H_2O)}]^+$ can be regarded as a distorted pentagonal bipyramid. Atoms O3, O1, O1*, N3, and N3* form a pentagonal plane. The two pyridyl groups occupy the trans positions. The crystallographically-required C_2-axis passes through the O3 and V1 atoms in the pentagonal plane, and the N1–V1–N1* moiety is virtually linear (179.9(2)°). The deviations of O1, O3, N3, O1*, N3*, and V1 atoms from the least-squares pentagonal plane are −0.343(2), 0.000(2), 0.507(2), 0.343, −0.507(2), and 0.000(2) Å, respectively, indicating a large distortion of the pentagonal plane. The dihedral angle between the N3–V1–N3* plane and the O1–V1–O1* plane is 31.83°. The bond distances are comparable with those found in other heptacoordinate vanadium(III) complexes.[3,4,7,17–21]

We were not able to obtain the crystals of the V(III)-bppdda complex with sufficient quality for X-ray crystallography. The structure of the bppdda complex was, therefore, estimated based on elemental analysis, the UV-visible spectrum, and the IR spectrum. Figure 3 shows the absorption and diffuse reflectance spectra of the bppdda complex. The band positions seem to correspond to each other, though the diffuse reflectance spectrum is poorly resolved. This observation suggests that the fundamental structure of the complex in the solid state is similar to that in solution. The very intense absorption band at 484 nm is typical for oxo-bridged dinuclear vanadium(III) complexes,[5] indicating that the isolated bppdda complex has a $\mathrm{V^{III}{-}O{-}V^{III}}$ unit. We thus tentatively formulated the isolated V(III)–bppdda complex as $[\mathrm{V^{III}_2(\mu\text{-}O)(bppdda)_2}]$. The coordi-

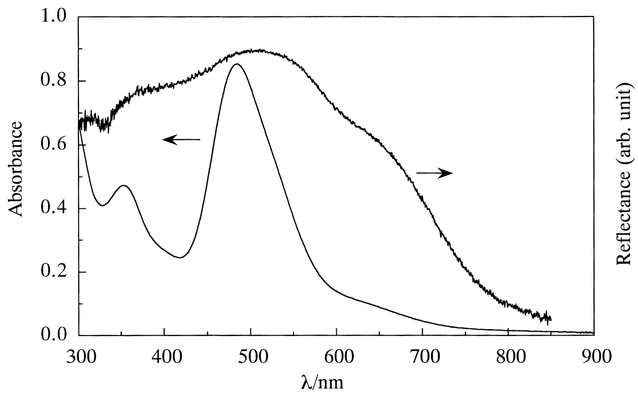


Fig. 3. The absorption (2.5 mmol/dm^3) and diffuse reflectance spectra of $[V^{III}_2(\mu\text{-}O)(bppdda)_2]\cdot 5H_2O$.

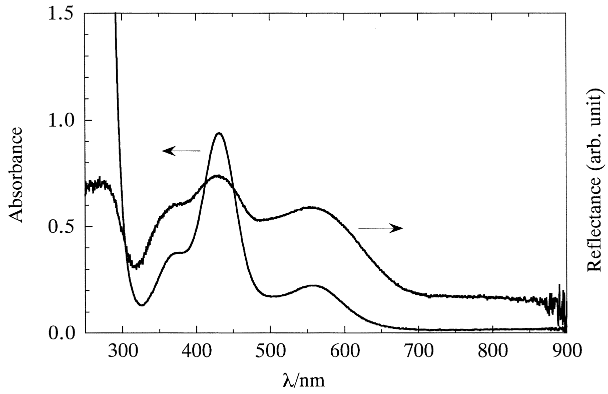


Fig. 4. The absorption (10 mmol/dm^3) and diffuse reflectance spectra of $Cs[V^{III}(tmdta)]\cdot H_2O$.

nation number of the bppdda complex is considered to be six, since all of the single μ-oxo dinuclear vanadium(III) complexes with a polydentate ligand have been known to adopt a hexacoordination.[5] The bppdda ligand in $[V^{III}_2(\mu\text{-}O)(bppdda)_2]$ is, thus, supposed to function as a pentadentate ligand.

Solution Properties. The coordination geometry of vanadium(III) complexes changes flexibly depending on the structure of the ligand, as mentioned above. The different coordination geometries would result in the different behavior of the complex in solution. Thus, it should be of interest to examine the solution properties of the present complexes.

The absorption spectrum of $Cs[V^{III}(tmdta)]$ in aqueous solution is compared with the diffuse reflectance spectrum of the complex in the solid state in Fig. 4. Both spectra correspond well with each other, indicating that the structure found in the solid state is maintained in an aqueous solution.

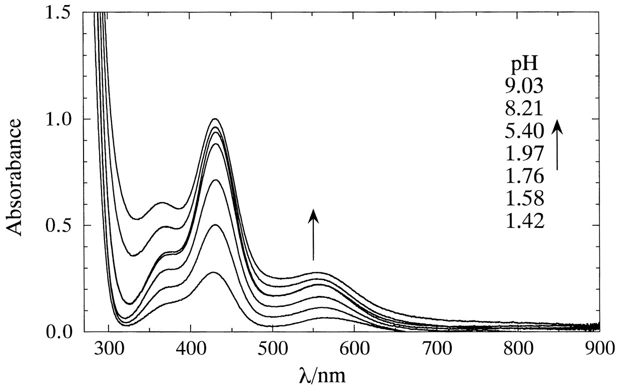


Fig. 5. The pH dependence of the absorption spectrum of $Cs[V^{III}(tmdta)]\cdot H_2O$ (10 mmol/dm^3).

It has been known that the heptacoordinate vanadium(III)–edta complex, $[V^{III}(edta)(H_2O)]^-$, and the hexacoordinate trdta complex, $[V^{III}(trdta)]^-$, exhibit different hydrolytic behaviors.[5] Namely, the edta complex yields a simple hydroxo complex, $[V^{III}(edta)(OH)]^{2-}$, on base hydrolysis, while the base hydrolysis of the trdta complex results in the formation of an oxo-bridged dinuclear complex, $[V_2(\mu\text{-}O)(trdta)_2]^{4-}$, in which trdta coordinates as a pentadentate ligand. It is, therefore, of interest to examine the hydrolytic behavior of $[V^{III}(tmdta)]^-$. Figure 5 shows the pH dependence of the absorption spectrum of $Cs[V^{III}(tmdta)]$. The pH of the 0.5 mmol/dm^3 solution of $Cs[V^{III}(tmdta)]$ was 5.40. The absorbance in the visible region slightly decreased by the addition of an acid down to pH 2, and rapidly decreased below pH 2. A partial release of the coordinated tmdta ligand by acid hydrolysis is likely to have occurred below pH 2. The band intensities were restored by returning the solution pH to neutral.

In a previous paper, we discussed how hexacoordinate vanadium(III) complexes with an aminopolycarboxylate ligand yield a μ-oxo dinuclear vanadium(III) complex on base hydrolysis, while heptacoordinate ones do not.[5] Contrary to a prediction based on the above finding, a very intense CT band due to V(III)–O–V(III) moiety around 460 nm, which is diagnostic to the formation of an oxo-bridged dinuclear vanadium(III) complex, was not observed, even at pH 9, though the absorbance in the 300–400 nm region increased with increasing the pH. This observation indicates that the present tmdta complex did not yield a μ-oxo dinuclear vanadium(III) complex on base hydrolysis. The increase in the absorbance in the 300–400 nm region is indicative of the formation of a hydroxo species, such as $[V^{III}(OH)(tmdta)]^{2-}$, in which tmdta coordinates as a quinquedentate fashion, since the similar spectral change observed for $[V^{III}(nta)(H_2O)_3]$ has been attributed to the formation of $[V^{III}(nta)(OH)_n(H_2O)_{3-n}]^{n-}$.[5] Above pH 9, a precipitate, which may be due to a formation of the insoluble vanadium(III) hydroxide, appeared. The above observations indicate that $[V^{III}(tmdta)]^-$ is moderately stable in solution.

Bpedda and bppdda have structures intermediate between edta and tpen, and trdta and tptn, respectively. It is therefore of interest to examine whether the bpedda/bppdda ligand set behaves as the edta/trdta ligand set or the tpen/tptn ligand set.

The absorption spectrum of $[V^{III}(bpedda)(H_2O)]ClO_4$ in aqueous solution is compared with the diffuse reflectance spectrum in the solid state in Fig. 6. Both spectral features correspond well with each other, indicating that the solid state structure is also kept in the solution. The band at 730 nm is diagnostic to the heptacoordination of the vanadium(III) complex.[4,5] Figure 7 shows the pH dependence of the absorption spectrum of the bpedda complex. The spectral change was reversible. The spectral feature scarcely changed from pH 1.8 to 5.2. Above pH 5.2, the intensities of the bands at 730 and 427 nm decreased, while those of the bands at 638 and 465 nm increased with increasing pH of the solution. The isosbestic

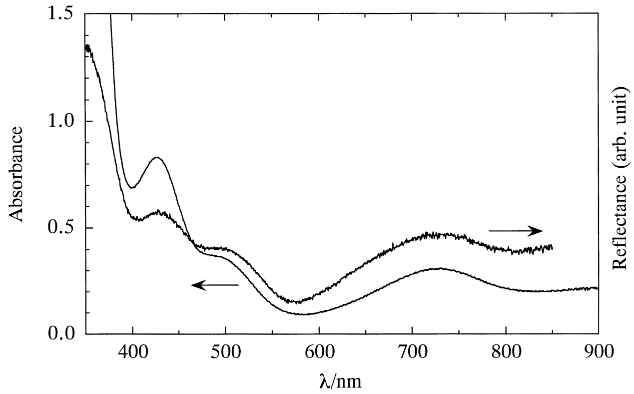


Fig. 6. The absorption (30 mmol/dm^3) and diffuse reflectance spectra of [V(III)(bpedda)(H_2O)].

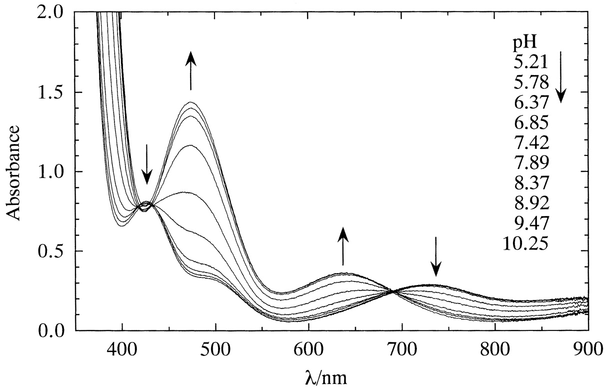


Fig. 7. The pH dependence of the absorption spectrum of [V^{III}(bpedda)(H_2O)] (30 mmol/dm^3).

points were observed at 693, 434, and 418 nm. The observed spectral change is similar to that for [V^{III}(edta)(H_2O)]$^-$,[5] indicating the acid dissociation equilibrium of the aqua ligand:

$$[\mathrm{V^{III}(bpedda)(H_2O)}]^- \rightleftarrows [\mathrm{V^{III}(OH)(bpedda)}]^{2-} + \mathrm{H^+}$$

When trdta was employed instead of edta as a chelating agent for the vanadium(III) complex, the hexacoordinate vanadium(III) complex, [V^{III}(trdta)]$^-$, was obtained.[4] This complex yields a μ-oxo dimer in an alkaline solution.[5] Similarly to trdta, bppdda yielded the μ-oxo dimer in an alkaline solution, which was successfully isolated as fine crystals. The corresponding monomer could not be isolated in this case due to its high solubility. It can thus be concluded that the vanadium(III) complexes with bpedda and bppdda show a behavior in solution similar to those with edta and trdta.

References

1 H. Michibata and K. Kanamori, in "Vanadium in the Environment, Vol. 30, Part 1, Chemistry and Biochemistry," ed by J. O. Nriagu, John Wiley & Sons, New York, (1998), Chapt. 10, pp. 217–249.

2 T. Ishii, I. Nakai, and K. Okoshi, in "Metal Ions in Biological Systems, Vol. 31, Vanadium and its Role in Life," ed by H. Sigel and A. Sigel, Marcel Dekker, New York, (1995), Chapt. 14.

3 a) M. Shimoi, Y. Saito, and H. Ogino, *Chem. Lett.*, **1989**, 1675. b) M. Shimoi, Y. Saito, and H. Ogino, *Bull. Chem. Soc. Jpn.*, **64**, 2629 (1991).

4 J. C. Robles, Y. Matsuzaka, S. Inomata, M. Shimoi, W. Mori, and H. Ogino, *Inorg. Chem.*, **32**, 13 (1993).

5 K. Kanamori, K. Ino, H. Maeda, K. Miyazaki, M. Fukagawa, J. Kumada, T. Eguchi, and K. Okamoto, *Inorg. Chem.*, **33**, 5547 (1994).

6 K. Kanamori, J. Kumada, M. Yamamoto, T. Okayasu, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **68**, 3445 (1995).

7 K. Kanamori, E. Kameda, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **69**, 2901 (1996).

8 K. Kanamori, E. Kameda, T. Kabetani, T. Suemoto, K. Okamoto, and S. Kaizaki, *Bull. Chem. Soc. Jpn.*, **68**, 2581 (1995).

9 H. Ogino, S. Kobayashi, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **43**, 97 (1970).

10 H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5021 (1960).

11 H. Toftlund and S. Yde-Andersen, *Acta Chem. Scand.*, **35**, 575 (1981).

12 H. Ogino, J.-J. Chung, and N. Tanaka, *Inorg. Nucl. Chem. Lett.*, **7**, 125 (1971).

13 G. M. Sheldrick, "SHELXS-97 and SHELXL-97. Program for refinement of crystal structures," University of Göttingen, Göttingen, Germany (1997).

14 Molecular Structure Corporation, "teXan. Single Crystal Structure Analysis Software. Version 1.7. MSC, 3200 Research Forest Drive," The Woodlands, TX 77381, USA (1995).

15 R. D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).

16 M. Shimoi, Y. Fujinawa, H. Ogino, K. Kanamori, and K. Kawai, *Bull. Chem. Soc. Jpn.*, **61**, 3491 (1988).

17 J. C. Robles, M. Shimoi, and H. Ogino, *Chem. Lett.*, **1992**, 309.

18 K. Kanamori, K. Yamamoto, T. Okayasu, M. Matsui, K. Okamoto, and W. Mori, *Bull. Chem. Soc. Jpn.*, **70**, 3031 (1997).

19 K. Okamoto, J. Hidaka, M. Fukagawa, and K. Kanamori, *Acta Crystallogr.*, **C48**, 1025 (1992).

20 M. Shimoi, S. Miyamoto, and H. Ogino, *Bull. Chem. Soc. Jpn.*, **64**, 2549 (1991).

21 H. Ogino, M. Shimoi, and Y. Saito, *Inorg. Chem.*, **28**, 3596 (1989).