Inorg. Chem. **1993,** *32,* 13–17

Syntheses and Structures of Vanadium(III) Complexes Containing 1,3-Diaminopropane-*N,N,N′,N′*-tetraacetate ($[V(trdta)]^-$) and 1,3-Diamino-2-propanol-*N,N,N′,N′*-tetraacetate ($[V_2(dpot)_2]^{2-}$)

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Received April 24, 1992

Vanadium(III) complexes with trdta, $Na[V(trdta)]\cdot 3H_2O$ and $K[V(trdta)]\cdot 4H_2O$, were synthesized by the reaction of vanadium(III) chloride with sodium and potassium salts of trdta, respectively, where trdta denotes 1,3-diaminopropane-*N,N,N′,N′*-tetraacetate. Crystal structure analysis of $Na[V(trdta)]\cdot 3H_2O$ showed that the complex contains a hexadentate trdta ligand and adopts a distorted octahedral geometry. This is the first example of a six-coordinate vanadium(III) complex containing a diamino polycarboxylate. Vanadium(III) complexes with dpot, $Na_2[V_2(dpot)_2]\cdot 5H_2O$, $K_2[V_2(dpot)_2]\cdot 7H_2O$, and $(NH_4)_2[V_2(dpot)_2]\cdot 7H_2O$, were synthesized by the reactions of vanadium(III) chloride with sodium, potassium, and ammonium salts of dpot, respectively, where dpot denotes 1,3-diamino-2-propanol-*N,N,N′,N′*-tetraacetate. An X-ray structural analysis of a single crystal of $K_2[V_2(dpot)_2]\cdot 7H_2O$ revealed that within the complex each vanadium atom assumes a novel seven-coordinate pentagonal-bipyramidal state. The dpot ion contains a deprotonated alkoxy group, which bridges two vanadium atoms, and a pendant carboxylic acid group. Both complex ions, $[V(trdta)]^-$ and $[V_2(dpot)_2]^{2-}$, exhibit thermochromism. Crystals of $Na[V(trdta)]\cdot 3H_2O$ ($C_{11}H_{20}N_2NaO_{11}V$) belong to the orthorhombic space group $P2_12_12_1$ with $a = 11.472$ (2) Å, $b = 16.561$ (3) Å, $c = 8.933$ (1) Å, $V = 1713.0$ (7) Å^3, $Z = 4$, and $R(F_o) = 0.049$ for 4246 reflections with $|F_o| \geq 3\sigma(F_o)$; those of $K_2[V_2(dpot)_2]\cdot 7H_2O$ ($C_{22}H_{42}K_2N_4O_{25}V_2$) belong to the monoclinic space group $P2_1/a$ with $a = 15.573$ (2) Å, $b = 12.601$ (2) Å, $c = 9.234$ (2) Å, $\beta = 96.98$ (2)°, $V = 1798.6$ (6) Å^3, $Z = 2$, and $R(F_o) = 0.066$ for 2684 reflections with $|F_o| \geq 3\sigma(F_o)$.

Introduction

Shepherd et al. reported that the vanadium(III) ions of the complex $[V_2(hedtra\text{-}H)_2]^{2-}$ [2] adopt seven-coordination.[3] Recently, we also reported that vanadium(III) forms seven-coordinate complexes with various diamino polycarboxylates. Thus, in the complexes $[V(edta)(H_2O)]^-$ [4] and $[V(cydta)(H_2O)]^-$,[5] edta and cydta act as hexadentate ligands, with the seventh coordination site of each complex being occupied by one molecule of water to form a capped trigonal prism. The complex $[V(hedtra)(H_2O)]$ also adopts a capped trigonal-prismatic structure, with the *N*-hydroxyethyl group and aqua ligand coordinating to the vanadium atom.[6] These results suggest (i) that diamino polycarboxylates, which may only form five-membered chelate rings, are not sufficiently large to enclose the vanadium(III) ion and (ii) that the vanadium(III) ion has a strong affinity for the hydroxy or deprotonated alkoxy group.

Herein the synthesis of vanadium(III) complexes containing trdta and dpot ligands is described. The trdta ligand, a derivative of edta in which the ethylenediamine moiety is replaced by 1,3-propanediamine, is expected to enclose the vanadium(III) ion more easily than does edta as a result of its enlarged diamine moiety. An X-ray crystal structural analysis was performed to determine whether the vanadium complex with the trdta ligand adopts a six- or seven-coordinate structure. The dpot ligand has the same framework as that of trdta but with the additional presence of a hydroxy group at the central carbon of the 1,3-propanediamine moiety. A crystal structural analysis was performed to determine whether the hydroxy group participates in coordination to the central metal ion. Coordination of either the hydroxy or the deprotonated alkoxy group to the vanadium(III) ion may lead to the formation of a complex with a structure quite different from those of the vanadium(III) complexes with edta or edta-like ligands.[3-6] In a preliminary communication the structure of the vanadium(III)–dpot complex was described.[7]

Experimental Section

Materials. H_4trdta was prepared in accordance with the literature methods.[8] H_4dpot (Tokyo Kasei Kogyo Co.) and vanadium(III) chloride were obtained commercially and used as received. All reactions were carried out under a nitrogen atmosphere.

Measurements. The infrared spectra were obtained using a JASCO IR-810 infrared spectrophotometer. The electronic spectra were recorded using a Shimadzu UV-260 spectrophotometer. Powder X-ray diffraction was measured using a Rigaku Geigerflex-2013 diffractometer. Magnetic susceptibility was measured by the SQUID method using a Quantum Design Magnetic Property Measurement System.

Preparation of $Na[V(trdta)]\cdot 3H_2O$. A suspension of H_4trdta (3.1 g, 10 mmol) in water (15 mL) was neutralized with 2.1 g (20 mmol) of Na_2CO_3. To this solution was added 1.6 g (10 mmol) of VCl_3 and the mixture stirred at room temperature for 30 min. The red precipitate that formed was isolated by filtration, washed successively with water, ethanol, and ether, and then allowed to dry in air. Yield: 54%. The red crystal

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(2) Abbreviations: $edta^{4-}$, ethylenediamine-*N,N,N′,N′*-tetraacetate; $hedtra^{3-}$, *N′*-(2-hydroxyethyl)ethylenediamine-*N,N,N′*-triacetate; hedtra-H^{4-}, deprotonated form of $hedtra^{3-}$; $cydta^{4-}$, *trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate; $dpot^{4-}$, 1,3-diamino-2-propanol-*N,N,N′,N′*-tetraacetate.

(3) Shepherd, R. E.; Hatfield, W. E.; Ghosh, D.; Stout, C. D.; Kristine, F. J.; Ruble, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 5511–5517.

(4) (a) Shimoi, M.; Saito, Y.; Ogino, H. *Chem. Lett.* **1989**, 1675–1678. (b) Shimoi, M.; Saito, Y.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2629–2634.

(5) Shimoi, M.; Miyamoto, S.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2549–2550.

(6) Ogino, H.; Shimoi, M.; Saito, Y. *Inorg. Chem.* **1989**, *28*, 3596–3600.

(7) Robles, J. C.; Shimoi, M.; Ogino, H. *Chem. Lett.* **1992**, 309–310.

(8) (a) Tanaka, N.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 877–879. (b) Ogino, H.; Takahashi, M.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 424–428. (c) Weyh, J. A.; Hamm, R. E. *Inorg. Chem.* **1968**, *7*, 2431–2435.

0020-1669/93/1332-0013$04.00/0

Table I. Crystallographic Data for Na[V(trdta)]·3H_2O and $K_2[V_2(dpot)_2]$·7H_2O

chem formula	$C_{11}H_{20}N_2NaO_{11}V$	$C_{22}H_{42}K_2N_4O_{25}V$
a, Å	11.472 (2)	15.573 (2)
b, Å	16.561 (3)	12.601 (2)
c, Å	8.933 (1)	9.234 (2)
β, deg		96.98 (2)
V, Å^3	1713.0 (7)	1798.6 (6)
Z	4	2
fw	430.22	942.66
space group	$P2_12_12_1$ (No. 19)	$P2_1/a$ (variant of No. 14)
T, °C	20	21
λ, Å	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	1.69	1.73
ρ_{calcd}, g cm^{-3}	1.68	1.74
μ(Mo Kα), cm^{-1}	5.94	9.01
R^a	0.049	0.066
$R_w{}^b$	0.047	0.095

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + aF_o{}^2]^{-1}$, where a = 0.0013 for Na[V(trdta)]·3H_2O and a = 0.003 for $K_2[V_2(dpot)_2]$·7H_2O.

for the X-ray crystal analysis was obtained by layering THF on an aqueous solution of the complex. Anal. Calcd for $C_{11}H_{20}N_2NaO_{11}V$: C, 30.71; H, 4.69; N, 6.51. Found: C, 30.56; H, 4.55; N, 6.47.

Preparation of K[V(trdta)]·4H_2O. The potassium salt was prepared in accordance with the procedure described for Na[V(trdta)]·3H_2O but using K_2CO_3 instead of Na_2CO_3. Stirring for 30 min afforded a pale green solid, which was isolated by filtration, washed successively with water, ethanol, and ether, and allowed to dry in air. Yield: 43%. Anal. Calcd for $C_{11}H_{22}KN_2O_{12}V$: C, 28.45; H, 4.78; N, 6.03. Found: C, 28.42; H, 4.70; N, 6.01.

Preparation of $K_2[V_2(dpot)_2]$·7H_2O. A suspension of H_4dpot (3.2 g, 10 mmol) in water (25 mL) was neutralized with K_2CO_3 (2.8 g, 20 mmol). To this solution was added VCl_3 (1.6 g, 10 mmol) and the mixture stirred for 30 min. The color of the mixture gradually changed from dark gray to chocolate brown. Evaporation of water from the solution under reduced pressure afforded a red-orange powder. The powder was washed with acetone and allowed to dry in air. Recrystallization of the complex was accomplished by dissolving the complex in water at 80 °C, heated using a water bath, followed by slow cooling to room temperature. The recrystallized complex was dark red-orange. Yield: 74%. Anal. Calcd for $C_{22}H_{42}K_2N_4O_{25}V_2$: C, 28.03; H, 4.50; N, 5.94. Found: C, 28.08; H, 4.49; N, 5.98.

Preparation of $Na_2[V_2(dpot)_2]$·5H_2O. The title compound was prepared by the same procedure as that for $K_2[V_2(dpot)_2]$·7H_2O but using Na_2CO_3 as opposed to K_2CO_3. Yield: 84%. Anal. Calcd for $C_{22}H_{38}N_4Na_2O_{23}V_2$: C, 30.21; H, 4.39; N, 6.41. Found: C, 29.80; H, 4.36; N, 6.52.

Preparation of $(NH_4)_2[V_2(dpot)_2]$·7H_2O. The title compound was prepared by the same procedure as that used for $K_2[V_2(dpot)_2]$·7H_2O but using $(NH_4)_2CO_3$ as opposed to K_2CO_3. Yield: 37%. Anal. Calcd for $C_{22}H_{50}K_2N_6O_{25}V_2$: C, 29.34; H, 5.61; N, 9.33. Found: C, 29.40; H, 5.20; N, 9.14.

X-ray Crystal Structural Determinations of K[V(trdta)]·3H_2O and $K_2[V_2(dpot)_2]$·7H_2O. Diffraction data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystallographic data for the complexes are listed in Table I. The reflection data were corrected for Lorentz and polarization factors. No correction was applied for absorption or extinction. Structures were solved using heavy-atom methods and parameters refined by block-diagonal least-squares methods. Anisotropic temperature factors were applied for the non-hydrogen atoms. One water molecule of the complex $K_2[V_2(dpot)_2]$·7H_2O was found at an inversion center. Thus the molecule was considered to be disordered about that position, at which the oxygen atom was then fixed. Hydrogen atom coordinates, excluding those of the water molecules, of Na[V(trdta)]·3H_2O were deduced from difference Fourier maps and refined using isotropic temperature factors. Those of $K_2[V_2(dpot)_2]$·7H_2O were calculated and fixed at those positions. The inverse chirality of Na[V(trdta)]·3H_2O afforded a larger *R* value (0.054) than that for the adopted chirality. For non-hydrogen and hydrogen atoms, values for the atomic scattering factors were those in refs 9 and 10, respectively. 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.[11]

Table II. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for Na[V(trdta)]·3H_2O

atom	*x*	*y*	*z*	B_{eqv},^{a} Å^2
V	1330.3 (3)	2455.3 (2)	2350.7 (4)	1.4
Na	4428 (1)	4868 (1)	1502 (1)	2.6
O(1)	2285 (2)	1639 (1)	3480 (2)	2.4
O(2)	2169 (3)	614 (2)	5066 (3)	5.0
O(3)	1414 (2)	3286 (1)	3914 (2)	2.3
O(4)	957 (2)	3669 (1)	6234 (2)	3.0
O(5)	864 (2)	1674 (1)	830 (2)	2.3
O(6)	335 (2)	1508 (1)	−1550 (2)	2.9
O(7)	2530 (2)	3035 (1)	1162 (2)	2.1
O(8)	2904 (2)	4175 (1)	−53 (3)	2.8
N(1)	−2 (2)	2024 (1)	3834 (2)	1.8
N(2)	226 (2)	3208 (1)	1016 (2)	1.6
C(1)	388 (3)	1196 (2)	4219 (4)	2.6
C(2)	1707 (3)	1140 (2)	4301 (3)	2.6
C(3)	−58 (2)	2538 (2)	5187 (3)	2.6
C(4)	828 (2)	3221 (1)	5156 (3)	2.0
C(5)	19 (2)	2798 (2)	−436 (3)	2.2
C(6)	428 (2)	1928 (1)	−442 (3)	1.9
C(7)	945 (2)	3947 (1)	785 (3)	2.0
C(8)	2221 (2)	3717 (1)	586 (3)	1.9
C(9)	−1155 (2)	1967 (2)	3032 (3)	2.8
C(10)	−1642 (2)	2735 (2)	2366 (4)	3.3
C(11)	−862 (3)	3428 (2)	1843 (3)	2.6
O(W1)	599 (2)	−15 (1)	738 (3)	3.2
O(W2)	4056 (2)	424 (1)	1973 (3)	3.3
O(W3)	3153 (2)	4543 (1)	3471 (3)	3.5

[a] The equivalent isotropic temperature factors for non-hydrogen atoms were computed by using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Table III. Interatomic Distances (Å) and Angles (deg) for Na[V(trdta)]·3H_2O

	Distances		
V–O(1)	2.011 (2)	V–O(3)	1.963 (2)
V–O(5)	1.951 (2)	V–O(7)	1.986 (2)
V–N(1)	2.145 (2)	V–N(2)	2.141 (2)
	Angles		
O(1)–V–O(3)	95.09 (9)	O(1)–V–O(5)	92.96 (9)
O(1)–V–O(7)	102.44 (8)	O(1)–V–N(1)	81.63 (9)
O(1)–V–N(2)	173.33 (8)	O(3)–V–O(5)	166.87 (9)
O(3)–V–O(7)	90.44 (8)	O(3)–V–N(1)	80.17 (8)
O(3)–V–N(2)	90.95 (8)	O(5)–V–O(7)	97.94 (8)
O(5)–V–N(1)	90.79 (8)	O(5)–V–N(2)	80.59 (8)
O(7)–V–N(1)	173.33 (8)	O(7)–V–N(2)	80.29 (8)
N(1)–V–N(2)	96.67 (8)		

Results and Discussion

Crystal Structure of Na[V(trdta)]·3H_2O. Tables II and III show the final atomic parameters and interatomic distances and angles, respectively. Figure 1 shows an ORTEP drawing of the complex anion. The trdta functions as a hexadentate ligand such that the geometry around the vanadium atom is that of a distorted octahedron. This is the first example of a six-coordinate vanadium(III) complex containing a diamino polycarboxylate. Its structure is in contrast to those of other vanadium(III) complexes containing edta-like ligands in that these usually adopt capped trigonal-prismatic structures.[4-7] Although the angle N(1)–V–N(2) (96.67 (3)°) is larger than 90° expected for a regular octahedron, four N–V–O angles of five-membered chelate rings are much less than 90°, ranging between 80.17 (8) and 81.63 (9)°. As a result, the O(3)–V–O(5) angle (193.13 (9)°) and O(1)–V–O(7) angle (102.44 (8)°) also show significant

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(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72–98, and Table 2.3.1, pp 149–150.

(10) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(11) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyuusho Houkoku* **1979**, *55*, 69–77.

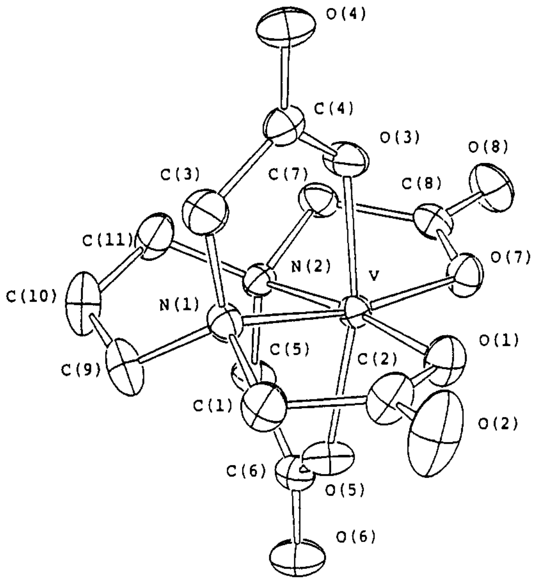

Figure 1. ORTEP diagram of the $[V(trdta)]^-$ anion.

Table IV. Comparison of Bond Angles for $[M^{III}(trdta)]^-$ Complexes

		angle, deg		
M(III)	$r_{M^{3+}}$,[a] Å	N(1)–M–N(2)	O(3)–M–O(5)	O(1)–M–O(7)
Co(III)[b]	0.685	99.0 (3)	179.6 (3)	92.6 (3)
Cr(III)[c]	0.765	95.8 (2)	184.3 (2)	99.7 (2)
V(III)[d]	0.780	96.67 (3)	193.13 (9)	102.44 (8)
Fe(III)[e]	0.785	94.3 (1)	184.6 (1)	112.5 (1)
Rh(III)[c]	0.805	98.3 (1)	180.3 (1)	97.6 (1)

[a] Reference 15. [b] Reference 12. [c] Reference 14. [d] This work. [e] Reference 13.

deviations from those of the regular octahedron. This suggests that the trdta ligand is still not of sufficient size to comfortably enclose the vanadium(III) ion. Consequently, a large coordination site exists on one side of the diamine chelate ring, which may be used to accommodate an additional ligand. The average V–O and V–N distances (1.978 and 2.143 Å) are shorter than the corresponding distances for seven-coordinate vanadium(III) complexes (2.054–2.061 and 2.222–2.246 Å)[4–6] in accordance with the difference of coordination numbers.

The structures of transition metal(III) complexes of trdta were reported for $K[Co(trdta)]\cdot 2H_2O$,[12] $Li[Fe(trdta)]\cdot 3H_2O$,[13] $Na[Cr(trdta)]\cdot 3H_2O$,[14] and $Na[Rh(trdta)]\cdot 3H_2O$,[14] the latter two of which are isomorphous with $Na[V(trdta)]\cdot 3H_2O$. The symmetry about Co(III) is that of an almost regular octahedron but with an expanded N–Co–N angle (99.0 (3)°). The other metals, however, attain octahedral symmetry with varying degrees of distortion, reflecting their large ionic radii, as indicated in Table IV. It should be noted that Rh(III), which has a larger ionic radius than both Fe(III) and V(III), attains higher octahedral symmetry than either of these metal ions. This may be a result of the low-spin d^6 configuration of the Rh(III) ion. It is of interest to note that the patterns of deviation from regular octahedral symmetry are quite different between the vanadium(III) and iron(III) complexes. Namely, the O(3)–V–O(5) angle of the vanadium(III) complex deviates from the octahedral angle to a greater extent than does the corresponding angle of the iron complex, and vice versa for the O(1)–V–O(7) angle.

Table V. Final Atomic Coordinates (×10⁴) and Equivalent Isotropic Temperature Factors for $K_2[V_2(dpot)_2]\cdot 7H_2O$

atom	*x*	*y*	*z*	B_{eqv},[a] Å²
K	4785 (1)	1059 (2)	7840 (3)	6.6
V	4054.7 (5)	4452.4 (7)	4344.1 (9)	1.5
O(1)	4629 (2)	5637 (3)	5592 (4)	1.9
O(2)	4116 (3)	3309 (3)	5862 (4)	2.3
O(3)	3441 (4)	2467 (4)	7501 (6)	4.1
O(4)	2834 (2)	3953 (3)	3412 (4)	2.7
O(5)	1438 (3)	4337 (5)	2804 (6)	4.1
O(6)	6047 (3)	4583 (3)	7443 (4)	2.3
O(7)	6410 (4)	4496 (4)	9833 (5)	4.3
O(8)	5628 (3)	8536 (4)	9444 (5)	3.7
O(9)	6489 (3)	9454 (3)	8182 (5)	3.5
N(1)	3036 (3)	5043 (3)	5748 (5)	1.7
N(2)	5705 (3)	6734 (3)	7493 (5)	1.5
C(1)	3346 (3)	6021 (4)	6550 (6)	1.9
C(2)	4306 (3)	5894 (4)	6928 (5)	1.8
C(3)	4757 (3)	6914 (4)	7459 (6)	2.0
C(4)	2899 (4)	4155 (4)	6749 (6)	2.2
C(5)	3524 (4)	3240 (4)	6714 (6)	2.2
C(6)	2231 (3)	5279 (5)	4775 (6)	2.3
C(7)	2137 (4)	4447 (5)	3567 (6)	2.6
C(8)	6059 (4)	6198 (4)	8867 (6)	2.3
C(9)	6171 (4)	5000 (5)	8698 (6)	2.5
C(10)	6149 (3)	7755 (4).	7309 (6)	2.1
C(11)	6047 (3)	8612 (4)	8440 (6)	2.1
O(W1)	6299 (3)	1039 (4)	9894 (5)	3.6
O(W2)	2240 (4)	2257 (4)	9413 (7)	4.5
O(W3)	937 (4)	2674 (5)	6455 (8)	5.9
O(W4)	5000	0	5000	13.6

[a] The equivalent isotropic temperature factors for non-hydrogen atoms were computed by using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$. The B_{ij}'s are defined by $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Table VI. Interatomic Distances (Å) and Angles (deg) for $K_2[V_2(dpot)_2]\cdot 7H_2O$[a]

	Distances		
V–O(1)	2.027 (4)	V–O(1ⁱ)	2.046 (4)
V–O(2)	2.004 (4)	V–O(4)	2.086 (4)
V–O(6ⁱ)	2.040 (4)	V–N(1)	2.292 (5)
V–N(2ⁱ)	2.326 (4)	V···Vⁱ	3.343 (2)
O···O(1ⁱ)	2.327 (7)		
	Angles		
O(1)–V–O(1ⁱ)	69.7 (1)	O(1)–V–N(1)	74.2 (2)
N(1)–V–O(4)	70.9 (2)	O(4)–V–N(2ⁱ)	74.2 (2)
N(2ⁱ)–V–O(1ⁱ)	74.7 (1)	O(2)–V–O(1)	98.7 (2)
O(2)–V–N(1)	79.3 (2)	O(2)–V–O(4)	92.0 (2)
O(2)–V–N(2ⁱ)	82.5 (2)	O(2)–V–O(1ⁱ)	88.8 (2)
O(6ⁱ)–V–O(1)	90.4 (2)	O(6ⁱ)–V–N(1)	105.9 (2)
O(6ⁱ)–V–O(4)	82.5 (2)	O(6ⁱ)–V–N(2ⁱ)	78.3 (2)
O(6ⁱ)–V–O(1ⁱ)	92.0 (1)	O(2)–V–O(6ⁱ)	170.5 (2)

[a] Key to the symmetry operation: (i) $1 - x$, $1 - y$, $1 - z$.

The conformation of the trimethylenediamine chelate ring is that of a skew-boat. The two in-plane acetate rings are more strained than the out-of-plane acetate rings, as is evident from their respective planarities: The maximum deviations from the least-squares planes of the former rings are 0.21 and 0.29 Å whereas those of the latter rings are 0.12 and 0.16 Å. This phenomenon is common among octahedral edta complexes.[16,17]

Crystal Structure of $K_2[V_2(dpot)_2]\cdot 7H_2O$. Tables V and VI show the final atomic coordinates and interatomic distances and angles. Figure 2 shows an ORTEP diagram of the complex anion. Crystal structural analysis revealed that the complex is dimeric and contains a center of inversion at the midpoint between the two vanadium atoms. No water molecules are coordinated to the vanadium center. The dpot ligand acts as a heptadentate ligand, with the deprotonated alkoxy group bridging two vanadium atoms

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(12) Nagao, R.; Marumo, R.; Saito, Y. *Acta Crystallogr.* **1972**, *B28*, 1852–1856.

(13) Yamamoto, T.; Mikata, K.; Miyoshi, K.; Yoneda, H. *Inorg. Chim. Acta* **1988**, *150*, 237–244.

(14) Herak, G.; Srdanov, G.; Djuran, M. I.; Radanovic, D. J.; Bruvo, M. *Inorg. Chim. Acta* **1984**, *83*, 55–64.

(15) (a) Shannon, R. D.; Prewitt, C. T. Kb *Acta Crystallogr.* **1969**, *B25*, 925–946. (b) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–771.

(16) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549–555.

(17) Radanovic, D. J. *Coord. Chem. Rev.* **1984**, *54*, 159–261.

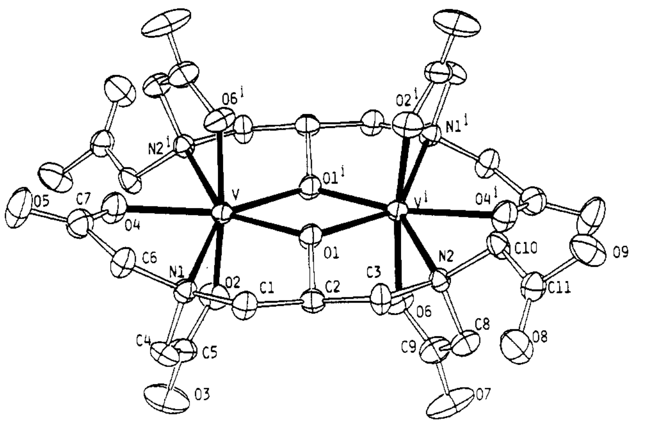

Figure 2. ORTEP diagram of the $[V_2(dpot)_2]^{2-}$ anion.

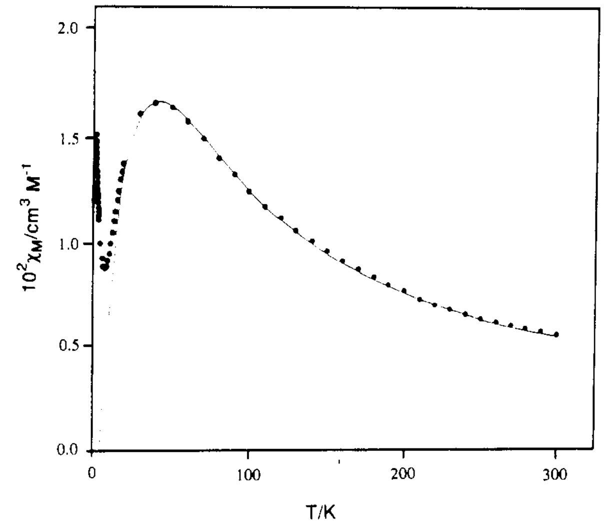

Figure 3. Temperature dependence of the magnetic susceptibility of $K_2[V_2(dpot)_2]\cdot7H_2O$.

Table VII. Electronic Absorption Spectral Data for Vanadium(III) Complexes with edta or edta-like Ligands

complex	abs max,[a] nm (ϵ, $M^{-1}\ cm^{-1}$)		
$[V(edta)(H_2O)]^-$	447 (28.7)	510 (11.3) sh	804 (10.2)
$[V(cydta)(H_2O)]^-$	447 (27.2)	510 (10.4) sh	822 (9.7)
$[V(hedtra)(H_2O)]$[b]	454 (19.4)	530 (10.3)	755 (9.2)
$[V(trdta)]^-$ [c]	365 (26.5)	438 (44.0)	554 (21.6)
$[V_2(dpot)_2]^{2-}$ [c]	420 (48.2) sh	530 (28.6)	840 (16.9)

[a] sh = shoulder. [b] Reference 6. [c] At 20 °C.

and one carboxylic acid group remaining uninvolved in coordination to the vanadium atoms. The difference between the bond distances of C(11)–O(8) and C(11)–O(9) (1.200 (8) vs 1.303 (7) Å) clearly shows that O(9) is protonated. The IR spectrum offers further evidence for the presence of a free carboxylic acid group and coordinated carboxylate as shown by the ν_{CO} absorption bands exhibited at 1720 and 1630 cm^{-1}, respectively. The large interatomic separation distance between the two vanadium atoms (3.343 (2) Å) indicates the absence of a V–V bond. Two dpot ligands surround two vanadium atoms affording distorted pentagonal-bipyramidal symmetry about each vanadium atom. The atoms lying along the equatorial plane are O(1), O(1^i), O(4), N(1), and N(2^i), where the superscript i denotes the symmetry operation $1 - x$, $1 - y$, $1 - z$. Among these atoms, the largest deviations from the least-squares plane are only 0.28 and –0.38 Å for N(1) and O(1), respectively. The sum of in-plane angles exceeds 360° by only 3.7°. This also shows the high planarity of these five atoms. The axial atoms are O(2) and O(6^i), and the bond angle O(2)–V–O(6^i) is 170.5°. Thus the geometry around the vanadium(III) ion may be well described by a pentagonal bipyramid.

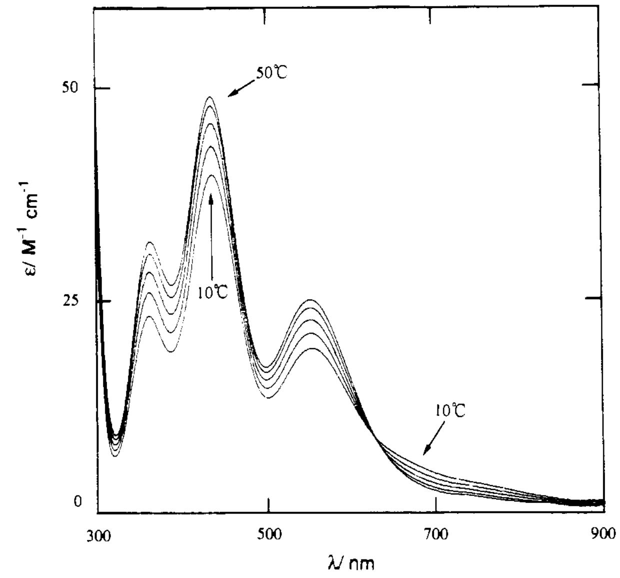

Figure 4. Temperature dependence of electronic spectra of an aqueous solution of $Na[V(trdta)]\cdot3H_2O$.

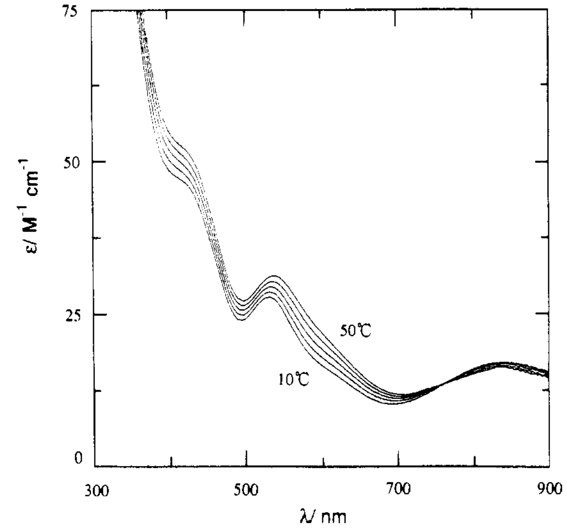

Figure 5. Temperature dependence of electronic spectra of an aqueous solution of $K_2[V_2(dpot)_2]\cdot7H_2O$.

The coordination structures around the vanadium(III) ions in $[V_2(hedtra\text{-}H)_2]^{2-}$ were described as slightly distorted pentagonal bipyramids.[3] However, as indicated in the description of the nonidealized pentagonal bipyramid by the former workers, the sums of the in-plane angles around each vanadium(III) ion are 375.5 and 374.5°, respectively. The sum of the in-plane angles for the dpot complex exceeds 360° only by 3.7°. Rather, the geometries around vanadium(III) ions of $[V_2(hedtra\text{-}H)_2]^{2-}$ resemble the geometry of $[V(edta)(H_2O)]^-$:[4] Each $[V(hedtra\text{-}H)]^-$ moiety adopts a distorted trigonal-prismatic structure with the deprotonated alkoxy oxygen, derived from the other half of the molecule, occupying a cap position, thus forming a capped trigonal prism.

Magnetic Susceptibility of $K_2[V_2(dpot)_2]\cdot7H_2O$. The magnetic susceptibility data for this compound between 1.9 and 300 K are shown in Figure 3. The electronic spin moments of the two vanadium(III) centers are weakly antiferromagnetically coupled. The sharp increase in susceptibility observed at temperatures below 9 K is most likely to be a result of the presence of traces of paramagnetic impurity, perhaps a vanadium(IV) species. The temperature dependence of the magnetic susceptibilities was analyzed on the basis of the spin-Hamiltonian $H = 2JS_1{\cdot}S_2$ ($S_1 = S_2 = 1$). The selected values of the parameters g and J, 1.88 and -14.5 cm^{-1}, respectively, provided the best fit to the experimental data given in Figure 3, as calculated from the following equation:

$$\chi_A = (Ng^2\mu_B^2/kT)[5 + \exp(-4J/kT)][5 + 3\exp(-4J/kT) + \exp(-6J/kT)]^{-1}$$

Electronic Spectra of Vanadium(III) Complexes with edta-like Ligands. Table VII lists the spectral data for vanadium(III) complexes with edta-like ligands. All complexes listed, except that of trdta, give three peaks situated around 450, 530, and 800 nm, the last of which is absent for this complex. This is diagnostic of the presence of a six-coordinate complex, as opposed to a seven-coordinate complex. Although the electronic spectra of the edta, cydta, and hedtra complexes show no temperature dependence, the trdta and dpot complexes exhibit thermochromism. Figure 4 shows the temperature dependence of the electronic spectra of an aqueous solution of $Na[V(trdta)]{\cdot}3H_2O$ between 10 and 50 °C. The spectral change exhibits an isosbestic point at 628 nm. Although there are several causes of thermochromic behavior,[18] a possible explanation in this case is the presence of an equilibrium between the six- and seven-coordinate species:

$$\underset{\text{six-coordinate species}}{[V(trdta)]^-} + H_2O \rightleftarrows \underset{\text{seven-coordinate species}}{[V(trdta)(H_2O)]^-}$$

The existence of the seven-coordinate species containing a water molecule at the seventh coordination site may be rationalized from the findings of the crystal structure analysis, where the complex was found to adopt a distorted octahedral geometry with a possible coordination site at the central vanadium(III) ion, where an extra ligand may be accommodated.

The potassium salt is a pale green powder, quite different in color from the sodium analogue. The potassium salt was found by powder X-ray diffraction analysis to be amorphous such that the possibility of performing a single-crystal structural analysis was excluded. It was thought that the green form of the complex may well be the aquated seven-coordinate complex in a solid form.

The dpot complex was also found to exhibit thermochromism. The spectral change shows an isosbestic point at 760 nm, as shown in Figure 5. Further study is warranted to determine the origin of the thermochromism.

Acknowledgment. The authors thank Professor Yoshitake Kido and Dr. Iwao Mogi (the Institute for Materials Science, Tohoku University) for the measurement of magnetic susceptibility. J.C.R. thanks the Ministry of Education, Science, and Culture of Japan for the award of a Mombusho Student Scholarship and the Japan Society for the Promotion of Science for the award of a JSPS-DOST Exchange Program Scholarship.

Supplementary Material Available: Tables S1–S10, giving full crystallographic and experimental data, hydrogen positional parameters, thermal parameters, interatomic distances, and bond angles for $Na[V(trdta)]{\cdot}3H_2O$ and $K_2[V_2(dpot)_2]{\cdot}7H_2O$ (15 pages). Ordering information is given on any current masthead page.

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[18] Sone, K.; Fukuda, Y. *Inorganic Thermochromism*; Springer-Verlag: Berlin, 1987.