Inorg. Chem. **1994,** *33,* 5547−5554

Relationship between Oxo-Bridged Dimer Formation and Structure of Vanadium(III) Amino Polycarboxylates

Kan Kanamori,[*,†] Kazuhito Ino,[†] Haruyo Maeda,[†] Keisuke Miyazaki,[†] Miharu Fukagawa,[†] Junko Kumada,[†] Taro Eguchi,[‡] and Ken-ichi Okamoto[§]

Departments of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930, Japan, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan, and University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received January 28, 1994[⊗]

The structures of vanadium(III) complexes with several amino polycarboxylates in the solid state as well as in aqueous solution have been investigated using electronic and Raman spectrophotometry and ^{1}H NMR relaxation time. The amino polycarboxylates employed were dtpa (diethylenetriamine-*N,N,N′,N″,N″*-pentaacetate), edta (ethylenediamine-*N,N,N′,N′*-tetraacetate), cydta (1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate), 1,3-pdta (1,3-propanediamine-*N,N,N′,N′*-tetraacetate), *S,S′*-edds (*S,S′*-ethylenediamine-*N,N′*-disuccinate), eddda (ethylenediamine-*N,N′*-diacetate-*N,N′*-di-3-propionate), tcta (1,4,7-triazacyclononane-1,4,7-triacetate), eed3a (*N*-ethylethylenediamine-*N,N′,N′*-triacetate), nta (nitrilotriacetate), and ida (iminodiacetate). The dtpa, tcta, and ida complexes, in addition to the edta, cydta, and nta complexes, the structures of which have been determined earlier, adopt heptacoordination in the solid state. The *S,S′*-edds and eddda complexes adopt hexacoordination as found for the 1,3-pdta complex. In aqueous solution, the hexacoordinate complexes yield the oxo-bridged dinuclear vanadium(III) complexes by hydrolysis, but the heptacoordinate ones do not. The vanadium(III) complex with eed3a, Na$_2$[V(eed3a)(SO$_4$)], is also found to adopt heptacoordination in the solid state, but it changes to the hexacoordinate complex in aqueous solution by releasing the sulfate ion.

Introduction

The interest of chemists in vanadium(III) compounds of biological systems was stimulated by Henze's discovery[1] that certain ascidians or sea squirts accumulate vanadium(III) ion to a great extent in their blood cells. Although many chemists as well as biologists have endeavored to clarify its biological role since then, the physiological function as well as the chemical formula has not yet been determined unequivocally.[2] In order to promote the understanding of the role of vanadium(III) in ascidian blood cells, development of the coordination chemistry of vanadium(III) should be requisite. However, vanadium(III) chemistry has progressed less than have vanadium(IV) and -(V) chemistries. It is of importance to study the properties of fundamental vanadium(III) complexes in solution as well as in the solid state.

Boeri and Ehrenberg observed an intense absorption band around 420 nm that can be due to a dimeric complex of vanadium(III) for the vanadocyte (vanadium-containing blood cell) hemolysate from *Ascidia obliqua*.[3] Recently, Anderson and Swinehart observed a similar intense absorption band for *A. ceratodes*.[4]

It has also been known that the hydrolytic species of aquavanadium(III) exhibits an intense absorption band around 420 nm.[5] A similar visible absorption band was observed for the intermediate of the reaction between vanadium(II) and vanadium(IV)[6] and for the intermediate of the oxidation reaction of vanadium(II).[7] In our previous paper,[8] we determined that this intense absorption band is due to a μ-oxo dimer rather than a bis(hydroxo) dimer. The relevance of the intense visible absorption band to the oxo bridging has been confirmed by the single-crystal X-ray analysis of [V$_2$(L-his)$_4$(O)]·2H$_2$O (L-his = L-histidinate).[9]

The vanadium(III) complex with ttha^{6-} (triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetate)[10] also yields a μ-oxo dinuclear complex on hydrolysis and exhibits a characteristic visible absorption band similar to those observed for the aqua[8] and L-his[9] vanadium(III) complexes, whereas the hydrolytic species of the vanadium(III)−edta complex shows a distinctly different absorption profile.[11] In order to clarify the difference in hydrolytic behavior between the vanadium(III) complexes with ttha and edta, a systematic examination of the solution properties of (amino polycarboxylato)vanadium(III) complexes is necessary.

In this paper, we report the study of the solution structure of several (amino polycarboxylato)vanadium(III) complexes based on electronic and Raman spectrophotometry and the NMR relaxation method. The amino polycarboxylate ligands em-

---

[†] Toyama University.
[‡] Osaka University.
[§] University of Tsukuba

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) Henze, M. *Hoppe-Seyler's Z. Physiol. Chem.* **1911**, *72*, 494.

(2) (a) Michibata, H.; Sakurai, H. In *Vanadium in Biological Systems*; Chasteen, N. D., Ed.; Kluwer: Dordrecht, The Netherlands, **1990**; pp 153−171. (b) Wever, R.; Kustin, K. *Adv. Inorg. Chem.* **1990**, *35*, 81. (c) Butler, A.; Carrano, C. *J. Coord. Chem. Rev.* **1991**, *109*, 61. (d) Michibata, H. *Adv. Biophys.* **1993**, *29*, 105.

(3) Boeri, E.; Ehrenberg, A. *Arch. Biochem. Physiol.* **1954**, *50*, 404.

(4) Anderson, D. H.; Swinehart, J. H. *Comp. Biochem. Physiol.* **1991**, *99A*, 585.

(5) (a) Pajdowski, L. *Rocz. Chem.* **1963**, *37*, 1351. (b) Pajdowski, L. *Rocz. Chem.* **1963**, *37*, 1363. (c) Pajdowski, L. *J. Inorg. Nucl. Chem.* **1966**, *28*, 433. (d) Pajdowski, L.; Jezowska-Trzebiatowska, B. *J. Inorg. Nucl. Chem.* **1966**, *28*, 443.

(6) (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1964**, *3*, 569. (b) Newton, T. W.; Baker, F. B. *J. Phys. Chem.* **1964**, *68*, 2.

(7) Dobson, J. C.; Sano, M.; Taube, H. *Inorg. Chem.* **1991**, *30*, 456.

(8) Kanamori, K.; Ookubo, Y.; Ino, K.; Kawai, K.; Michibata, H. *Inorg. Chem.* **1991**, *30*, 3832.

(9) Kanamori, K.; Teraoka, M.; Maeda, H.; Okamoto, K. *Chem. Lett.* **1993**, 1731.

(10) Myser, T. K.; Shepherd, R. E. *Inorg. Chem.* **1987**, *26*, 1544.

(11) Kristine, F. J.; Shepherd, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 6562.

0020-1669/94/1333-5547$04.50/0

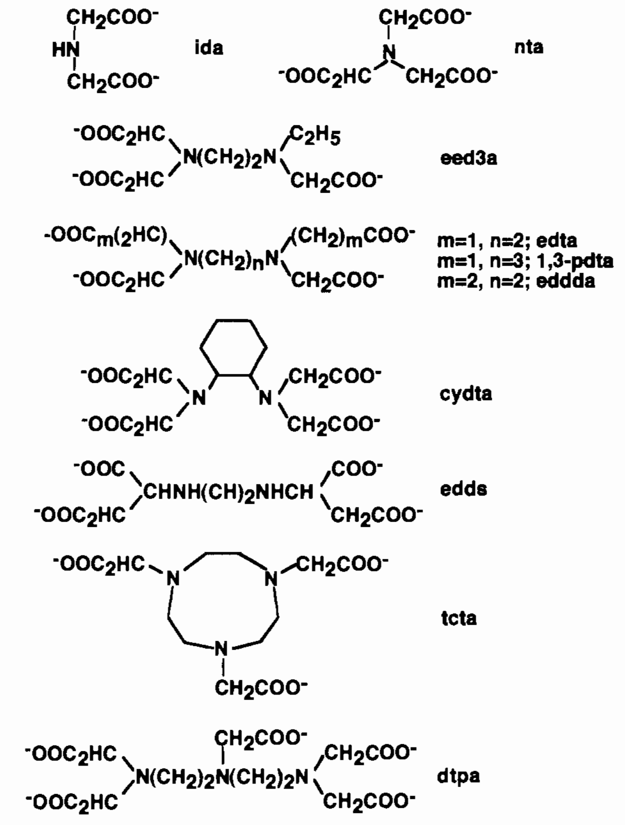

Figure 1. Amino polycarboxylate ligands.

ployed in the present study are illustrated in Figure 1 with their abbreviations.

Experimental Section

Preparation of Ligands. H_4cydta, H_4edta, H_5dtpa, H_2ida, and H_3nta were purchased commercially and used as received. H_3eed3a was prepared from *N*-ethylethylenediamine and monochloroacetic acid according to the ordinary method. Because the free ligand preparation yielded little crystalline product, the reaction solution from which NaCl was removed as much as possible was used for the preparation of the vanadium(III) complex. H_4(*S,S'*-edds),[12] Ba_2(1,3-pdta),[13] H_4eddda·$3H_2O$,[14] and H_3tcta[15] were prepared according to literature methods.

Preparation of Complexes. Preparations of air-sensitive vanadium(III) complexes were carried out under an argon atmosphere using standard Schlenk techniques. K[V(edta)(H_2O)]·$2H_2O$,[16] Na[V(cydta)(H_2O)]·$2H_2O$,[17] and [V(nta)($H_2O)_3$]·$4H_2O$[18] were prepared according to the methods in the literature.

KV(Hdtpa)(H$_2$O). A suspension of H_5dtpa (4.0 g, 10 mmol), $BaCO_3$ (3.0 g, 15 mmol), and K_2CO_3 (1.4 g, 10 mmol) in 50 cm^3 of water was warmed to remove evolved CO_2. To this suspension was added a solution of $V_2(SO_4)_3$[19] (2.0 g, 5 mmol) in 30 cm^3 of water. The mixture was stirred at 60 °C for 1 day. Precipitated $BaSO_4$ was removed by filtration. The reddish brown filtrate was concentrated to 20 cm^3. Fine green needle crystals were obtained by adding ethanol. The yield was more than 80%. Anal. Calcd for $C_{14}H_{21}N_3KO_{11}V$: C, 33.78; H, 4.26; N, 8.45. Found: C, 33.83; H, 4.17; N, 8.30.

Na[V(1,3-pdta)]·3H$_2$O. This complex was prepared by a method different from that in the literature.[20] $V_2(SO_4)_3$ (2.0 g, 5 mmol) was suspended in 50 cm^3 of water. The suspension was stirred at 80 °C for 1 day to give a green solution. This solution was added to a suspension of Ba_2(1,3-pdta) (5.8 g, 10 mmol) and Na_2SO_4 (1.6 g, 5 mmol) in 20 cm^3 of water. The mixture was stirred at 60 °C for 1 day. A white precipitate of $BaSO_4$ was removed by filtration. The filtrate was concentrated to ca. 10 cm^3. The reddish purple crystals were obtained by adding 1,4-dioxane slowly. The yield was nearly quantitative. Anal. Calcd for $C_{11}H_{20}N_2NaO_{11}V$: C, 30.71, H, 4.69, N, 6.51. Found: C, 30.95, H, 4.72, N, 6.49.

K[V(*S,S'*-edds)]·H$_2$O. To a suspension of H_4(*S,S'*-edds) (1.5 g, 5 mmol) and $BaCO_3$ (1.5 g, 7.5 mmol) in 30 cm^3 of water was added a solution of $V_2(SO_4)_3$ (1 g, 2.5 mmol) in 30 cm^3 of water. The mixture was warmed at 60 °C for 1 day. After the precipitated $BaSO_4$ was removed by filtration, KCl (0.37 g, 5 mmol) solution was added to the filtrate. The solution was evaporated to dryness. Bluish purple crystals were obtained by recrystallization from water by adding ethanol. The crystals were sometimes contaminated by a brown oil. Yield: 40%. Anal. Calcd for $C_{10}H_{14}N_2KO_9V$: C, 30.31; H, 3.57; N, 7.07. Found: C, 30.00; H, 3.45; N, 6.90.

K[V(eddda)]·2H$_2$O. A suspension of H_4eddda·$3H_2O$ (3.8 g, 10 mmol), $BaCO_3$ (3.0g, 15 mmol), and KOH (0.6 g, 10 mmol) in 50 cm^3 of water was warmed at 50 °C until the evolution of CO_2 gas stopped. To this solution was added a solution of $V_2(SO_4)_3$ (2.0 g, 5 mmol) in 30 cm^3 of water. The mixture was stirred at 60 °C for 1 day. A white precipitate of $BaSO_4$ was removed by filtration. The filtrate was evaporated to dryness. The crude material obtained was dissolved in the minimum amount of water. A bluish green powder was obtained by adding methanol to the solution. Yield: 78%. Anal. Calcd for $C_{12}H_{20}N_2KO_{10}V$: C, 32.58; H, 4.56; N, 6.33. Found: C, 32.33; H, 4.43; N, 6.23.

V(tcta)(H$_2$O)$_5$. A suspension of H_3tcta (3.1 g, 10 mmol), $BaCO_3$ (2.0g, 10 mmol), and $BaCl_2$·$2H_2O$ (1.2 g, 5 mmol) in 20 cm^3 of water was warmed at 50 °C until the evolution of CO_2 gas stopped. To this solution was added a solution of $V_2(SO_4)_3$ (2.0 g, 5 mmol) in 50 cm^3 of water. The mixture was warmed at 60 °C for 1 day. Precipitated $BaSO_4$ was removed by filtration. The filtrate was concentrated to 20 cm^3. Pale brown needlelike crystals were deposited by adding a 1:1 mixture of acetonitrile and 1,4-dioxane to the solution. Yield: 51%. Anal. Calcd for $C_{12}H_{28}N_3O_{11}V$: C, 32.66; H, 6.41; N, 9.52. Found: C, 32.74; H, 6.31; N, 9.39.

Na[VO(eed3a)]·3H$_2$O. To the reaction solution (200 cm^3) of H_3eed3a was added a solution of $VOSO_4$·$3H_2O$ (37 g, 0.17 mol) in 100 cm^3 of water. The pH of the solution was adjusted to 6–7 by adding 0.5 N NaOH. The solution was concentrated to 100 cm^3 under reduced pressure and then evaporated spontaneously at ambient temperature. The blue crystals deposited were washed with 50% ethanol and dried. The product was recrystallized from water/ethanol. Anal. Calcd for $C_{10}H_{21}N_2NaO_{10}V$: C, 29.79; H, 5.25; N, 6.95. Found: C, 29.74; H, 5.23; N, 6.92.

Na$_2$[V(eed3a)(SO$_4$)]·2H$_2$O. A solution of Na[VO(eed3a)]·$3H_2O$ (8.1 g, 20 mmol) in 30 cm^3 of water was added to a solution of $Na_2S_2O_4$ (2.2 g, 10 mmol) in 20 cm^3 of water. The color of the solution became deep brown immediately. After the mixture was stirred for 3 h, the solution was concentrated to 20 cm^3. To this solution was added 30 cm^3 of methanol, and the mixture was kept at 40 °C for 1 day. The thin orange crystals deposited were collected by filtration, washed with methanol, and then dried. Yield: 43%. Anal. Calcd for $C_{10}H_{19}N_2Na_2O_{12}SV$: C, 24.60; H, 3.92; N, 5.74. Found: C, 24.84; H, 3.95; N, 5.75.

NaV(ida)$_2$(H$_2$O)$_2$. A suspension of H_2ida (2.7 g, 20 mmol), $BaCO_3$ (3.0 g, 15 mmol), and Na_2CO_3 (0.5 g, 5 mmol) in 50 cm^3 of water was warmed to remove evolved CO_2 gas. To this suspension was added a solution (30 cm^3) of $V_2(SO_4)_3$ (2.0 g, 5 mmol). The mixture was stirred at 40 °C for 5 h. After the precipitated $BaSO_4$ was removed by filtration, the filtrate was concentrated to ca. 5 cm^3. A brown powder was obtained by adding methanol and holding the solution at 40 °C for 1 day. Yield: 35%. Anal. Calcd for $C_8H_{14}N_2NaO_{10}V$: C, 25.81; H, 3.80; N, 7.53. Found: C, 25.72; H, 3.55; N, 7.39.

Measurements. Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer using excitation by an Ar$^+$ ion laser

---

(12) Neal, J. A.; Rose, N. J. *Inorg. Chem.* **1968**, *7*, 2405.
(13) Weyh, J. H.; Hamm, R. E. *Inorg. Chem.* **1968**, *7*, 2431.
(14) Byers, W.; Douglas, B. E. *Inorg. Chem.* **1972**, *11*, 1470.
(15) Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413.
(16) Shimoi, M.; Saito, Y.; Ogino, H. *Chem. Lett.* **1989**, 1675.
(17) Shimoi, M.; Miyamoto, S.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2549.
(18) Okamoto, K.; Hidaka, J.; Fukagawa, M.; Kanamori, K. *Acta Crystallogr.* **1992**, *C48*, 1025.
(19) Claunch, J. C.; Jones, M. M. *Inorg. Synth.* **1963**, *7*, 92.
(20) Robles, J. C.; Matsuzaka, Y.; Inomata, S.; Shimoi, M.; Mori, W.; Ogino, H. *Inorg. Chem.* **1993**, *32*, 13.

Table 1. Crystallographic Data for K[V(*S*,*S*′-edds)]·H_2O

formula	$C_{10}H_{14}N_2O_9VK$	T, K	296
fw	396.28	λ, Å	0.710 73
crystal system	monoclinic	ϱ_{calc}, g/cm^3	1.81
space group	$P2_1$	$F(000)$	808
crystal dimens, mm^3	0.38 × 0.40 × 0.50	μ, cm^{-1}	9.9
a, Å	9.687(4)	$2\theta_{max}$, deg	60
b, Å	17.445(3)	R^a	0.052
c, Å	9.295(4)	$R_w{}^b$	0.059
β, deg	112.14(2)	$R'^{\,a,c}$	0.054
V, Å^3	1454.8(10)	$R_w'^{\,b,c}$	0.061
Z	4		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$. ^{c} Refinement in the enantiomeric parameters.

line, 514.5 or 488.0 nm. Infrared spectra were recorded on a JASCO FT/IR-8000S. The samples used for Raman and infrared measurements were in the form of KBr disks. The disks were spun to avoid thermal decomposition induced by the laser illumination for the Raman measurements.

Electronic absorption and reflectance spectra were recorded on a JASCO Ubest-50 UV/vis spectrophotometer.

^{1}H spin–lattice relaxation times (T_1's) were measured at 20.4 MHz by using a JEOL (FSE-60SS) pulsed NMR spectrometer. In order to determine T_1 at 20 °C, we applied a $\pi/2$ pulse(comb)$-\tau-\pi/2$ pulse sequence generated by a computer program. The observed magnetization recovery could then be reproduced by an exponential curve with a time constant of T_1. Aqueous solutions of ca. 6 mmol dm^{-3} were used for the T_1 measurements. At least two T_1 values were measured for each sample and determined within ±5% error.

X-ray Structure Determination. A crystal of K[V(*S*,*S*′-edds)]·H_2O was mounted on a glass fiber, coated with epoxy as a precaution against solvent loss, and centered on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the range $14 < 2\theta < 20°$. Systematic absence led to the space group $P2_1$ (No. 4). Crystallographic data are summarized in Table 1. The intensity data were collected by the ω-2θ scan mode up to $2\theta = 60°$. A total of 4381 unique reflections of 4623 measured reflections were collected, 4112 of which were considered as observed [$F_o > 3\sigma(F_o)$]. Data reduction and application of Lorentz, polarization, and linear decay corrections (correction factor on I: 1.000–1.005) and empirical absorption corrections based on a series of ψ scans (minimum and maximum transmission factors: 0.85 and 1.00) were carried out using the Enraf-Nonius Structure Determination Package.[21]

The structure was solved by a direct method[21] and conventional difference Fourier techniques. The structure was refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included in the calculation. One of two independent K atoms (K2 and K3) exhibited positional disorder and was best modeled with two positions (occupancy factors: K2, $^7/_8$; K3, $^1/_8$). All the calculations were done on a VAX computer using the crystallographic package MOLEN.[22] Non-hydrogen atom coordinates are listed in Table 2.

Results and Discussion

Structures of Monomeric Complexes. As the basis for discussing the structures of (amino polycarboxylato)vanadium(III) complexes in aqueous solution, it is necessary to determine the structures in the solid state.

The structures of K[V(edta)(H_2O)][16] and K[V(cydta)(H_2O)][17] have been determined X-ray crystallographically. These complexes assume a heptacoordinate structure described as a capped trigonal prism. The complex consists of a hexadentate edta or cydta ligand and a water molecule as the seventh ligand. We have briefly reported the structure of [V(nta)(H_2O)$_3$], in which the heptacoordination is completed by a quadridentate nta ligand and three coordinated water molecules.[18] In this case, the coordination polyhedron can be described as a capped octahedron.

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms of K[V(*S*,*S*′-edds)]·H_2O ($B_{eq} = (8\pi^2/3)\sum\sum U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$)

atom	x	y	z	B_{eq}
V1	0.5630(1)	0.133	0.2047(1)	1.76(1)
O10	0.6574(5)	0.1153(2)	0.4267(4)	2.41(8)
O11	0.7252(6)	0.0481(3)	0.6423(5)	3.4(1)
O12	0.4454(4)	0.0348(3)	0.1761(5)	2.35(8)
O13	0.4719(5)	−0.0898(3)	0.2172(5)	3.21(9)
O14	0.3823(5)	0.1908(3)	0.1651(5)	3.0(1)
O15	0.2904(6)	0.3066(4)	0.1560(7)	4.6(1)
O16	0.6917(5)	0.2279(3)	0.2339(5)	2.61(9)
O17	0.7454(7)	0.3251(3)	0.1124(6)	4.2(1)
N10	0.7150(5)	0.0540(3)	0.1769(5)	1.86(8)
N11	0.5344(6)	0.1574(3)	−0.0284(5)	2.5(1)
C10	0.7120(6)	0.0554(3)	0.5061(6)	2.0(1)
C11	0.7682(6)	−0.0087(4)	0.4311(7)	2.3(1)
C12	0.6928(6)	−0.0163(3)	0.2534(6)	2.1(1)
C13	0.5246(6)	−0.0272(4)	0.2096(6)	2.1(1)
C14	0.6856(7)	0.0424(4)	0.0093(7)	2.8(1)
C15	0.6582(7)	0.1216(4)	−0.0647(6)	3.1(1)
C16	0.3533(7)	0.2600(4)	0.1042(6)	2.9(1)
C17	0.3963(8)	0.2772(5)	−0.0341(8)	3.6(2)
C18	0.5415(8)	0.2433(4)	−0.0330(7)	3.0(1)
C19	0.6695(7)	0.2695(4)	0.1115(7)	2.5(1)
V2	0.8785(1)	0.40251(6)	0.5994(1)	1.83(2)
O20	1.0382(5)	0.3443(3)	0.5737(6)	3.13(9)
O21	1.1971(5)	0.2530(3)	0.5880(6)	3.7(1)
O22	0.9109(6)	0.3586(3)	0.8115(5)	2.70(9)
O23	0.9425(6)	0.2476(3)	0.9386(5)	3.5(1)
O24	0.9476(5)	0.5001(3)	0.7035(5)	2.62(9)
O25	0.9866(5)	0.6244(3)	0.7001(6)	3.1(1)
O26	0.8359(5)	0.4519(3)	0.3886(5)	2.69(8)
O27	0.6934(6)	0.5372(3)	0.2191(5)	3.7(1)
N20	0.7573(5)	0.2982(3)	0.5395(5)	1.98(9)
N21	0.6592(5)	0.4441(3)	0.5430(5)	2.02(9)
C20	1.0801(7)	0.2734(4)	0.5959(6)	2.4(1)
C21	0.9801(7)	0.2143(4)	0.6257(7)	2.6(1)
C22	0.8466(7)	0.2440(3)	0.6626(6)	2.2(1)
C23	0.9027(7)	0.2855(4)	0.8196(6)	2.4(1)
C24	0.6027(6)	0.3090(4)	0.5316(7)	2.6(1)
C25	0.5491(7)	0.3860(4)	0.4488(8)	2.7(1)
C26	0.8979(6)	0.5697(4)	0.6598(6)	2.2(1)
C27	0.7350(6)	0.5820(4)	0.5653(7)	2.4(1)
C28	0.6535(6)	0.5168(4)	0.4555(7)	2.3(1)
C29	0.7300(7)	0.5008(4)	0.3407(7)	2.4(1)
K1	0.0522(2)	0.2781(1)	0.2497(2)	3.67(3)
K2	0.1773(2)	0.9598(1)	0.9726(2)	2.91(3)
K3	0.1654(8)	0.9316(5)	0.9416(8)	1.1(1)
OW1	0.1167(6)	0.4271(3)	0.1827(7)	4.1(1)
OW2	0.0954(9)	0.1042(4)	0.9892(9)	8.1(2)

The heptacoordinate structure has also been found for [Fe(edta)(H_2O)]$^-$.[23] It has been recognized that the heptacoordination in this complex results from the small chelate-ring size of edta, being insufficiently large to encircle the Fe(III) ion. It can then be expected that expansion of the chelate-ring size would result in a normal hexacoordinate octahedral structure. This expectation has been realized for [Fe(1,3-pdta)]$^-$, which contains a six-membered chelate ring composed of the 1,3-propanediamine moiety and [Fe(eddda)]$^-$, which contains two six-membered chelate rings made up of the two propionate sidearms.[24] A similar trend can be expected for the vanadium

---

(21) Enraf-Nonius Structure Determination Package (SDP); Enraf-Nonius: Delft, The Netherlands, 1978.

(22) Fair, C. K. *MOLEN, International Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(23) (a) Hoard, J. L.; Lind, M.; Silverton, S. V. *J. Am. Chem. Soc.* **1961**, *83*, 2770. (b) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316. (c) Lind, M.; Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 34. (d) Solans, X.; Font Altaba, M. *Acta Crystallogr.* **1984**, *C40*, 635.

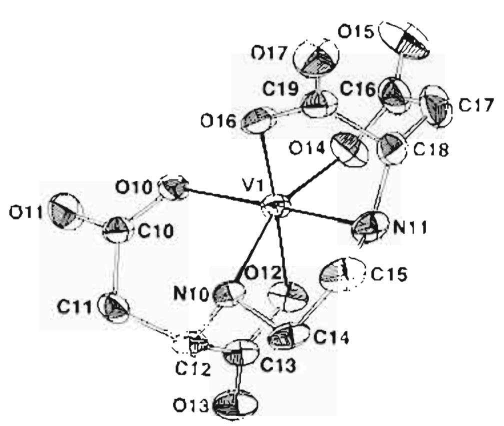

Figure 2. ORTEP drawing of the non-hydrogen atoms of [V(*S,S'*-edds)]$^-$ (1).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [V(*S,S'*-edds)]$^-$ (1)

	Bond Lengths		
V1–O10	1.942(4)	V1–O12	2.026(6)
V1–O14	1.927(5)	V1–O16	2.023(5)
V1–N10	2.107(5)	V1–N11	2.120(5)
	Bond Angles		
O10–V1–O12	91.0(2)	O10–V1–O14	108.5(2)
O10–V1–O16	88.3(2)	O10–V1–N10	87.2(2)
O10–V1–N11	161.0(2)	O12–V1–O14	89.5(2)
O12–V1–O16	176.3(2)	O12–V1–N10	79.0(2)
O12–V1–N11	100.6(2)	O14–V1–O16	94.2(2)
O14–V1–N10	160.8(2)	O14–V1–N11	86.8(2)
O16–V1–N10	97.4(2)	O16–V1–N11	79.2(2)
N10–V1–N11	80.4(2)		

(III) complexes. In fact, the [V(1,3-pdta)]$^-$ complex has a hexacoordinate structure.[20]

The structure of the vanadium(III) complex with *S,S'*-edds, which has the same diamine backbone as edta but two longer sidearms than edta, has been determined by X-ray crystal structure analysis. There are two crystallographically independent complex anions (1 and 2) in the unit cell. Each complex anion has very similar geometric parameters. The perspective view of [V(*S,S'*-edds)]$^-$ (1) is shown in Figure 2. The important bond distances and angles are summarized in Table 3. The complex anion adopts a distorted octahedral structure. The molecular dimensions of [V(*S,S'*-edds)]$^-$ are similar to those obtained for [Fe(*S,S'*-edds)]$^-$.[25] The G rings in the equatorial plane are composed of the six-membered chelates while the axially disposed R rings are composed of the five-membered chelates. Considering that there is more strain in the G plane for five-membered rings than for six-membered rings,[26] it is reasonable that the present edds complex preferentially adopts the structure having two six-membered chelate rings in the G plane. The deviation from a regular octahedron is a little larger in this complex than in [V(1,3-pdta)]$^-$; for example, the O10–V–O14 angle is 108.5(2)° in the edds complex but the corresponding angle for the 1,3-pdta complex is 102.44(8)°.[20]

Crystals of sufficient quality for X-ray analysis were not obtained for the eddda, tcta, dtpa, eed3a, and ida complexes. Therefore, the solid-state structures of these complexes were determined using the reflectance, infrared, and Raman spectra.

Ogino et al.[20] have pointed out that heptacoordinate vanadium(III) complexes exhibit an absorption band in the 800 nm region, although the band is absent for hexacoordinate complexes. The diffuse reflectance spectrum of the eddda complex is shown in Figure 3a. The spectrum of the eddda complex resembles that of K[V(*S,S'*-edds)] and has no band in the 800 nm region. This observation indicates that the eddda complex assumes a hexacoordinate octahedral structure with a hexadentate eddda ligand, [V(eddda)]$^-$. On the other hand, the reflectance spectra of the dtpa, tcta, eed3a, and (ida)$_2$ complexes (Figure 3b–e) exhibit a pronounced band in the 800 nm region, suggesting that these complexes adopt heptacoordination.

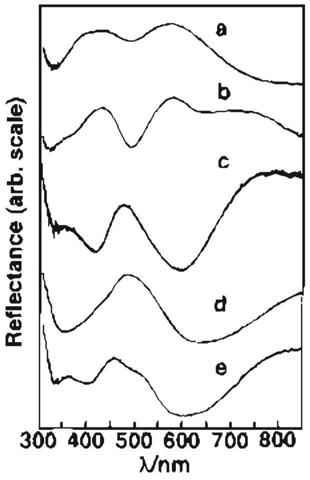

Figure 3. Diffuse reflectance spectra: (a) eddda complex; (b) dtpa complex; (c) tcta complex; (d) eed3a complex; (e) (ida)$_2$ complex.

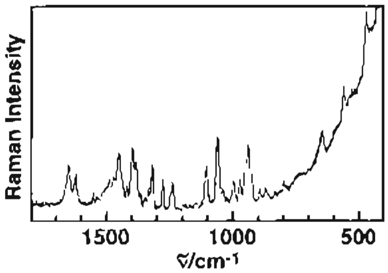

Figure 4. Raman spectrum of $Na_2[V(eed3a)(SO_4)]\cdot 2H_2O$. Spectral conditions: spectral bandwidth 5 cm^{-1}, laser, Ar$^+$ ion, 514.5 nm, 250 mW.

For the dtpa complex, the elemental analysis and the infrared band at 1727 cm^{-1} that is assignable to the C=O stretching vibration of a protonated carboxylate group suggest that one of the five carboxylate groups of dtpa does not coordinate to the metal center. Although the heptacoordination can be completed by the remaining seven donor atoms, a ^{1}H NMR relaxation study (vide infra) indicated that there are one or two water molecules in the coordination sphere, at least in aqueous solution.

The complex with a quinquedentate ligand, eed3a, was isolated as a complex containing a sulfate anion. We have shown that if a sulfate coordinates to a metal center in a monodentate fashion or exists as a free ion, a very intense band appears at 980 cm^{-1} in the SO_4^{2-} stretching region, whereas if a sulfate coordinates in a bidentate fashion, the most intense band appears around 1010 cm^{-1}.[27] As shown in Figure 4, the present V–eed3a–SO_4^{2-} complex has an intense Raman band at 1058 cm^{-1} and a weak band at 996 cm^{-1}, indicating that the sulfate coordinates in a bidentate fashion. The bidentate coordination of the sulfate anion in addition to the quinquedentate coordination of the eed3a chelate would result in the heptacoordination of the complex, [V(eed3a)(SO$_4$)]$^{2-}$.

---

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

(25) Pavelcik, F.; Kettman, V. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1376.

(26) Radanovic, D. J.; Douglas, B. E. *Inorg. Chem.* **1975**, *14*, 5.

(27) Kanamori, K.; Kunita, N.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2574.

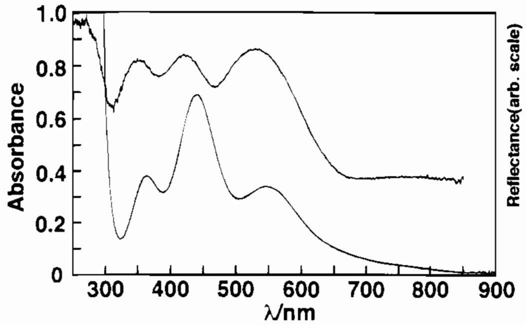

Figure 5. Diffuse reflectance (upper) and absorption (lower) spectra of Na[V(1,3-pdta)]·$3H_2O$.

Because the vanadium(III) complexes are substitution labile, the structure found in the solid state is not necessarily maintained as it is in aqueous solution. We, therefore, compared the absorption spectra of the present (amino polycarboxylato)-vanadium(III) complexes with the corresponding reflectance spectra to estimate the structures in aqueous solution. Each complex, except the eed3a one, showed an absorption spectrum corresponding fairly well to the respective reflectance spectrum with respect to the number and positions of the bands. A typical example is shown in Figure 5 for $[V(1,3\text{-pdta})]^-$. Although the 1,3-pdta complex seems to be subject to hydrolysis to some extent in aqueous solution as will be discussed in the next section, the fairly good agreement between the electronic spectra observed for the solid and solution samples allows us to conclude that the basic structure of the complex does not change on dissolution; i.e., the predominant species in the solution is not a heptacoordinate one but a hexacoordinate one. On the same basis, we considered that the predominant species in the solution of the other (amino polycarboxylato)vanadium(III) complexes, except for the eed3a complex, also have the same coordination numbers as those found in the solid states.

The color of the eed3a complex changes from orange in the solid state to deep brown on dissolution in water. This deep brown color is indicative of the formation of the oxo-bridged dinuclear complex, as will be discussed later in detail.

Estimation of the Number of Coordinated Water Molecules Based on ^{1}H NMR Spin–Lattice Relaxation Time. In order to determine the number of the coordinated water molecules in the (amino polycarboxylato)vanadium(III) complexes, ^{1}H NMR spin–lattice relaxation times were measured. So far, T_1 measurements of water protons have been used to estimate the number of coordinated water molecules for several paramagnetic complexes.[28–33]

The observed relaxation rate, $[T_1^{-1}]_{\rm obs}$, of the aqueous solution of paramagnetic complexes can be expressed as the sum of the contribution from the coordinated water molecule(s), $[T_1^{-1}]_{\rm p}$, that from water molecules in the second coordination sphere, $[T_1^{-1}]_{\rm s}$, and that from the bulk water, $[T_1^{-1}]_{\rm b}$:

$$[T_1^{-1}]_{\rm obs} = [T_1^{-1}]_{\rm p} + [T_1^{-1}]_{\rm s} + [T_1^{-1}]_{\rm b}$$

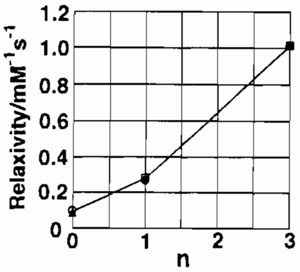

Figure 6. Correlation between relaxivity (T_1^{-1}/M) and number of coordinated water molecules (n): ○, $[V(\text{eddda})]^-$; ▲, $[V(S,S'\text{-edds})]^-$; □, $[V(\text{edta})(H_2O)]^-$; ●, $[V(\text{cydta})(H_2O)]^-$; ■, $[V(\text{nta})(H_2O)_3]$.

The third term can be neglected because, generally, $[T_1^{-1}]_{\rm b} \ll [T_1^{-1}]_{\rm p}$, $[T_1^{-1}]_{\rm s}$. $[T_1^{-1}]_{\rm p}$ and $[T_1^{-1}]_{\rm s}$ depend on several parameters as follows:

$$[T_1^{-1}]_{\rm p,s} \propto nM\mu_{\rm eff}^2\tau_{\rm c}r^{-6}$$

where n is the number of coordinated water molecules, M is the molar concentration of paramagnetic complexes, $\mu_{\rm eff}$ is the effective magnetic moment of the metal ion, and r is the internuclear distance between the metal ion and the water protons. The correlation time, $\tau_{\rm c}$, can be expressed by the sum of the contributions from the rotational correlation time of the complex considered, $\tau_{\rm r}$, the electron spin relaxation time of the paramagnetic ion, $\tau_{\rm S}$, and the exchange lifetime between water molecules in the coordination sphere and those in the bulk, $\tau_{\rm M}$:

$$\tau_{\rm c}^{-1} = \tau_{\rm r}^{-1} + \tau_{\rm S}^{-1} + \tau_{\rm M}^{-1}$$

Because all the complexes studied here have similar sizes, it is probable that the values of $[T_1^{-1}]_{\rm s}$ can be assumed to be similar. Thus, the observed variation in $[T_1^{-1}]_{\rm obs}$ can be attributed to the variation in $[T_1^{-1}]_{\rm p}$. Among the parameters that determine $[T_1^{-1}]_{\rm p}$, $\mu_{\rm eff}$ and r will be regarded as constant because all the complexes have similar ligands. If we assume that $\tau_{\rm c}$ will not vary significantly among the complexes, $[T_1^{-1}]_{\rm obs}/M$ (relaxivity) is then directly proportional to n. We chose the observed T_1^{-1}/M values for $[V(S,S'\text{-edds})]^-$ (0.09 mM^{-1} s^{-1}) and $[V(\text{eddda})]^-$ (0.10 mM^{-1} s^{-1}), those for $[V(\text{edta})(H_2O)]^-$ (0.29 mM^{-1} s^{-1}) and $[V(\text{cydta})(H_2O)]^-$ (0.27 mM^{-1} s^{-1}), and that for $[V(\text{nta})(H_2O)_3]$ (1.0 mM^{-1} s^{-1}) as the standard values of relaxivities when n = 0, 1, and 3, respectively. These values are considered to be appropriate for the standard values, because these complexes are structurally characterized. These standard values are plotted against n in Figure 6. The approximate linear relationship between the relaxivity and n implys that aquation is not significant, and so the number of the coordinated water molecules does not change seriously on dissolution of these complexes. This conclusion is consistent with the fact that the electronic spectra of the edta and cydta complexes[20] as well as the nta complex do not show temperature dependence, implying an equilibrium in solution. The approximate number of coordinated water molecules can then be estimated on the basis of this figure for complexes whose structures are unknown. A slight deviation from the straight line would be due to a minor extent of aquation of the eddda and edds complexes or a variation in $\tau_{\rm c}$, especially in $\tau_{\rm r}$, of the complexes.

Ogino et al.[20] have pointed out that the 1,3-pdta complex exhibits thermochromism and attributed it to an equilibrium between the hexa- and the aquated heptacoordinate species. According to Figure 6, it follows that the observed relaxivity of the 1,3-pdta complex (0.20 mM^{-1} s^{-1}) corresponds to ca. 0.5 coordinated water molecule. This fact is consistent with

---

(28) Whidby, J. F.; Leyden, D. E. *Anal. Chim. Acta* **1970**, *51*, 25.
(29) Bloch, J.; Navon, G. *J. Inorg. Nucl. Chem.* **1980**, *42*, 693.
(30) Oakes, J.; Smith, E. G. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 299.
(31) Oakes, J.; Smith, E. G. *J. Chem. Soc., Faraday Trans 1* **1983**, *79*, 643.
(32) Chang, C. A.; Brittain, H. G.; Telser, J.; Tweedle, M. F. *Inorg. Chem.* **1990**, *29*, 4468.
(33) Kanamori, K.; Ukita, N.; Kawai, K.; Taguchi, S.; Goto, K.; Eguchi, T.; Kishita, M. *Inorg. Chim. Acta* **1991**, *186*, 205.

the proposed equilibrium, but it appears more likely that the aquated species is a hexacoordinate one having an uncoordinated acetate arm, since the observed electronic spectral change is small in the 800 nm region.

The observed T_1^{-1} value of the dtpa complex is 0.42 mM^{-1} s^{-1}. This indicates that ca. 1.4 coordinated water molecules on an average coordinate to vanadium(III) in aqueous solution. An equilibrium between the monoaqua and diaqua species would likely exist in the aqueous solution. Because the dtpa complex takes a heptacoordinate structure, the dtpa ligand seems to act as a quinquedentate or hexadentate ligand in the aqueous solution.

The observed T_1^{-1} value of the tcta complex is 1.0 mM^{-1} s^{-1}, which is close to that observed for $[V(nta)(H_2O)_3]$. The tcta complex in aqueous solution can then be formulated as $[V(tcta)(H_2O)_3]$, in which the tcta ligand acts in a tetradentate fashion. It is known that the hexadentate coordination of the tcta ligand results in a significant distortion from an octahedron to a trigonal prism.[34] The V(III)–tcta complex seems to avoid steric distortion by leaving the two carboxylate groups uncoordinated.

For the ida complex, the observed T_1^{-1} value is 0.84 mM^{-1} s^{-1}, indicating that ca. 2.5 coordinated water molecules on an average coordinate to vanadium(III). Taking into account the fact that the complex assumes a heptacoordinate structure, we may assume that one of the two ida ligands in the complex coordinates in a bidentate fashion and the other equilibrates between bidentate and tridentate coordination.

In conclusion, T_1^{-1} measurements are very useful for estimating the number of coordinated water molecules in aqueous solutions of paramagnetic vanadium(III) complexes.

Relationship between Oxo-Bridged Dimer Formation and Structure of the Monomeric Complex. The ttha complex of vanadium(III) forms the oxo-bridged dinuclear complex on hydrolysis.[8,10] This dinuclear complex exhibits an intense absorption band due to the oxo-to-V(III) charge transfer at 450 nm. In the Raman spectrum upon resonance with the CT band, the first overtone of the V–O–V antisymmetric stretching vibration is strongly resonance enhanced at 1494 cm^{-1}. We examined oxo-bridged dimer formation for the (amino polycarboxylato)vanadium(III) complexes by using the CT absorption band in the 450 nm region and the resonance-enhanced Raman bands as the markers for oxo-bridged dimer formation. Oligomerization was not taken into consideration in the present systems for the following reasons: (i) in general, oligomerization in solution is less important in vanadium(III) chemistry than in vanadium(IV) and -(V) chemistries; in fact, the hydrolytic behavior of aquavanadium(III) has been explained without oligomers,[35] though the earlier study[5c] suggested the presence of a hydroxo-bridged trimer; (ii) if oligomerization would occur to some extent for the aqua species, it would be scarcely expected for the (amino polycarboxylato)vanadium(III) complexes having a less free coordination sites for oligomerization than the aqua species.

Figure 7 shows the absorption spectra of the edta complex as a function of pH. From pH 1.8 to 7.5, the spectrum does not show any considerable pH dependence. As the pH of the solution is increased above 7.5, the intensities of the bands at 447 and 780 nm decrease, new bands appear at 405, 497, and 700 nm, and the intensities of these bands increase. In this spectral change, the three isosbestic points are found at 422, 460, and 775 nm. This spectral change does not depend on the concentration of the complex. Although the earlier study[11] proposed the existence of the oxo-bridged dimer in addition to the hydroxo species, the above observations strongly indicate that only one equilibrium exists in the aqueous solution:

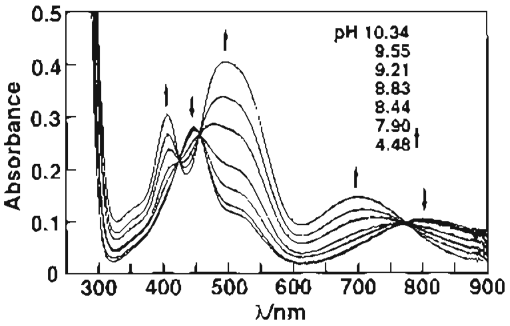

Figure 7. Absorption spectra of $[V(edta)(H_2O)]^-$ (10.2 mM) as a function of pH.

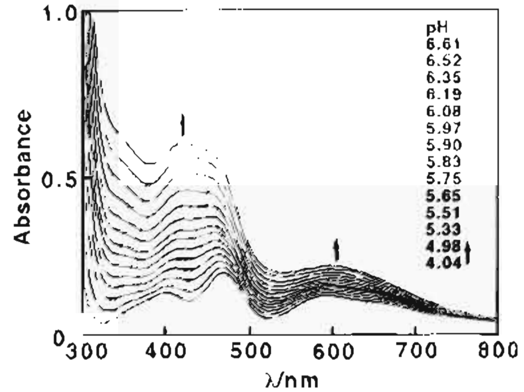

Figure 8. Absorption spectra of $[V(nta)(H_2O)_3]$ (10.4 mM) as a function of pH.

$$[V(edta)(H_2O)]^- \rightleftharpoons [V(edta)(OH)]^{2-} + H^+$$

The Raman spectrum of the basic solution of the edta complex also shows no evidence of oxo-bridged dimer formation. The band at 700 nm observed for the higher pH solution suggests that the hydroxo species assumes heptacoordination dominantly. The cydta complex shows a spectral change similar to that observed for the edta complex, indicating that the hydrolytic behavior of the cydta complex is the same as that of the edta complex.

Figure 8 shows the absorption spectra of the nta complex as a function of pH. The absorbances in the whole visible region increase with increasing solution pH. There is no indication of the formation of an oxo-bridged dimer. Therefore, the observed hydrolytic behavior of the nta complex can be interpreted by the successive deprotonation of the coordinated water molecules:

$$[V(nta)(H_2O)_3] \rightleftharpoons [V(nta)(OH)(H_2O)_2]^- + H^+$$

$$[V(nta)(OH)(H_2O)_2]^- \rightleftharpoons [V(nta)(OH)_2(H_2O)]^{2-} + H^+$$

Further increase in the solution pH resulted in precipitation of vanadium(III) hydroxide.

The absorption spectrum of the 1,3-pdta complex shows a pH dependence which is completely different from those observed for the edta, cydta, and nta complexes. The spectral change caused by the hydrolysis of the 1,3-pdta complex depends on the concentration of the complex. Figure 9 shows the spectral change observed for the 15.2 mM solution. A very

---

(34) Wieghardt, K.; Bossek, U.; Chaudhuri, P.; Hermann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

(35) Brito, F.; Gonçalves, *An. Quim.* **1982**, *78*, 104.

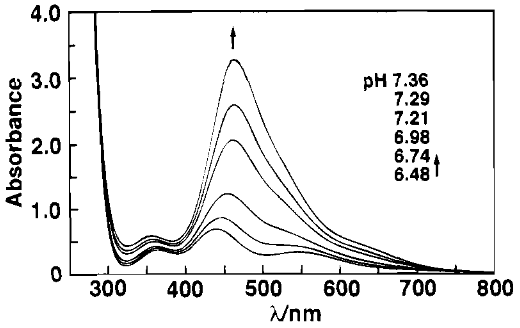

Figure 9. Absorption spectra of $[V(1,3\text{-pdta})]^-$ (15.2 mM) as a function of pH.

strong band appears at 465 nm and grows with increasing pH. For the 1.25 mM solution, the band at 465 nm is not clearly observed. The observation of the band at 465 nm which is attributable to the CT transition of the V—O—V moiety and the concentration dependence of the spectral change clearly indicate the formation of an oxo-bridged dimer. The resonance Raman spectrum with the 465 nm band (Figure 10) confirms the oxo-bridged dimer formation. The resonance Raman characteristics are very similar to those observed for $[V_2O(ttha)]^{2-}$, in which the oxo and decadentate ttha ligands bridge two metal centers.[8] The dominant band at 1470 cm^{-1} can be assigned to the first overtone of ν_{as}(V—O—V), and the bands at 745 and 422 cm^{-1} are assignable to ν_{as}(V—O—V) and ν_s(V—O—V), respectively. The hydrolytic equilibria of the 1,3-pdta complex can then be expressed as

$$[V(1,3\text{-pdta})]^- + H_2O \rightleftharpoons [V(1,3\text{-pdta})(OH)]^{2-} + H^+$$

$$2[V(1,3\text{-pdta})(OH)]^{2-} \rightleftharpoons [\{V(1,3\text{-pdta})\}_2(\mu\text{-O})]^{4-} + H_2O$$

Because the *S,S'*-edds and eddda complexes show visible and Raman characteristics similar to those observed for the 1,3-pdta complex, it can be reasonably concluded that these complexes also form the oxo-bridged dimer on hydrolysis. The electrochemical properties of vanadium(III) complexes with 1,3-pdta and edta have been discussed.[36]

It is worthwhile to note that the vanadium(III) complexes having a hexacoordinate structure form the oxo-bridged dimer on hydrolysis, but those having a heptacoordinate structure do not. This difference in the hydrolytic behavior between the hexa- and heptacoordinate species can be interpreted by assuming a dihydroxo-bridged intermediate in the oxo-bridged dimer formation reaction:

$$[VL]^{n-} \rightleftharpoons [VL(OH)]^{(n+1)-} + H^+$$

$$2[VL(OH)]^{(n+1)-} \rightleftharpoons [\{VL(OH)\}_2]^{2(n+1)-}$$

$$[\{VL(OH)\}_2]^{2(n+1)-} \rightleftharpoons [\{VL\}_2O]^{2(n+1)-}$$

If the dihydroxo-bridged intermediate is formed by the association of two hydroxo species, the resultant species would be a heptacoordinate one. Because heptacoordination has been found for several vanadium(III) complexes as shown above, the heptacoordinate intermediate would be likely to be formed. Then, the dihydroxo-bridged intermediate would be converted into an oxo-bridged dimer by the subsequent dehydration reaction, since it is presumed that the dihydroxo-bridged complex is not particularly stable for vanadium(III) complexes. On the other hand, the association of heptacoordinate hydroxo species would result in an octacoordinate intermediate that is considered to be very unfavorable due to steric requirements. In fact, the dtpa and tcta complexes, the structures of which were estimated to be heptacoordinate on the basis of the absorption band in the 800 nm region, do not exhibit the CT absorption band due to the oxo-bridged dimer on hydrolysis.

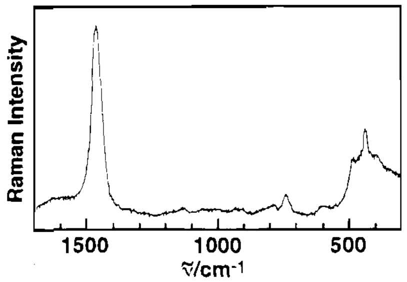

Figure 10. Resonance Raman spectrum of $[V(1,3\text{-pdta})]^-$ in aqueous solution (pH 7.8). Spectral conditions: spectral bandwidth 5 cm^{-1}, laser, Ar^+ ion, 514.5 nm, 200 mW.

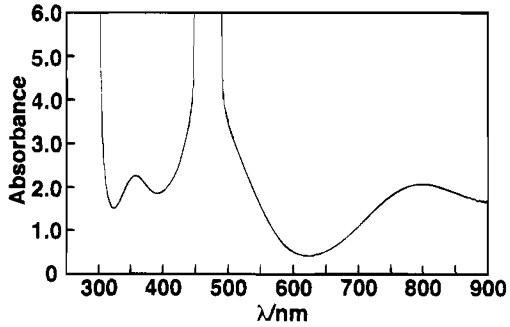

Figure 11. Absorption spectrum of a saturated solution of the $(ida)_2$ complex.

The color of $Na_2[V(eed3a)(SO_4)]$ changes from orange in the solid state to intense brown on dissolution in water. This intense color is bleached by addition of acid to the solution, suggesting that the intense brown color observed at higher pHs is due to the oxo-bridged dimer. The resonance Raman spectrum confirmed the presence of the oxo-bridged dimer in solution. It is thus likely that the eed3a complex exists dominantly as a hexacoordinate species in aqueous solution. Considering the weak ligand-field strength of the sulfate anion, the predominant monomeric species that is present in an acidic aqueous solution would be the hexacoordinate aquo species $[V(eed3a)(H_2O)]$.

Releasing one of the four carboxylato groups from coordination relaxes the strain in the chelate-ring system of the edta complex. This relaxation results in hexacoordination, proved by the fact that the quinquedentate coordination of Hedta results in a hexacoordinate iron(III) complex, although the full coordination of edta generally results in a heptacoordinate iron(III) complex.[37] It is also known that *N*-(hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate (hedta), which acts as a quinquedentate ligand, forms the hexacoordinate iron(III) complex.[38] Therefore, the heptacoordinate structure of the eed3a complex in the solid state seems to be forced by the bidentate coordination of a sulfate ion.

The ida complex exhibits an interesting absorption feature. Figure 11 shows the absorption spectrum of a saturated solution of the ida complex. In addition to the spectral feature due to the heptacoordinate species, a very intense band appears at 470 nm. This intense band disappears on slight dilution of the solution. These facts suggest that a hexacoordinate species coexists as a very minor component along with the heptacoor-

---

(36) Boddin, M.; Kanamori, K.; Ino, K.; Meier, R.; Mitzenheim, S. Manuscript in preparation.

(37) Kennard, C. H. L. *Inorg. Chim. Acta* 1967, *1*, 347.

(38) Lippard, S. J.; Schugar, H.; Walling, C. *Inorg. Chem.* **1967**, *6*, 1825.

dinate species in aqueous solution and it gives an oxo-bridged dimer upon hydrolysis.

Resonance Raman Characteristics. For the oxo-bridged iron(III) complexes the Fe−O−Fe symmetric stretching is strongly enhanced in the resonance Raman spectra, although the antisymmetric stretching is very weak or not observed.[39] On the contrary, for the oxo-bridged vanadium(III) complexes with the amino polycarboxylates, the V−O−V antisymmetric stretching is resonance-enhanced to an extent similar to that of the symmetric stretching. Furthermore, the first overtone of the V−O−V antisymmetric stretching is strongly resonance-enhanced. This difference in the resonance Raman characteristics between the iron(III) and vanadium(III) complexes may reflect the difference in the structure of the bridging moiety in the CT excited state. Hirakawa and Tsuboi have elucidated that the equilibrium conformation of the molecule is distorted along the normal coordinate for the Raman band that is resonance-enhanced in the transition from the ground to the excited state.[40] It can then be assumed that the structure of the bridging moiety of the oxo-bridged vanadium(III) complexes in the CT excited state is antisymmetrically distorted, namely the $V^{4+}{=}O{-}V^{2+}$ type.

Conclusion. In this investigation several (amino polycarboxylato)vanadium(III) complexes were newly prepared. The structure of the *S,S'*-edds complex has been determined by single-crystal X-ray analysis. The other complexes have been characterized on the basis of their electronic and vibrational spectra. The measurement of ^{1}H NMR spin−lattice relaxation time can also provide useful information about the number of coordinated water molecules and hence the structure of the vanadium(III) complexes in aqueous solution.

It has been noted that some (aminopolycarboxylato)vanadium(III) complexes yield an oxo-bridged dimer but some do not. This work has proven that the difference in solution behavior is related to the coordination number of the monomeric complexes: a hexacoordinate monomer yields an oxo-bridged dimer upon hydrolysis whereas a heptacoordinate one does not. A probable mechanism for the dimerization reaction has been proposed.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research No. 04640573 from the Ministry of Education, Science, and Culture of Japan and was supported financially by the Izumi Science and Technology Foundation. We wish to thank Dr. Yuriko Abe for her valuable discussions concerning the formation reaction of the oxo-bridged dimer.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, and hydrogen positional parameters (5 pages). Ordering information is given on any current masthead page.

---

(39) For example: Shiemko, A. K.; Loehr, T. M.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1986**, *108*, 2437.

(40) Hirakawa, A. Y.; Tsuboi, M. *Science* **1975**, *188*, 359.