Heptacoordinate Vanadium(III) Complexes Containing a Didentate Sulfate Ligand. X-Ray Structures of $[V_2(SO_4)_3\{N,N'\text{-bis(2-pyridylmethyl)-1,2-ethanediamine}\}_2]$ and $[V(SO_4)\{N,N,N',N'\text{-tetrakis(2-pyridylmethyl)-1,2-ethanediamine}\}]^+$ and Their Solution Properties

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Several vanadium(III) complexes with a tetradentate *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen) or a hexadentate *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen) ligand were prepared and characterized by UV-vis and Raman spectroscopy. Of these complexes, the structures of two vanadium(III) complexes with a didentate sulfate were determined by X-ray crystallography. $[V_2(SO_4)_3(\text{bispicen})_2]$ crystallizes in the monoclinic space group *C*2/*c* with $a = 25.083(7)$, $b = 24.236(5)$, $c = 15.708(5)$ Å, $\beta = 114.96(2)°$, $Z = 8$, and $R = 0.087$. The complex containing the $[V(SO_4)(\text{tpen})]^+$ cation crystallizes in the orthorhombic space group *Aba*2 with $a = 20.1836(8)$, $b = 19.793(1)$, $c = 15.6107(7)$ Å, $Z = 8$, and $R = 0.069$. Both complexes adopt a heptacoordinate pentagonal bipyramidal structure in which the didentate sulfate is situated in the pentagonal plane. The heptacoordinate structure of the tpen-SO_4^{2-} complex is stable in an aqueous solution, whereas the bispicen-SO_4^{2-} complex is easily aquated to yield a hexacoordinate oxo-bridged dinuclear species.

The coordination chemistry of vanadium has attracted the increasing attention of chemists as well as biologists with regard to its biological and physiological functions.[1,2] Vanadium is now recognized to be an essential trace element to higher animals. Biologically relevant oxidation states are vanadium(III), (IV), and (V). Among these oxidation states, vanadium(III) is generally unstable to air-oxidation. It is well known that several kinds of invertebrates, tunicates[3] and fan worms,[4] sequester the vanadium ion from sea water, and accumulate it as the unstable vanadium(III) form in their body. The physiological role of vanadium(III) in tunicates, however, is still a controversial issue. Another pending problem is why tunicates chose sulfate as a counter ion of vanadium(III) instead of chloride, which is the most abundant anion in sea water.[5] With regard to this problem, Frank et al. have proposed that the coordination of sulfate has the effect of dramatically lowering the ionic strength at high intracellular vanadium(III).[6] Since sulfate, but not chloride, is a potential didentate ligand, the structure of sulfato vanadium(III) complexes would depend on its coordination mode, monodentate or didentate. In this paper we examine the effect of sulfate on the coordination geometry of vanadium(III) complexes.

Experimental

Compound Preparations: All of the reagents were commercially available and used without further purification. All of the synthetic procedures involving vanadium(III) complexes were performed under an Ar atmosphere using standard Schlenk techniques or in a N_2-filled glove box.

Ligands: *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen)[7] and *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen)[8] were prepared according to literature methods.

$[VCl_2(\text{bispicen})]Cl$ (1): A methanol solution (8 cm^3) of VCl_3 (0.79 g; 5 mmol) was mixed with a methanol solution (4 cm^3) of bispicen (1.21 g; 5 mmol). The resulting purple-brown solution was evaporated to dryness. The residue was dissolved in 6 cm^3 of water. Green crystals (**1**) were deposited by adding methanol (15 cm^3) and acetone (20 cm^3) to a brown aqueous solution, and allowing it to stand at 60 °C. Yield 56%. Anal. Calcd for $C_{14}H_{18}N_4Cl_3V$=$[VCl_2(\text{bispicen})]Cl$: C, 42.02; H, 4.55; N, 14.02%. Found: C, 42.28; H, 4.71; N, 14.01%.

$[V_2(\mu\text{-}O)Cl_2(\text{bispicen})_2]Cl_2\cdot 2H_2O\cdot CH_3OH$ (2): An aqueous solution (20 cm^3) of bispicen (1.21 g; 5 mmol) was added to a solution (20 cm^3) of VCl_3 (0.79 g; 5 mmol), resulting in a brown solution. The pH of the solution was adjusted to 4.5 by adding 1 mol dm^{-3} of LiOH. After the solution was evaporated to dryness, the residue was redissolved in 2 cm^3 of water. To the solution was added 10 cm^3 of methanol and 40 cm^3 of acetone; the resulting solution was then kept at 60 °C. Brown crystals (**2**) were obtained in 62% yield. Anal. Calcd for $C_{29}H_{44}N_8O_4Cl_4V_2$=$[V_2OCl_2(\text{bispicen})_2]Cl_2\cdot 2H_2O\cdot CH_3OH$: C, 42.86; H, 5.47; N, 13.79%. Found: C, 42.79; H, 5.59; N, 13.83%.

$[V_2(SO_4)_3(\text{bispicen})_2]\cdot 1/4H_2O\cdot 3/8CH_3OH\cdot DMF$ (3): To an aqueous solution (20 cm^3) of bispicen (1.21 g; 5 mmol) was added a solution (25 cm^3) of $V_2(SO_4)_3$[9] (0.98 g; 2.5 mmol). The resulting dark-purple-brown solution was acidified to pH 2.5 by the addition of 2 mol dm^{-3} of H_2SO_4. The color of the solution changed to yellowish brown. The solution was evaporated to dryness. After the residue was dissolved in a small amount of water, methanol (15 cm^3) and *N*,*N*-dimethylformamide (DMF) (15 cm^3) were added to it. The solution was kept standing at 65 °C; then, orange crystals (**3**) were deposited. Yield 44%. Anal. Calcd for $C_{31.375}H_{45}N_9O_{13.625}S_3V_2$=[$V_2(SO_4)_3$(bispicen)$_2$]·1/4$H_2O$·3/8$CH_3OH$·DMF: C, 39.07; H, 4.71; N, 13.07%. Found: C, 38.74; H, 4.94; N, 12.94%.

[V_2OBr_4(tpen)]·3H_2O·CH_3OH (4): A VBr_3 solution was obtained by a double decomposition of $V_2(SO_4)_3$ (0.78 g; 2 mmol) and $BaBr_2·2H_2O$ (2 g; 6 mmol) in H_2O. After precipitated barium sulfate was removed by filtration, the filtrate was evaporated to dryness. The residue was dissolved in methanol, and a methanol solution of tpen (0.85 g; 2 mmol) was added to it, resulting in a dark-purple solution. The solution was concentrated to ca. 10 cm^3, and 30 cm^3 of acetone was added. Purple powder (**4**) was deposited when the solution was kept standing at 60 °C for several hours. Yield 45%. Anal. Calcd for $C_{27}H_{38}N_6Br_4O_5V_2$=[$V_2OBr_4$(tpen)]·3$H_2O$·$CH_3OH$: C, 34.20; H, 4.05; N, 8.87%. Found: C, 34.11; H, 4.08; N, 8.87%.

[V(SO_4)(tpen)](HSO_4)$_{0.75}$(SO_4)$_{0.125}$5/4H_2O (5): A suspension of tpen (1.0 g; 2.4 mmol) in 15 cm^3 of water was mixed with an aqueous solution (25 cm^3) of $V_2(SO_4)_3$ (0.46 g; 1.2 mmol); then a green powder was deposited. The pH of the mixture was adjusted to 2.4 by the addition of 1 mol dm^{-3} of H_2SO_4. The green powder was dissolved to give an orange solution. The solution was concentrated to ca. 4 cm^3, and 20 cm^3 of ethanol was added to it. Yellow crystals (**5**) were obtained by allowing the solution to stand at 70 °C. Yield 68%. Anal. Calcd for $C_{26}H_{30.5}N_6O_{8.75}S_{1.875}V$=[V($SO_4$)(tpen)]($HSO_4$)$_{0.75}$($SO_4$)$_{0.125}$·5/4$H_2O$: C, 46.04; H, 4.54; N, 12.39%. Found: C, 45.69; H, 4.73; N, 11.76%.

Measurements: UV-vis spectra were recorded on a JASCO Ubest 50 spectrophotometer. Raman spectra were recorded on a JASCO R-800 using an Ar^+ ion laser (514.5 nm) or on a JASCO RFT-200 using a YAG laser (1064 nm).

X-Ray Structure Determination: The crystallographic data for complexes **3** and **5** are summarized in Table 1. Each of the crystals was mounted on a glass fiber and centered on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo *Kα* radiation. The unit-cell parameters were determined by a least-squares refinement using diffraction angles of 25 reflections in the range of $41 < 2\theta < 45°$ for **3** and of $23 < 2\theta < 44°$ for **5**. Data reduction and the application of Lorentz, polarization, linear decay correction (correction factor on *I*: 1.000 to 1.154 for **3** and 1.000 to 1.014 for **5**), and empirical absorption corrections based on a series of ψ scans (minimum and maximum transmission factors: 0.89 to 1.00 for **3** and 0.97 to 1.00 for **5**) were carried out.[10)] The structures were solved by a direct method[10)] and conventional difference Fourier techniques. The structures were refined by full-matrix least-squares techniques on F. All non-hydrogen atoms, except for O21, O22, O23, O24, and O25 for **5**, were refined anisotropically. The water oxygen (site occupancy factor (occ)=1/4) and methanol (occ=3/8) atoms in **3** had a positional disorder. In **5**, the counter anions (occ=3/4 for HSO_4, occ=1/8 for SO_4) and two water oxygen atoms (occ=3/4 and 1/2) also had a positional disorder. All of the calculations were performed on a VAX computer using the crystallographic package MOLEN.[10)] The non-hydrogen atom coordinates for **3** and **5** are listed in Tables 2 and 3, respectively. (Lists of the structure factors, complete bond distances and angles, and anisotropic thermal parameters are deposited as Document No. 69060 at the Office of the Editor of Bull. Chem. Soc. Jpn.)

The numbers of the solvent of crystallization in **3** and **5** shown in the preparation section followed the result of the X-ray analysis. The number of protons in **5** was estimated based on the number of sulfate anions found in the X-ray analysis and the electric neutrality.

Results and Discussion

Bispicen Complexes: The green (**1**) and brown (**2**)

Table 1. Crystallographic Data

	3	**5**
Formula	$C_{28}H_{36}O_{12}S_3V_2·C_3H_7NO·0.375CH_4O·0.25H_2O$	$C_{26}H_{28}N_6O_4SV·0.75HSO_4·0{,}125SO_4·1.25H_2O$
Formula wt	964.34	678.20
Crystal system	Monoclinic	Orthorhombic
Space group	C_2/c (No. 15)	*Aba*2 (No. 41)
a/Å	25.083(7)	20.1836(8)
b/Å	24.236(5)	19.7933(13)
c/Å	15.708(5)	15.6107(7)
β/°	114.96(2)	
V/Å^3	8568(4)	6236.5(6)
Z	8	8
D_{calcd}/g cm^{-3}	1.48	1.25
Crystal size/mm	0.35 × 0.57 × 0.25	0.20 × 0.25 × 0.50
λ(Mo *Kα*)/Å	0.71073	0.71073
μ(Mo *Kα*)/cm^{-1}	6.2	4.6
Scan width/°	0.8+0.51 tan θ	0.6+0.50 tan θ
Temp/K	296	296
2θ range/°	0—60	0—60
Reflections		
Total	13384	4941
$F_o > 3\sigma(F_o)$	8229	2922
F(000)	3984	2452
No. of variables	544	389
$R^{a)}(R_w)^{b)}$	0.087 (0.095)	0.069 (0.071)

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

Table 2. Final Atomic Coordinates and Equivalent Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms of **3** ($B_{eq}=(8\pi^2/3)\Sigma\Sigma U_{ij}a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
V1	0.18951(4)	0.41771(4)	0.12643(6)	2.29(2)	C1p3	0.5032(3)	0.4047(3)	0.4863(5)	4.0(2)
V2	0.38502(4)	0.34600(4)	0.36540(6)	2.59(2)	C2p3	0.5597(3)	0.4267(4)	0.5161(6)	5.8(2)
S1	0.14826(6)	0.37061(6)	0.2435(1)	2.75(3)	C3p3	0.5922(4)	0.4139(4)	0.4658(7)	6.3(2)
S2	0.35839(7)	0.26553(6)	0.2330(1)	3.08(3)	C4p3	0.5686(3)	0.3787(4)	0.3912(6)	5.3(2)
S3	0.32896(7)	0.45635(6)	0.2413(1)	3.19(3)	C5p3	0.5126(3)	0.3574(3)	0.3666(5)	4.3(2)
O11	0.1951(2)	0.3509(2)	0.2146(3)	2.98(8)	N21	0.4036(2)	0.4122(3)	0.4694(4)	4.2(1)
O12	0.1373(2)	0.4266(2)	0.1981(3)	3.51(9)	N22	0.3070(2)	0.3522(2)	0.3930(3)	3.4(1)
O13	0.0964(2)	0.3371(2)	0.2032(3)	4.3(1)	C21	0.4661(3)	0.4152(4)	0.5390(5)	4.9(2)
O14	0.1711(2)	0.3749(2)	0.3434(3)	4.2(1)	C22	0.3648(3)	0.4133(4)	0.5192(5)	5.1(2)
O21	0.4161(2)	0.2925(2)	0.2939(3)	3.35(9)	C23	0.3042(3)	0.4033(4)	0.4451(5)	5.0(2)
O22	0.3189(2)	0.2958(2)	0.2677(3)	3.8(1)	C24	0.3012(3)	0.2988(4)	0.4371(5)	4.6(2)
O23	0.3418(2)	0.2778(2)	0.1364(3)	4.6(1)	N1p4	0.4051(2)	0.2872(2)	0.4722(3)	3.3(1)
O24	0.3607(3)	0.2073(2)	0.2524(4)	5.8(2)	C1p4	0.3610(3)	0.2739(3)	0.4963(4)	3.6(1)
O31	0.2685(2)	0.4424(2)	0.2275(3)	3.5(1)	C2p4	0.3685(3)	0.2360(4)	0.5670(5)	4.8(2)
O32	0.3632(2)	0.4042(2)	0.2623(3)	3.6(1)	C3p4	0.4235(4)	0.2126(4)	0.6149(5)	5.1(2)
O33	0.3542(3)	0.4921(2)	0.3212(4)	5.6(2)	C4p4	0.4685(3)	0.2247(3)	0.5901(5)	4.5(2)
O34	0.3279(2)	0.4799(2)	0.1565(3)	4.6(1)	C5p4	0.4578(3)	0.2627(3)	0.5178(5)	3.7(1)
N1p1	0.1676(2)	0.5065(2)	0.1148(3)	3.0(1)	N1d1	0.6600(5)	0.3315(5)	0.7287(8)	5.6(2)
C1p1	0.1640(3)	0.5343(3)	0.0390(4)	3.3(1)	O1d1	0.7262(8)	0.3069(9)	0.874(1)	7.7(5)
C2p1	0.1541(3)	0.5908(3)	0.0291(5)	4.4(2)	O2d1	0.577(1)	0.360(1)	0.751(2)	6.8(6)
C3p1	0.1479(3)	0.6201(3)	0.1003(5)	4.3(2)	C1d1	0.678(1)	0.385(1)	0.767(2)	6.3(6)
C4p1	0.1521(3)	0.5912(3)	0.1802(5)	4.0(2)	C2d1	0.617(1)	0.298(1)	0.664(2)	8.0(8)
C5p1	0.1622(3)	0.5349(3)	0.1840(4)	3.4(1)	C3d1	0.698(2)	0.304(3)	0.775(4)	11(2)
N11	0.2120(2)	0.4545(2)	0.0188(3)	3.1(1)	C4d1	0.629(2)	0.375(2)	0.752(3)	6.1(8)
N12	0.2274(2)	0.3497(2)	0.0795(3)	3.1(1)	C5d1	0.703(3)	0.351(3)	0.721(4)	11(2)
C11	0.1717(3)	0.4988(3)	−0.0342(4)	3.9(1)	N1d2	0.000	0.4636(7)	0.250	7.5(4)
C12	0.2187(3)	0.4125(3)	−0.0458(4)	4.3(1)	O1d2	0.448(2)	0.037(2)	0.231(3)	8(1)
C13	0.2568(3)	0.3672(3)	0.0189(4)	4.1(1)	O2d2	0.990(1)	0.477(1)	0.092(2)	8.4(8)
C14	0.1811(3)	0.3073(3)	0.0349(5)	4.3(2)	C1d2	0.014(1)	0.420(1)	0.301(2)	6.5(6)
N1p2	0.1137(2)	0.3833(2)	0.0200(3)	3.3(1)	C2d2	0.002(1)	0.452(1)	0.340(2)	6.7(6)
C1p2	0.1208(3)	0.3322(3)	−0.0095(5)	4.1(2)	C3d2	0.500	0.022(2)	0.250	6(1)
C2p2	0.0728(4)	0.3027(4)	−0.0752(6)	5.8(2)	C4d2	0.466(2)	0.003(2)	0.272(3)	6.5(9)
C3p2	0.0173(4)	0.3253(4)	−0.1082(6)	6.4(2)	O1m	0.4534(8)	0.4691(8)	0.736(1)	7.5(5)
C4p2	0.0099(3)	0.3777(5)	−0.0777(6)	6.1(2)	C1m	0.500	0.5019(9)	0.750	7.6(5)
C5p2	0.0587(3)	0.4055(3)	−0.0135(5)	4.4(2)	O1w	0.535(1)	0.349(1)	0.748(2)	7.4(7)
N1p3	0.4793(2)	0.3718(2)	0.4122(3)	3.2(1)					

vanadium(III) complexes were isolated in the reaction of VCl_3 with bispicen. The vanadium(III) ion can take a heptacoordinate structure as well as a normal hexacoordinate one. It has been proposed that the electronic spectrum is diagnostic to the coordination number of vanadium(III) complexes;[11,12] i.e., the heptacoordinate vanadium(III) complexes exhibit a band in the longer wavelength region (typically 700—900 nm), while hexacoordinate ones do not. Since the diffuse reflectance spectrum of **1** does not exhibit a band characteristic to heptacoordinate vanadium(III) complexes in the longer wavelength region, but shows a band at 582 nm and a shoulder at around 450 nm, **1** is likely to take a hexacoordinate structure. Taking the result of the elemental analysis into consideration, it is reasonably deduced that the green complex **1** is a hexacoordinate complex, formulated as $[VCl_2(bispicen)]Cl$.

The reflectance spectrum of **2** shows intense bands at 543 and 664 (shoulder) nm, which can be assigned to the charge-transfer (CT) transition of the V–O–V moiety.[12,13] Further, the Raman spectrum exhibits resonance-enhanced bands at 717 and 1423 cm^{-1} (Fig. 1(A)), which can also be assigned to the antisymmetric V–O–V stretching vibration and its overtone, respectively.[12—14] These spectral characteristics together with the elemental analysis indicate, therefore, that the brown complex **2** is an oxo-bridged dinuclear complex, $[V_2(\mu\text{-}O)Cl_2(bispicen)_2]Cl_2$.

The color of $[V_2(\mu\text{-}O)Cl_2(bispicen)_2]^{2+}$ changes slightly in water. The CT bands exhibit a blue-shift from 543 and 664 nm in the solid state to 496 and 600 nm, respectively. This shift would be due to an aquation of the coordinated chloro ligands. Contrary to the case of $[V_2(\mu\text{-}O)Cl_2(bispicen)_2]^{2+}$, the color of $[VCl_2(bispicen)]^+$ dramatically changes from light green to dark brown upon dissolving it in water. The visible absorption spectrum of this dark-brown solution exhibits intense bands at the same position as $[V(\mu\text{-}O)Cl_2(bispicen)_2]Cl_2$ in water. This indicates that aquation followed by olation of $[VCl_2(bispicen)]^+$ occurs to yield the oxo-bridged dinuclear complex.

The yellow complex (**3**) was obtained from the reaction in a dilute H_2SO_4 solution using sulfate as a counter anion.

Table 3. Final Atomic Coordinates and Equivalent Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms of **5** ($B_{eq}=(8\pi^2/3)\Sigma\Sigma U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}
V	0.76662(6)	0.21186(6)	0.275	2.85(2)
S	0.6887(1)	0.2802(1)	0.3866(2)	3.26(3)
O1	0.6720(3)	0.2422(3)	0.3039(4)	3.5(1)
O2	0.6810(4)	0.3508(3)	0.3751(5)	6.2(2)
O3	0.6529(3)	0.2526(4)	0.4572(4)	4.1(1)
O4	0.7611(3)	0.2611(3)	0.3902(4)	4.2(1)
N1	0.8277(4)	0.1378(4)	0.1997(5)	4.3(2)
N2	0.7062(4)	0.1917(4)	0.1544(4)	3.4(1)
C1	0.7907(6)	0.1090(5)	0.1239(6)	4.8(2)
C2	0.7503(5)	0.1643(5)	0.0863(6)	4.3(2)
N11	0.7463(4)	0.1157(4)	0.3336(5)	4.0(1)
C11	0.7846(6)	0.0625(5)	0.3097(6)	4.6(2)
C12	0.7707(7)	−0.0039(6)	0.3317(8)	6.4(3)
C13	0.7165(7)	−0.0157(6)	0.3797(7)	6.1(3)
C14	0.6755(6)	0.0384(5)	0.4077(6)	5.3(2)
C15	0.6921(5)	0.1031(5)	0.3829(6)	4.4(2)
C16	0.8459(5)	0.0821(5)	0.2600(8)	5.4(2)
N21	0.8724(3)	0.2284(4)	0.3074(5)	4.2(2)
C21	0.9168(4)	0.2091(6)	0.2456(7)	4.7(2)
C22	0.9835(5)	0.2220(6)	0.2552(9)	6.5(3)
C23	1.0070(5)	0.2556(8)	0.3248(9)	7.1(3)
C24	0.9618(5)	0.2764(6)	0.3850(9)	5.9(3)
C25	0.8944(5)	0.2612(5)	0.3766(6)	4.7(2)
C26	0.8893(5)	0.1737(6)	0.1721(8)	5.2(2)
N31	0.7775(4)	0.3032(4)	0.1975(5)	3.6(1)
C31	0.7338(5)	0.3107(4)	0.1324(6)	3.9(2)
C32	0.7348(6)	0.3657(5)	0.0788(7)	5.2(2)
C33	0.7821(6)	0.4155(5)	0.0911(7)	5.2(2)
C34	0.8269(6)	0.4084(5)	0.1578(8)	6.0(3)
C35	0.8239(5)	0.3514(5)	0.2084(7)	4.6(2)
C36	0.6803(5)	0.2574(5)	0.1248(6)	3.9(2)
N41	0.6269(5)	0.0718(5)	0.0500(6)	6.2(2)
C41	0.6063(6)	0.1266(5)	0.0972(7)	5.2(2)
C42	0.5496(6)	0.1624(6)	0.0786(9)	6.9(3)
C43	0.5087(8)	0.1402(7)	0.012(1)	8.8(4)
C44	0.5303(7)	0.0825(7)	−0.039(1)	8.6(4)
C45	0.5880(8)	0.0536(7)	−0.0167(9)	8.8(4)
C46	0.6493(5)	0.1437(5)	0.1738(6)	4.2(2)
O1w	0.0731(8)	0.0695(8)	0.300(1)	11.8(6)
O2w	0.000(1)	0.468(1)	0.284(2)	15.2(9)
S2	0.0571(2)	0.0827(2)	0.0640(4)	8.7(1)
O21	0.0637(7)	0.1435(7)	0.090(1)	11.5(4)[a]
O22	0.0826(9)	0.0275(9)	0.083(1)	14.9(6)[a]
O23	−0.0109(8)	0.0754(8)	0.026(1)	10.7(4)[a]
O24	0.094(1)	0.095(1)	−0.020(1)	9.8(6)[a]
O25	0.022(1)	0.061(1)	0.157(2)	11.1(7)[a]

a) Isotropic thermal parameters (B/Å^2).

An X-ray structural analysis reveals that **3** contains a sulfate-bridged dimeric unit. Figures 2(A) and 2(B) show perspective views around V1 and the bridging moiety, respectively, of **3**. Two of the three sulfate ions in **3** coordinate to each vanadium center as a didentate ligand and the other sulfate ion bridges two vanadium centers. Each vanadium center adopts a heptacoordination, which is distinct from the hexacoordination of the chloro complex, $[VCl_2(bispicen)]Cl$. The geometries around each vanadium atom are essentially the same.

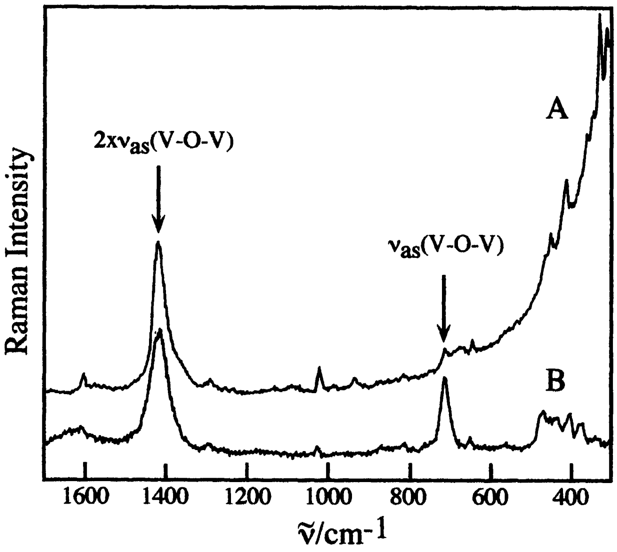

Fig. 1. Resonance Raman spectra of **2** in KBr disk (A) and of the aqueous solution (0.85 mmol dm^{-3}, pH 3.5) of **3** (B).

The heptacoordinate vanadium(III) complexes can take a capped trigonal prism,[15,16] a capped octahedron,[17] or a pentagonal bipyramid.[11] As shown in Fig. 2(A), the vanadium(III) atom in **3** is present in a distorted pentagonal bipyramidal structure. Namely, one oxygen atom (O31) of the bridging sulfate ion and a pyridyl nitrogen atom (N1p2) occupies the apical positions. The two oxygen atoms of the didentate sulfate (O12 and O13), the two amino nitrogen atoms (N11 and N12), and one pyridyl nitrogen atom (N1p1) of bispicen complete the pentagonal plane. The deviations of these atoms from the least-squares pentagonal plane are −0.247(4) Å (O11), 0.282(4) Å (O12), −0.184(5) Å (N1p1), 0.0512(5) Å (N11), and 0.098(5) Å (N12), and the V1 atom locates at −0.0343(9) Å on this pentagonal plane. Similar deviations are also discerned for the other V2 species: O21, −0.122(4) Å; O22, 0.184(5) Å; N1p3, 0.010(5) Å; N21, 0.086(6) Å; N22, −0.158(5) Å, and V2, 0.037(1) Å. Then, the coordination polyhedron adopted by the vanadium atoms in $[V_2(SO_4)_3(bispicen)_2]$ can be described as a distorted pentagonal bipyramid.

Figure 3 shows the reflectance spectrum of $[V_2(SO_4)_3(bispicen)_2]$ in the solid state. The spectrum exhibits a band at 850 nm, being consistent with the criterion for the heptacoordinate vanadium(III) stated above.[11,12]

Table 4 lists the selected bond distances and angles around V1 of $[V_2(SO_4)_3(bispicen)_2]$. The dimensions around V2 are not significantly different from those around V1. The distance between V1 and N1p1 (the pyridyl nitrogen in the pentagonal plane) is longer than that between V1 and N1p2 (the pyridyl nitrogen in the axial position). Further, it is reasonable that the didentate sulfate ligand with a small bite angle is preferentially located in the equatorial plane. These are consistent with a pentagonal bipyramidal structure.

In $[V_2(SO_4)_3(bispicen)_2]$, the linear tetradentate bispicen ligand binds the vanadium(III) center in an unsymmetrical

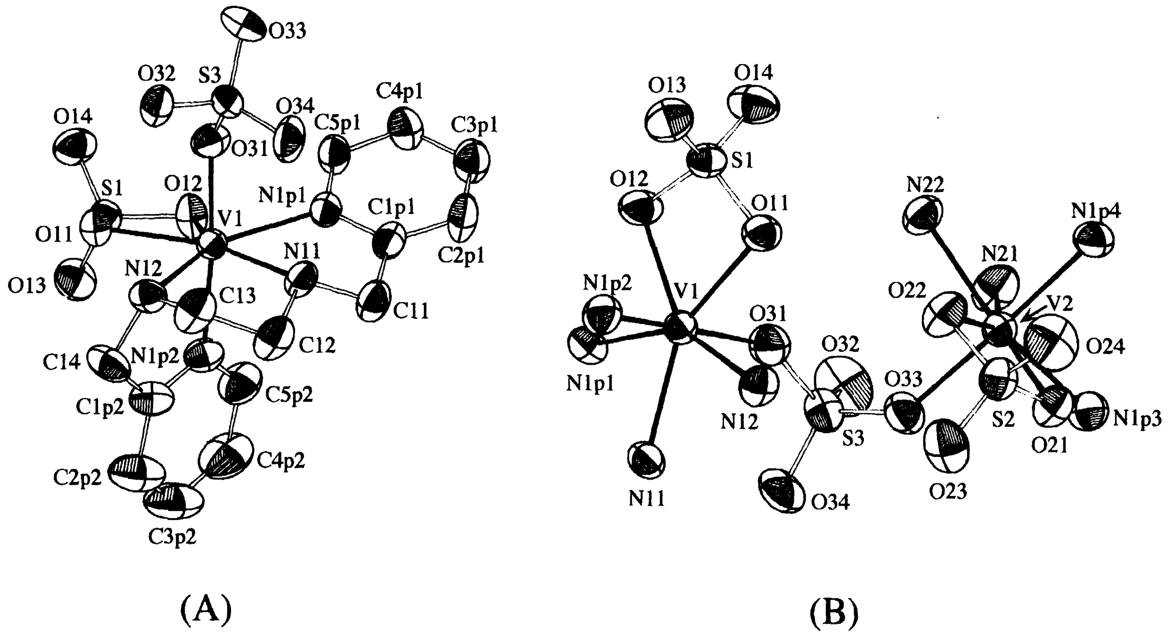

Fig. 2. Perspective views of $[V_2(SO_4)_3(bispicen)_2]$ in **3**. A, around V1; B, the bridging moiety.

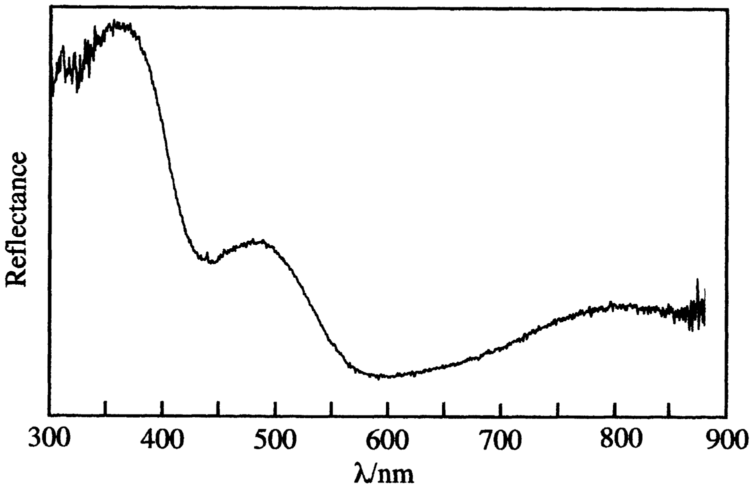

Fig. 3. Diffuse reflectance spectrum of **3**.

Table 4. Selected Bond Distances (Å) and Angles (degree) for **3**

	Bond distances		
V1–O11	2.096(4)	V1–O12	2.067(5)
V1–O31	2.038(4)	V1–N1p1	2.209(5)
V1–N11	2.185(6)	V1–N12	2.180(6)
V1–N1p2	2.104(4)		
	Bond angles		
O31–V1–O11	86.6(2)	N11–V1–N12	75.9(2)
O31–V1–O12	100.1(2)	N12–V1–O11	73.8(2)
O31–V1–N1p1	84.5(2)	N1p2–V1–O11	90.2(2)
O31–V1–N11	90.0(2)	N1p2–V1–O12	84.6(2)
O31–V1–N12	93.8(2)	N1p2–V1–N1p1	102.2(2)
O11–V1–O12	66.6(2)	N1p2–V1–N11	89.4(2)
O12–V1–N1p1	75.5(2)	N1p2–V1–N12	78.9(2)
N1p1–V1–N11	71.0(2)		

fashion that corresponds to the *cis-β* form in an octahedral complex. For octahedral complexes, the symmetric *cis-α* coordination is regarded as being the most stable coordination mode for linear tetradentate ligands that form solely five-membered chelate rings. This is exemplified by manganese,[18—22] chromium,[23] and iron[24] complexes with bispicen and its *N*-methyl substituted derivative. The only example of the *cis-β* coordination of bispicen has been found in $[Cr_2(\mu\text{-}OH)_2(bispicen)_2](ClO_4)_4$, which contains one *cis-α* skeleton and one *cis-β* skeleton.[25] Since the vanadium(III) complexes are substitution labile, the bispicen ligand should coordinate to the vanadium(III) center in the most stable mode and, therefore, the *cis-β* coordination mode is considered to be more favorable than the *cis-α* one in the pentagonal bipyramidal complex.

Similarly to $[VCl_2(bispicen)]Cl$, the heptacoordinate yellow bispicen-SO_4^{2-} complex, $[V_2(SO_4)_3(bispicen)_2]$, changes immediately to a dark-brown species in water. This solution exhibits an intense band at 504 nm in the visible absorption spectrum, indicating the formation of an oxo bridge. The resonance Raman spectrum, which corresponds well to that of $[\mathrm{V_2(\mu\text{-}O)Cl_2(bispicen)_2}]\mathrm{Cl_2}$ in the solid state, also confirms the formation of the oxo-bridged dinuclear species in water (Fig. 1(B)). In order to know whether the heptacoordinate species containing a didentate sulfate would exist in aqueous solution, the pH dependence of the absorption spectrum was examined for $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$ in an aqueous solution containing a large excess of sulfate (Fig. 4). The intensity of the 504-nm band, which is due to the charge-transfer transition of the V–O–V moiety,[12,13] decreases with decreasing the pH of the solution. At pH 2.70, the 504-nm band becomes extinct, indicating that the concentration of the oxo-bridged dimer is negligible. The band at 850 nm is not detectable even in this condition. The non-resonance Raman spectrum of $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$ in water, obtained by excitation with a YAG laser (1064 nm), exhibits a band at 983 $\mathrm{cm^{-1}}$ due to a free sulfate ion. These observations suggest that the coordinated sulfate ions in $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$ are likely to be displaced by water molecules to yield a hexacoordinate species in aqueous solution.

Contrary to the aqueous solution, the solution of $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$ in 99% DMF clearly exhibits a band at 850 nm, as depicted in the inset of Fig. 4, indicating that the heptacoordinate structure is preserved in the DMF solution of a low water content.

Tpen Complexes: The mononuclear complexes with tpen or tpen derivatives have been characterized crystallographically for $[\mathrm{Ni(tpen)}](\mathrm{ClO_4})_2\cdot 2/3\mathrm{H_2O}$,[26] $[\mathrm{Fe(tpen)}](\mathrm{ClO_4})_2\cdot n\mathrm{H_2O}$ (n=0 or 2/3),[27] and $[\mathrm{Fe(mtpen)}](\mathrm{ClO_4})_2\cdot 2/3\mathrm{H_2O}$ (mtpen=*N*- 6- methyl- 2- pyridylmethyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethylenediamine).[28] The pentadentate coordination of the tpen derivative has been found in $[\mathrm{Fe(H_2O)L}](\mathrm{PF_6})_2\cdot\mathrm{H_2O}$ (L=*N*,*N*′- bis(6- methyl- 2- pyridylmethyl)- *N*,*N*′- bis(2- pyridylmethyl)ethylenediamine).[29] These complexes all have a hexacoordinate octahedral structure. Furthermore, it is known that tpen tends to act as a bridging ligand together with additional bridging groups, such as hydroxide, oxide, or carboxylate, giving dinuclear complexes; e.g., $[\mathrm{(VO)_2(\mu\text{-}OH)(tpen)}]^{2+}$,[30] $[\mathrm{Cr_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(tpen)}]^{3+}$,[31] $[\mathrm{Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2CCH_3)(tpen)}]^{3+}$,[32,33] and $[\mathrm{(MO)_2(\mu\text{-}O)_2(tpen)}]^{2+}$ (M=Mo and W).[34] Although a dinuclear vanadium(III)–tpen complex without any additional bridging groups has been reported and formulated as $[\mathrm{V_2Cl_6(tpen)}]$,[30] its structure has not been well characterized.

The purple vanadium(III)–tpen complex **4** obtained here shows intense CT absorption bands at 492 nm and a shoulder at around 605 nm, that are characteristic to the oxo-bridged dinuclear vanadium(III) complex.[12,13] The resonance Raman spectrum also exhibits bands due to ν_{as} (V–O–V) and $2\times\nu_{\mathrm{as}}$ (V–O–V) at 692 and 1367 $\mathrm{cm^{-1}}$, respectively. These spectral features together with the elemental analysis indicate that **4** can be formulated as $[\mathrm{V_2(\mu\text{-}O)Br_4(tpen)}]$.

Figure 5 depicts the perspective view of the complex cation, $[\mathrm{V(SO_4)(tpen)}]^+$, in **5**. The sulfate ligand binds to the vanadium center as a didentate ligand, and tpen acts as a pentadentate ligand with a pendant pyridyl group. The vanadium center adopts a heptacoordinate pentagonal bipyramidal structure similar to $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$. The pentagonal plane of $[\mathrm{V(SO_4)(tpen)}]^+$ is completed by the didentate sulfate (O1 and O4), and one pyridyl group (N21) and the diamine ring (N1 and N2) of the tpen ligand. The deviations of these atoms from the least-square pentagonal plane are −0.124(6) Å (O1), −0.151(6) Å (O2), 0.381(8) Å (N21), −0.449(8) Å (N1), and 0.343(7) Å (N2), and the V atom locates at −0.042(1) Å on this pentagonal plane. As summarized in Table 5, the dimensions of the coordination polyhedron of $[\mathrm{V(SO_4)(tpen)}]^+$ correspond well to those found in $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$. Recently, the X-ray structure of $[\mathrm{Fe^{II}(SO_4)(tpen)}]$ has been reported briefly,[35] though this complex has a hexacoordinate structure with a monodentate sulfate ligand.

Contrary to $[\mathrm{V_2(SO_4)_3(bispicen)_2}]$, the heptacoordinate structure of $[\mathrm{V(SO_4)(tpen)}]^+$ is stable, even in an aqueous

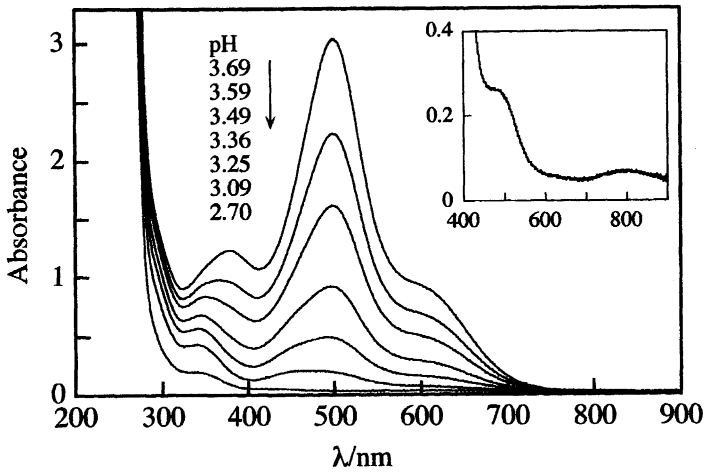

Fig. 4. Absorption spectra of **3** as a function of pH ($[\mathrm{V^{3+}}]$=0.002 mol dm^{-3} and $[\mathrm{SO_4^{2-}}]$=0.67 mol dm^{-3}). The inset; absorption spectrum of **3** in 99% dimethylformamide.

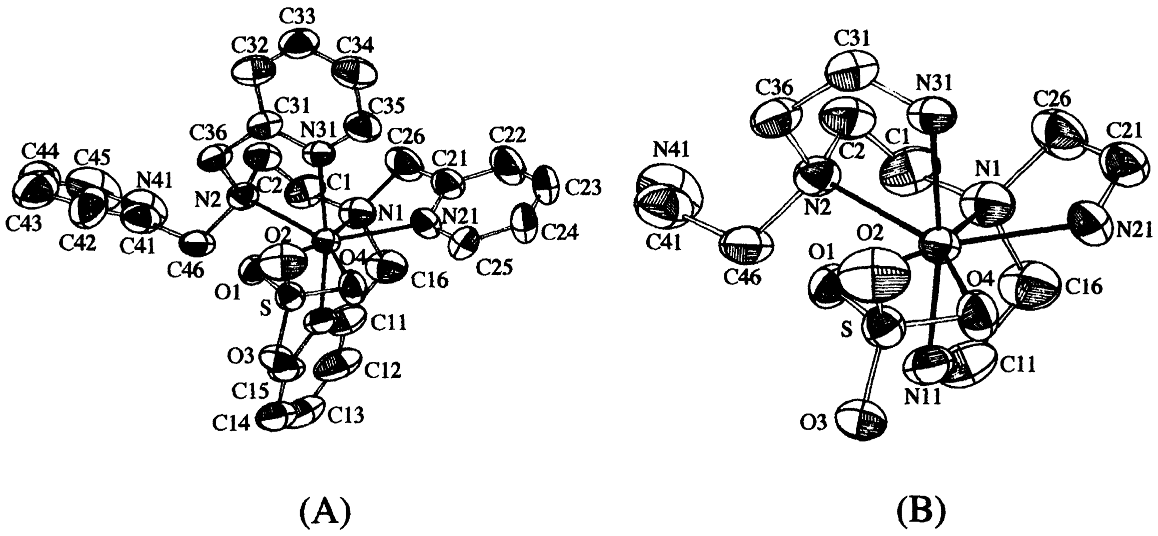

Fig. 5. A, perspective view of the complex cation in **5**; B, pyridine rings are omitted for clarity.

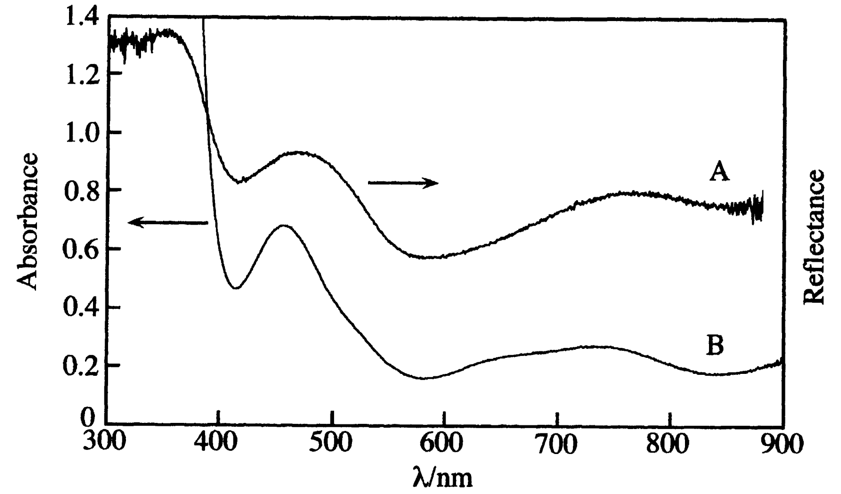

Fig. 6. Diffuse reflectance (A) and absorption (24 mmol dm^{-3}, pH 2.94) (B) spectra of **5**.

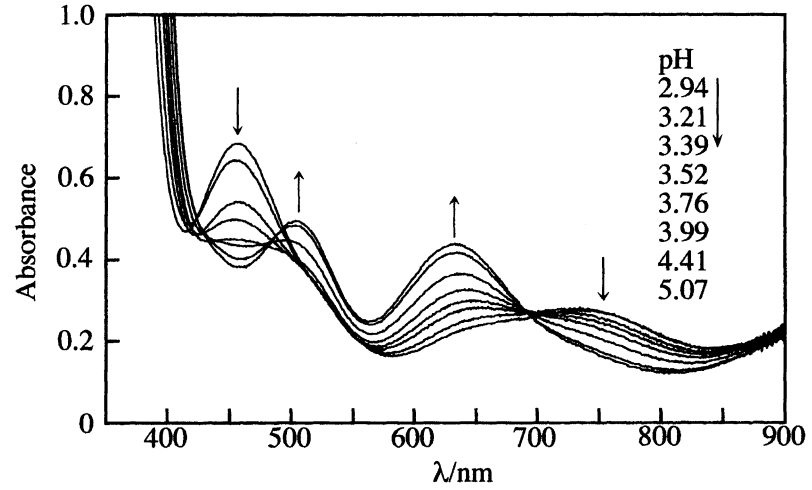

Fig. 7. Absorption spectra of **5** (25 mmol dm^{-3}) as a function of pH.

solution. As shown in Fig. 6, the absorption spectrum of **5** in an aqueous solution corresponds well to the reflectance spectrum in the solid state, suggesting that the heptacoordinate complex is still a dominant species in an aqueous solution.

Table 5. Selected Bond Distances (Å) and Angles (degree) for **5**

	Bond distances		
V–O1	2.053(6)	V–N31	2.188(7)
V–O4	2.050(6)	S–O1	1.532(6)
V–N1	2.248(8)	S–O2	1.418(7)
V–N2	2.280(7)	S–O3	1.428(7)
V–N11	2.152(7)	S–O4	1.511(6)
V–N21	2.219(7)		
	Bond angles		
O1–V–O4	67.5(2)	N1–V–N2	75.3(3)
O1–V–N1	144.8(3)	N1–V–N11	75.5(3)
O1–V–N2	74.7(2)	N1–V–N21	71.8(3)
O1–V–N11	89.3(3)	N1–V–N31	101.2(3)
O1–V–N21	143.3(3)	N2–V–N11	95.4(3)
O1–V–N31	88.5(3)	N2–V–N21	136.8(3)
O4–V–N1	143.1(3)	N2–V–N31	75.0(3)
O4–V–N2	141.3(2)	N11–V–N21	102.5(3)
O4–V–N11	92.1(3)	N11–V–N31	170.4(3)
O4–V–N21	77.4(3)	N21–V–N31	84.7(3)
O4–V–N31	95.6(3)		

A close examination of the absorption spectrum, however, indicates that weak additional bands appear at around 500 and 630 nm. In order to obtain information concerning the species in aqueous solution, the pH dependence of the absorption spectrum of $[V(SO_4)(tpen)]^+$ was examined. We pointed out earlier for the aminopolycarboxylate complexes of vanadium(III) that the hexacoordinate complexes yield an oxo-bridged dinuclear complex on base hydrolysis, while the heptacoordinate ones do not.[12] As shown in Fig. 7, the intensities of the additional bands at 506 and 633 nm increase with increasing the pH of the solution, while those of the bands at 458 and 744 nm decrease. This spectral change somewhat resembles that found for the heptacoordinate edta complex, $[V(edta)(H_2O)]^-$.[12] In the case of the edta complex, the bands at 421 and 804 nm become weakened while the bands at 496 and 700 nm grow with increasing the pH of the solution. This spectral change of the edta complex has been explained by hydrolysis of the coordinated aqua ligand. Furthermore, in contrast to $[V_2(SO_4)_3(bispicen)_2]$, $[V(SO_4)(tpen)]^+$ does not exhibit an intense charge-transfer band due to an oxo-bridged dimer, even at higher pHs, as in the case of $[V(edta)(H_2O)]^-$. The above properties of **5** in water imply that the heptacoordinate structure is preserved even at a higher pH region. Then, the heptacoordinate complexes containing a hexadentate tpen, [V(tpen)a] (a=monodentate SO_4^{2-}, OH_2, or OH^-), in addition to the cation in **5** are species that are likely to exist in a solution of the vanadium(III)–tpen-SO_4^{2-} system.

In order to compare the properties of the V^{3+}–tpen-SO_4^{2-} complex with those of V^{3+}–tpen-X^- (X=halogen), we have attempted to isolate a mononuclear tpen complex using chloride or bromide as a counter ion. This attempt has not been successful so far. It must be emphasized, however, that the V^{3+}–tpen-X^- (X=Cl or Br) system shows the absorption spectral behavior completely different from those for the V^{3+}–tpen-SO_4^{2-} system. A reaction between VX_3 (X=Cl or Br) and tpen in 1 : 1 molar ratio develops a deep-purple color, and the absorption maxima agrees with that of the purple tpen complex **4**, indicating the formation of the $V_2(\mu$-O)(tpen) species. The CT band due to the V–O–V moiety can be discerned even at pH 1.2. On the other hand, the CT band was not observed in the V^{3+}–tpen-SO_4^{2-} system, as stated above. This fact suggests a pronounced effect of sulfate to suppress the formation of the oxo-bridged dinuclear complex.

Heptacoordination of Vanadium(III) Complex: The heptacoordinate structure has been found in several vanadium(III) complexes containing an aminopolycarboxylate ligand, such as edta,[15] cydta,[16] and nta.[17] It has been considered that the heptacoordination of these complexes results from the insufficiently large chelate-ring system of the aminopolycarboxylates to encircle the vanadium(III) center. In other words, the above multidentate ligands enforce the vanadium(III) center to adopt a heptacoordinate structure. In the present bispicen system, however, the bispicen ligand does not compel the heptacoordinate structure to the vanadium atom, as evidenced from the existence of the hexacoordinate bispicen complexes, $[VCl_2(bispicen)]Cl$ and $[V_2(\mu$-$O)Cl_2(bispicen)_2]Cl_2$. Therefore, the heptacoordinate structure of $[V_2(SO_4)_3(bispicen)_2]$ can be considered to be a consequence of the didentate coordination of the sulfate ligand. The present result indicates that sulfate binding can possibly change the coordination number of vanadium(III) complexes.

In the tpen system, the heptacoordinate structure seems to exist without a didentate coordination of sulfate, indicating that the coordination of tpen is mainly responsible for the heptacoordinate structure. As indicated in the previous section, however, it appears that the sulfate ion seems to play a role in stabilizing the monomeric heptacoordinate structure.

Since tunicate blood cells contain a large amount of sulfate together with vanadium(III), and have a high acidity (pH 2—4),[36] the present findings would be of importance with regard to the status of the vanadium(III) ion in tunicate.

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