4308 *Inorg. Chem.* **1992**, *31*, 4308–4313

Complexes of Vanadium(III) and Vanadium(IV) Containing Bipyridine and Tetrachlorocatecholate Ligands. Insights into the Tunicate Vanadium(III) Coordination Environment

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Received March 26, 1992

The reaction between $V(acac)_3$, tetrachlorocatechol, and bipyridine has been found to give $V(bpy)(Cl_4Cat)_2$. Crystallographic characterization on the complex [triclinic, space group $P\bar{1}$, $a = 7.911$ (2) Å, $b = 8.982$ (2) Å, $c = 17.981$ (3) Å, $\alpha = 80.05$ (1)°, $\beta = 88.60$ (1)°, $\gamma = 88.76$ (2)°, $V = 1257.9$ (5) Å^3, $Z = 2$, $D_{calcd} = 1.845$ g cm^{-3}, $R = 0.065$ and $R_w = 0.076$ for 2914 observed reflections] has shown that the complex molecule has a trigonal prismatic structure with a twist angle between triangular faces of 3.2°. The complex appears to result from oxidation of V(III) species formed initially in the reaction. More immediate product isolation gave $V(bpy)(acac)(Cl_4Cat)$. Crystallographic characterization of a thin platelike crystal of the complex obtained as a dichloromethane solvate, $V(bpy)(acac)(Cl_4Cat)\cdot CH_2Cl_2$ [monoclinic, $P2_1/n$, $a = 13.864$ (3) Å, $b = 8.407$ (2) Å, $c = 22.898$ (5) Å, $\beta = 90.87$ (2)°, $V = 2668.6$ (10) Å^3, $Z = 4$, $D_{calcd} = 1.581$ g cm^{-3}, $R = 0.056$ and $R_w = 0.074$ for 896 observed reflections], has shown that the complex molecule is octahedral and monomeric in structure. Addition of the PPh_4^+ cation to the reaction mixture described above gave crystals of $(PPh_4)[V(bpy)(Cl_4Cat)_2]$, the V(III) analog of $V(bpy)(Cl_4Cat)_2$. The anion was also formed as the $CoCp_2^+$ salt by cobaltocene reduction of the neutral V(IV) complex. Electrochemical characterization on both $V(bpy)(Cl_4Cat)_2$ and $V(bpy)(Cl_4Cat)_2^-$ has shown that the V(III)/V(IV) couple occurs at −0.50 V (vs Fc/Fc$^+$). Attempts at displacing the Cl_4Cat ligands from both the V(III) and V(IV) forms of the complex with excess bipyridine failed. The implications of this observation to the characterization of tunicate V(III) are discussed.

Introduction

The coordination chemistry of vanadium with catecholate and semiquinonate ligands is rich and interesting. Shilov has reported that species containing V(II) complexed with catechol are highly reductive and capable of reducing dinitrogen to ammonia.[1] Catechol oxidation reactions have been reported for complexes containing vanadium in a higher oxidation state.[2] Some of the most intriguing vanadium–catechol chemistry that has been carried out recently has been in the context of studies on vanadium tunichrome model complexes.[3,4] Tunicates have the ability to sequester vanadium in unusually high concentrations.[5,6] Blood cell concentrations of the metal approach 0.10 M, an increase of 10^8 over the concentration of V(V) in sea water.[7] The coordination environment remains unknown, but studies have shown that vanadium concentrations are associated with concentrations of a class of organic molecules known as tunichromes.[8] The tunichromes have catechol and pyrogallol functionalities that make them ideally suited for metal ion coordination.[3,5,9,10] Vanadium has been shown to have a high affinity for catecholate oxygen donor ligands and it is not unreasonable to imagine that the tunichromes chelate with vanadium as polycatecholate ligands.[3,5] The metal is stored as V(III) with a small fraction in the form of V(IV).[11,12] It is surprising that the metal is present in such a reduced form, and when it is coordinated with catecholate oxygens, nucleophilicity is enhanced.[3,13] An assay used by Hawkins to study the distribution and oxidation state of the metal takes advantage of the intense visible transitions of $[V(bpy)_2Cl]_2O^{2+}$ formed when cells containing the metal are treated with 2,2′-bipyridine.[12,14] This implies either that vanadium may be displaced from its catecholate coordination environment by the nitrogen donor ligand or that a significant quantity of the vanadium is complexed by other ligands that render the metal ion more accessible to the bipyridine. We now report complexes of V(III) and V(IV) containing bipyridine and tetrachlorocatecholate ligands along with the results of a competitive bonding study.

Experimental Section

Materials. Tetrachlorocatechol (H_2Cl_4Cat) was prepared by the chlorination of catechol and sublimed before use. 2,2′-Bipyridine (bpy) and tris(acetylacetonato)vanadium(III) ($V(acac)_3$) were purchased from Aldrich and used as received.

$V(bpy)(Cl_4Cat)_2$. $V(acac)_3$ (1.08 g, 3.0 mmol) and 2,2′-bipyridine (0.471, 3.0 mmol) were dissolved in dichloromethane (40 mL), and

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(1) Isalva, S. A.; Nikonova, L. A.; Shilov, A. E. *Nouv. J. Chim.* **1981**, *5*, 21.

(2) (a) Tatsuno, Y.; Nakamura, C.; Saito, T. *J. Mol. Catal.* **1987**, *42*, 57. (b) Casellato, U.; Tamburini, S.; Vigato, P. A.; Vidali, M.; Fenton, D. E. *Inorg. Chim. Acta* **1984**, *84*, 101. (c) Galeffi, B.; Postel, M.; Grand, A.; Rey, P. *Inorg. Chim. Acta* **1989**, *160*, 87.

(3) (a) Bulls, A. R.; Pippin, C. G.; Hahn, F. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 2627. (b) Kime-Hunt, E.; Spartalian, K.; Carrano, C. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1270.

(4) Hawkins, C. J.; Kabanos, T. A. *Inorg. Chem.* **1989**, *28*, 1084.

(5) Smith, M. J.; Kim, D.; Horenstein, B.; Nakanishi, K.; Kustin, K. *Acc. Chem. Res.* **1991**, *24*, 117.

(6) Kustin, K.; Robinson, W. E.; Smith, M. J. *Invertebr. Reprod. Dev.* **1990**, *17*, 1.

(7) (a) Macara, I. G.; McLeod, G. C.; Kustin, K. *Comp. Biochem. Physiol., B: Comp. Biochem.* **1979**, *63B*, 299. (b) Hawkins, C. J.; James, G. A.; Parry, D. L.; Swinehart, J. H.; Wood, A. L. *Comp. Biochem. Physiol.* **1983**, *76B*, 559.

(8) Oltz, E. M.; Pollack, S.; Delohery, T.; Smith, M. J.; Ojika, M.; Lee, S.; Kustin, K.; Nakanishi, K. *Experientia* **1989**, *45*, 186.

(9) (a) Oltz, E. M.; Bruening, R. C.; Smith, M. J.; Kustin, K.; Nakanishi, K. *J. Am. Chem. Soc.* **1988**, *110*, 6162. (b) Lee, S.; Frankel, R.; Chang, M.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1988**, 785.

(10) Hawkins, C. J. *Pure Appl. Chem.* **1988**, *60*, 1267.

(11) Lee, S.; Kustin, K.; Robinson, W. E.; Frankel, R. B.; Spartalian, K. *J. Inorg. Biochem.* **1988**, *33*, 183.

(12) Brand, S. G.; Hawkins, C. J.; Marshall, A. T.; Nette, G. W.; Parry, D. L. *Comp. Biochem. Physiol.* **1989**, *93B*, 425.

(13) Cooper, S. R.; Koh, Y. G.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(14) Brand, S. G.; Edelstein, N.; Hawkins, C. J.; Shalimoff, G.; Snow, M. R.; Tiekink, E. R. T. *Inorg. Chem.* **1990**, *29*, 434.

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tetrachlorocatechol (1.60 g, 6.0 mmol) dissolved in dichloromethane (30 mL) was added dropwise under an atmosphere of Ar over the period of 1 h. A fine red-brown precipitate formed that was later identified as polymeric $VO(bpy)(Cl_4Cat)$. The precipitate was filtered from the solution, and the filtrate was slowly evaporated to a small volume, giving dark blue-green plates of $V(bpy)(Cl_4Cat)_2$. Yields for the reaction were variable and dependent upon the quantity of $VO(bpy)(Cl_4Cat)$ precipitate formed.

Anal. Calcd for $C_{22}H_8N_2O_4Cl_8V$: C, 37.81; H, 1.15; N, 4.01. Found: C, 38.58; H, 1.16; N, 4.08.

IR (KBr, cm^{-1}): 1447 (m), 1265 (s), 1250 (sh), 997 (m), 810 (m), 791 (m), 768 (m), 602 (m).

$V(bpy)(acac)(Cl_4Cat)$. The reaction to form $V(bpy)(Cl_4Cat)_2$ was repeated with the difference that the solution containing tetrachlorocatechol was added over the period of a few minutes and the solution was reduced in volume over a short period of time without filtration. The concentrated solution was then filtered to remove $VO(bpy)(Cl_4Cat)$ and $V(bpy)(Cl_4Cat)_2$, and the filtrate was evaporated to give thin purple plates of $V(bpy)(acac)(Cl_4Cat)$ formed as a dichloromethane solvate.

Anal. Calcd for $C_{22}H_{17}N_2O_4Cl_6V$: C, 43.43; H, 2.71; N, 4.71. Found: C, 43.65; H, 2.94; N, 4.54.

IR (KBr, cm^{-1}): 1569 (m, br), 1519 (m, br), 1434 (s), 1376 (m), 1357 (m, br), 1253 (m), 979 (m), 809 (m), 785 (m), 769 (m), 734 (m).

$VO(bpy)(Cl_4Cat)$. $VO(acac)_2$ (0.53 g, 2.0 mmol) and 2,2′-bipyridine (0.62 g, 4.0 mmol) were dissolved in tetrahydrofuran (100 mL). A solution of tetrachlorocatechol (1.06 g, 4.0 mmol) in tetrahydrofuran (30 mL) was added dropwise. The solution was stirred for several hours, and the dark red-brown precipitate of $VO(bpy)(Cl_4Cat)$ was separated from the solution by filtration (0.90 g, 95% yield).

Anal. Calcd for $C_{16}H_8N_2O_3Cl_4V$: C, 40.98; H, 1.72; N, 5.97. Found: C, 41.76; H, 1.75; N, 5.84.

IR (KBr, cm^{-1}): 1443 (s, sh), 1430 (vs), 1250 (m), 981 (m), 885 (s, br), 810 (m), 788 (m), 763 (m), 733 (m).

$(CoCp_2)[V(bpy)(Cl_4Cat)_2]$. $V(bpy)(Cl_4Cat)_2$ (0.154 g, 0.221 mmol) and cobaltocene (0.040 g, 0.21 mmol) were combined in a N_2-filled glovebox and dissolved in 50 mL of tetrahydrofuran. During a period of several hours, a green-brown precipitate of $(CoCp_2)[V(bpy)(Cl_4Cat)_2]$ separated from the solution. The complex was isolated by filtration and dried under a flow of dry Ar.

$(PPh_4)[V(bpy)(Cl_4Cat)_2]$. $V(acac)_3$ (1.045 g, 3.0 mmol), 2,2′-bipyridine (0.47 g, 3.0 mmol), and $(PPh_4)Br$ were dissolved in dichloromethane (80 mL) under N_2. Tetrachlorocatechol (1.60 g, 6.0 mmol) dissolved in CH_2Cl_2 (50 mL) was added with stirring. The volume of the solution was reduced with a slow flow of Ar, and the complex crystallized from solution as green-brown plates. Chemical analyses indicated that the complex crystallized as a dichloromethane solvate, $(PPh_4)[V(bpy)(Cl_4Cat)_2]\cdot 2CH_2Cl_2$.

Anal. Calcd for $C_{48}H_{32}N_2O_4PCl_{12}V$: C, 47.72; H, 2.67; N, 2.32. Found: C, 47.24; H, 2.58; N, 2.30.

Physical Measurements. Electronic spectra were recorded either on a Perkin-Elmer Lambda 9 spectrophotometer or on a Hewlett Packard 8451A diode array spectrophotometer. Infrared spectra were obtained on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer-controlled electroanalysis system; solution rest potentials were determined using a PAR potentiostat. A platinum-disk working electrode and a platinum-wire counter electrode were used. A Ag/Ag^+ reference electrode was used that consisted of an *n*-butanenitrile solution of $AgNO_3$ in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport for measurements made in acetonitrile. Tetrabutylammonium tetrafluoroborate was used as the supporting electrolyte, and the ferrocene/ferrocenium couple was used as an internal standard. With this experimental arrangement the Fc/Fc^+ couple appeared at 0.013 V (vs Ag/Ag^+). Measurements made in dichloromethane solution were referenced to a Ag/Ag^+ electrode prepared with $AgPF_6$ with tetrabutylammonium hexafluorophosphate used as the electrolyte. In this case, the Fc/Fc^+ couple appeared at 0.270 V. X-Band EPR spectra were recorded on a Varian E-109E spectrometer using a 100-kHz modulation frequency and calibrated with the DPPH resonance at a g value of 2.0037.

Crystallographic Structure Determination of $V(bpy)(acac)(Cl_4Cat)$. Dark purple crystals of $V(bpy)(acac)(Cl_4Cat)$ were obtained as layered thin plates upon crystallization from dichloromethane. Peak scans indicated that the crystals formed as intimate twins. A fragment from a cluster of plates was found to be a single crystal, but with small volume due to the thin platelike crystal habit. After extensive study of several crystalline samples of the complex, including samples recrystallized from different solvents, this crystal was judged to be the most suitable for crystallographic study, despite its marginal quality. At the outset of this investigation, the form of the complex was unknown. It was hoped that the structure determination would establish composition and provide, at least, gross features of molecular structure. The crystal was coated with an amorphous resin to retard decomposition in air. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table I. Data were collected by θ–2θ scans on a Seimens P3 diffractometer within the angular range 3.0–40.0° over two independent quadrants. Few observations appeared above a 2θ value of 35°, and further data collection above 40° seemed futile. The 896 observed averaged reflections were sufficient to solve the structure and to allow anisotropic refinement of heavy atoms and atoms within the coordination sphere. Atom locations were determined using direct methods. A molecule of dichloromethane appeared on final difference Fourier maps and was included in the refinement. Final cycles of least-squares refinement converged with discrepancy indices of R = 0.056 and R_w = 0.074. Final positional parameters for the non-hydrogen atoms of $V(bpy)(acac)(Cl_4Cat)$ are listed in Table II. Tables containing full listings of atom positions and anisotropic displacement parameters are available as supplementary material.

Table I. Crystallographic Data for $V(bpy)(Cl_4Cat)_2$ and $V(bpy)(acac)(Cl_4Cat)\cdot CH_2Cl_2$

	$V(bpy)(Cl_4Cat)_2$	$V(bpy)(acac)(Cl_4Cat)$
fw	698.8	637.0
color	blue-green	purple
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	7.911 (2)	13.864 (3)
b (Å)	8.982 (2)	8.407 (2)
c (Å)	17.981 (3)	22.898 (5)
α (deg)	80.05 (1)	90.00
β (deg)	88.60 (1)	90.87 (2)
γ (deg)	88.76 (2)	90.00
V (Å^3)	1257.9 (5)	2668.6 (10)
Z	2	4
D_{calcd} (g cm^{-3})	1.845	1.581
μ (mm^{-1})^a	1.27	1.00
R, R_w	0.065, 0.076	0.056, 0.074
GOF	1.58	1.94

^{a} Radiation Mo Kα (λ = 0.710 73 Å); T = 294–297 K.

Crystallographic Structure Determination of $V(bpy)(Cl_4Cat)_2$. Dark blue-green crystals of $V(bpy)(Cl_4Cat)_2$ were obtained as thin plates from a dichloromethane solution. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table I. Data were collected by θ–2θ scans within the angular range 3.0–50.0°. Atom locations were determined by direct methods. Final cycles of least-squares refinement converged with discrepancy indices of R = 0.065 and R_w = 0.076. Final positional parameters for non-hydrogen atoms of the $V(bpy)(Cl_4Cat)_2$ molecule are listed in Table III. Tables containing full listings of atom positions and anisotropic displacement parameters are available as supplementary material.

Results

The use of 2,2′-bipyridine in the characterization of sequestered vanadium(III) in tunicates has prompted study of the reaction between bipyridine and vanadium catecholate complexes that might resemble species formed by coordination through oxygen atoms of the tunichrome catechol or pyrogallol rings. We have used the tetrachlorocatecholate ligand due to the more positive oxidation potential of Cl_4Cat relative to unsubstituted catecholate or alkyl-substituted catecholates.[15] This feature may result in reduced complexes that are less air sensitive than similar compounds studied earlier with the 3,5-di-*tert*-butylcatecholate (DBCat) ligand.[16,17] Bis(tetrachlorocatecholato)(bipyridine)-

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(15) Zirong, D.; Bhattacharya, S.; McCusker, J. K.; Hagen, P. M.; Hendrickson, D. N.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 870.

(16) Galeffi, B.; Postel, M. *Nouv. J. Chim.* **1984**, *8*, 481.

(17) Kabanos, T. A.; White, A. J. P.; Williams, D. J.; Woolins, J. D. *J. Chem. Soc., Chem. Commun.* **1992**, 17.

Table II. Atomic Coordinates for V(bpy)(acac)(Cl_4Cat)

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq) (Å^2)
V	3417 (2)	1429 (3)	1256 (1)	61 (2)^a
Cl1	−111 (3)	857 (7)	1178 (3)	116 (3)^a
Cl2	−999 (3)	2325 (7)	32 (3)	124 (3)^a
Cl3	340 (4)	3839 (7)	−880 (3)	124 (3)^a
Cl4	2561 (3)	3906 (6)	−651 (2)	96 (2)^a
O1	2030 (7)	1189 (11)	1246 (5)	68 (5)^a
O2	3139 (7)	2381 (10)	479 (4)	55 (5)^a
O3	3644 (7)	3436 (12)	1670 (6)	76 (6)^a
O4	3599 (7)	368 (12)	2043 (5)	63 (5)^a
Cl	1609 (14)	1796 (20)	747 (9)	61 (5)
C2	2215 (15)	2440 (18)	340 (7)	47 (5)
C3	1815 (12)	3083 (18)	−145 (8)	60 (5)
C4	814 (12)	3062 (18)	−255 (8)	65 (5)
C5	253 (12)	2364 (19)	158 (8)	69 (6)
C6	613 (13)	1726 (19)	669 (8)	68 (5)
N1	3629 (9)	−887 (14)	921 (5)	56 (6)^a
C7	4515 (14)	−1257 (22)	726 (7)	58 (5)
C8	4698 (13)	−2789 (22)	526 (7)	85 (6)
C9	3973 (12)	−3928 (21)	511 (7)	73 (6)
C10	3091 (12)	−3534 (21)	688 (7)	73 (6)
C11	2936 (13)	−2011 (22)	896 (7)	62 (6)
N2	4919 (9)	1305 (16)	1056 (5)	60 (6)^a
C12	5237 (13)	−26 (25)	784 (8)	64 (6)
C13	6166 (13)	−223 (22)	607 (7)	80 (6)
C14	6806 (14)	968 (23)	714 (8)	98 (7)
C15	6519 (13)	2329 (22)	992 (7)	83 (6)
C16	5575 (14)	2485 (23)	1153 (8)	77 (6)
C17	3865 (12)	5472 (21)	2369 (8)	103 (7)
C18	3766 (12)	3674 (25)	2222 (11)	76 (7)
C19	3773 (12)	2561 (26)	2623 (10)	97 (7)
C20	3725 (12)	954 (27)	2517 (10)	73 (7)
C21	3770 (12)	−170 (21)	3014 (8)	105 (7)

[a] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

vanadium(IV) and its vanadium(III) analog have been synthesized, and reactions directed at replacement of the catecholate ligands with bipyridine have been investigated.

Table III. Atomic Coordinates for V(bpy)(Cl_4Cat)$_2$

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)^a (Å^2)
V	371 (2)	7553 (2)	7526 (1)	33 (1)
O1	−406 (7)	8029 (6)	8477 (3)	38 (2)
O2	−574 (8)	5654 (6)	7977 (3)	42 (2)
O3	−210 (7)	9577 (6)	7080 (3)	39 (2)
O4	−676 (7)	7180 (7)	6624 (3)	42 (2)
N1	2654 (8)	8546 (8)	7762 (4)	34 (2)
N2	2299 (8)	6138 (8)	7203 (4)	39 (2)
C1	−1124 (9)	6914 (10)	8954 (5)	37 (3)
C2	−1210 (10)	5585 (10)	8661 (5)	41 (3)
C3	−1929 (13)	4281 (11)	9099 (5)	51 (3)
Cl1	−1999 (5)	2680 (3)	8703 (2)	84 (1)
C4	−2482 (12)	4345 (11)	9806 (5)	50 (3)
Cl2	−3375 (4)	2755 (4)	10356 (2)	79 (1)
C5	−2430 (11)	5704 (13)	10093 (5)	54 (4)
Cl3	−3208 (4)	5742 (4)	11008 (1)	76 (1)
C6	−1789 (11)	7003 (11)	9672 (5)	45 (3)
Cl4	−1730 (5)	8677 (4)	9990 (2)	78 (1)
C7	−967 (9)	9745 (10)	6414 (5)	35 (3)
C8	−1201 (10)	8429 (10)	6142 (5)	38 (3)
C9	−1984 (10)	8390 (11)	5467 (5)	42 (3)
Cl5	−2242 (4)	6691 (3)	5180 (2)	63 (1)
C10	−2470 (10)	9783 (11)	5037 (5)	45 (3)
Cl6	−3371 (3)	9778 (3)	4175 (1)	61 (1)
C11	−2233 (11)	11107 (11)	5301 (5)	44 (3)
Cl7	−2894 (4)	12794 (3)	4768 (2)	72 (1)
C12	−1514 (11)	11123 (10)	5994 (5)	44 (3)
Cl8	−1141 (3)	12748 (3)	6327 (2)	66 (1)
C13	4118 (10)	7896 (10)	7588 (5)	40 (3)
C14	5645 (11)	8473 (12)	7716 (6)	56 (4)
C15	5699 (14)	9740 (13)	8037 (7)	67 (4)
C16	4216 (13)	10443 (12)	8204 (6)	57 (4)
C17	2702 (12)	9798 (11)	8065 (5)	47 (3)
C18	3914 (10)	6510 (10)	7270 (5)	40 (3)
C19	5259 (12)	5599 (13)	7081 (7)	60 (4)
C20	4861 (17)	4345 (14)	6795 (7)	79 (5)
C21	3173 (15)	3958 (13)	6728 (6)	65 (4)
C22	1956 (14)	4889 (11)	6931 (6)	54 (4)

[a] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Electrochemical Potentials ($E_{1/2}$, V vs Fc^+/Fc (ΔE_p, mV))^a for Selected Vanadium Complexes

complex	V^{IV}/V^{V}	V^{III}/V^{IV}	V^{II}/V^{III}	ref
V(bpy)(Cl_4Cat)$_2$	+0.92^b +0.83^c	−0.35 (79) −0.50 (69)	−1.74 (83) −1.90 (100)	*d*
V(phen)(DBCat)$_2$	+0.02	−1.29		17
V(bpy)(acac)(Cl_4Cat)	+0.06 (84)	−0.50 (73)	−1.75 (72)	*d*
V(acac)$_2$(Cat)		−0.62		4
V(acac)$_2$(DBCat)		−0.77		4
V(TRENCAM)$^{2-}$	+0.13	−0.94		3a
V(Cl_4Cat)$_3^{2-}$	+0.28 (92)	−1.14 (92)	−2.35	22
V(L)^e	+0.38	−0.50	−2.41	20
V(BBPEN)	+1.11	+0.27	−1.79	21

[a] Potentials referenced to NHE have been converted by assuming that the Fc^+/Fc couple occurs at +0.40 vs NHE. [b] Acetonitrile. [c] Dichloromethane. [d] This work. [e] L is the trianion of 1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane.

V(bpy)(Cl_4Cat)$_2$. The reaction described in the Experimental Section which produced V(bpy)(Cl_4Cat)$_2$ as a product was carried out with V(acac)$_3$ in the interest of obtaining the V(III) form of the complex. Electrochemical characterization on neutral V(bpy)(Cl_4Cat)$_2$ has shown that it undergoes irreversible oxidation at +0.83 V (vs Fc/Fc^+). At this potential, it is not clear whether oxidation occurs at the metal to give the V(V) cation, V^V(bpy)(Cl_4Cat)$_2^+$, or at one of the quinone ligands to give a semiquinonate complex product, V^{IV}(bpy)(Cl_4SQ)(Cl_4Cat)$^+$. Reduction of the complex occurs reversibly at −0.50 (69) V to give the V(III) anion, V^{III}(bpy)(Cl_4Cat)$_2^-$. Potentials for these processes and for electrochemical reactions of related complexes are listed in Table IV. Complexes related to the neutral V(IV) form had been reported earlier with 3,5-di-*tert*-butylcatechol,[16] and the electrochemistry of V(phen)(DBCat)$_2$ shows dramatically the effect of substituent differences on the quinone ligands.[17] With the alkyl substituents of the DBCat ligands, both redox processes are shifted negatively by approximately 0.8 V. Redox processes that occur at the quinone ligands or from orbitals that have significant quinone ligand electronic contributions are typically shifted positively for the chloronated catecholate ligands relative to the alkyl-substituted catechols.[15,18] This effect appears for the ligand-based redox processes of Cr(bpy)(Q)$_2$ and Fe(bpy)(Q)$_2$ (Q = DBQ, Cl_4Q), where the quinone ligands are either semiquinonate or catecholate in the redox series (1) and

$$\mathrm{M(bpy)(SQ)_2^+} \overset{e^-}{\rightleftarrows} \mathrm{M(bpy)(SQ)(Cat)} \overset{e^-}{\rightleftarrows} \mathrm{M(bpy)(Cat)_2^-} \tag{1}$$

metal ions remain in the trivalent form. Shifts in the range of redox potentials for V(bpy)(Cl_4Cat)$_2$ and V(phen)(DBCat)$_2$ are difficult to view as metal-based processes (eq 2), although EPR

$$\mathrm{V^V(bpy)(Cat)_2^+} \overset{e^-}{\rightleftarrows} \mathrm{V^{IV}(bpy)(Cat)_2} \overset{e^-}{\rightleftarrows} \mathrm{V^{III}(bpy)(Cat)_2^-} \tag{2}$$

spectra clearly define the charge distribution of V^{IV}(bpy)(Cl_4Cat)$_2$ and reduction must occur at the metal. The absence of a significant shift for the V(TRENCAM)$^{2-}$ redox series compared with V(Cl_4Cat)$_3^{2-}$ (Table IV) indicates that ligand field effects for the two catecholate ligands should be roughly comparable, and the reduction potentials are not sufficiently negative for reduction of the bipyridine or phenanthroline ligands. Oxidation of the neutral V(IV) complexes may occur at the metal or at one of the catecholate ligands. The more negative oxidation potential

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(18) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552.

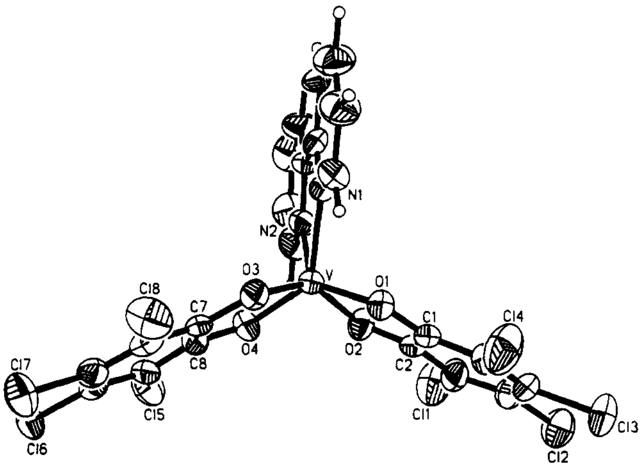

Figure 1. View of the trigonal prismatic $V(bpy)(Cl_4Cat)_2$ molecule.

Table V. Selected Bond Lengths and Angles for $V(bpy)(Cl_4Cat)_2$

	Lengths (Å)		
V–O1	1.917 (6)	V–O2	1.917 (6)
V–O3	1.907 (6)	V–O4	1.922 (6)
V–N1	2.115 (7)	V–N2	2.100 (7)
O1–C1	1.329 (9)	O2–C2	1.310 (10)
O3–C7	1.336 (10)	O4–C8	1.358 (10)
N1–C13	1.340 (11)	N1–C17	1.334 (13)
N2–C18	1.341 (10)	N2–C22	1.335 (13)
C1–C2	1.389 (13)	C1–C6	1.397 (12)
C2–C3	1.415 (12)	C3–Cl1	1.714 (11)
C3–C4	1.345 (14)	C4–Cl2	1.743 (10)
C4–C5	1.406 (16)	C5–Cl3	1.748 (10)
C5–C6	1.376 (13)	C6–Cl4	1.699 (11)
C7–C8	1.372 (13)	C7–C12	1.399 (11)
C8–C9	1.382 (12)	C9–Cl5	1.711 (10)
C9–C10	1.403 (12)	C10–Cl6	1.722 (9)
C10–C11	1.372 (14)	C11–Cl7	1.725 (9)
C11–C12	1.385 (13)	C12–Cl8	1.705 (10)
C13–C14	1.365 (13)	C13–C18	1.471 (13)
C14–C15	1.363 (17)	C15–C16	1.371 (15)
C16–C17	1.388 (15)	C18–C19	1.399 (13)
C19–C20	1.363 (19)	C20–C21	1.400 (18)
C21–C22	1.347 (16)		
	Angles (deg)		
O1–V–O2	79.9 (3)	O1–V–O3	88.0 (2)
O2–V–O3	143.1 (3)	O1–V–O4	135.8 (2)
O2–V–O4	84.5 (2)	O3–V–O4	80.3 (3)
O1–V–N1	84.9 (3)	O2–V–N1	129.5 (2)
O3–V–N1	83.1 (2)	O4–V–N1	134.8 (3)
O1–V–N2	133.9 (3)	O2–V–N2	82.1 (3)
O3–V–N2	128.7 (3)	O4–V–N2	83.5 (3)
N1–V–N2	74.8 (3)		

of $V(phen)(DBCat)_2$ may indicate that it is ligand-based

$$V^{IV}(bpy)(SQ)(Cat)^+ \overset{e^-}{\rightleftarrows} V^{IV}(bpy)(Cat)_2 \qquad (3)$$

but contracted V–O and V–N bond lengths observed in the structure determination of $V(phen)(DBCat)_2^+$ seem to point to V(V). It is of interest that the average catecholate C–O lengths were also found to contract upon oxidation to $V(phen)(DBCat)_2^+$, to values of 1.32 Å typical of disordered or delocalized $ML_2(SQ)(Cat)$ species.[15]

Structural characterization of $V(bpy)(Cl_4Cat)_2$ revealed that the complex molecule has a very regular trigonal prismatic coordination geometry. A view of the molecule is shown in Figure 1, and bond distances and angles are listed in Table V. The twist angle between triangular faces of the prism as defined by Steifel is 3.2°.[19] Values of 60 and 0° would be expected for regular antiprismatic (octahedral) and prismatic geometries, respectively. As a complex of d^1 V(IV), it has no strong ligand field preference for structure, and trigonal distortions have been noted previously for V(IV) catecholate complex molecules.[3a] The crystal packing arrangement shown in Figure 2 displays pairing interactions between quinone ligands that result in rows and planes of paired molecules. These intermolecular interactions appear responsible for the unusual coordination geometry of $V(bpy)(Cl_4Cat)_2$ in the solid state and for the plate-shaped habit of crystals of the complex. Structural characterization of $V(phen)(DBCat)_2$ and $V(phen)(DBCat)_2^+$ has shown that both complexes have distorted octahedral geometries.[17] Electronic spectra of $V(bpy)(Cl_4Cat)_2$ in the visible region (Figure 3) consist of two bands at 732 nm (3900 M^{-1} cm^{-1}) and 450 nm (3000 M^{-1} cm^{-1}). These shift slightly to 758 and 475 nm in dichloromethane and to 730 and 471 nm in tetrahydrofuran solutions. The solution EPR spectrum of the complex shows the typical isotropic eight-line pattern of V(IV) complexes with a *g* value of 1.960 and hyperfine coupling of 78 G.

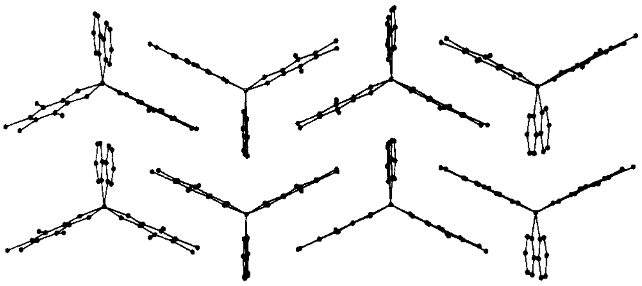

Figure 2. Diagram showing intermolecular interactions on the crystallographic *ac* plane of $V(bpy)(Cl_4Cat)_2$.

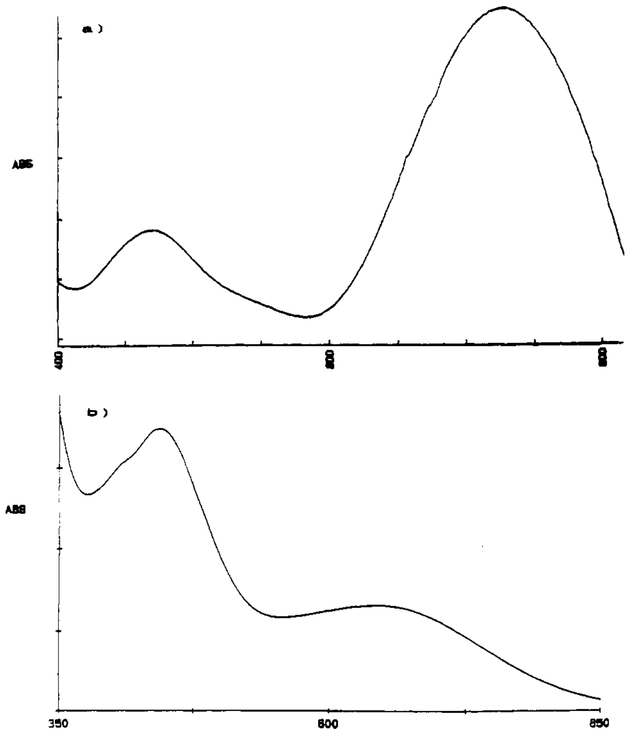

Figure 3. Electronic spectra of $V(bpy)(Cl_4Cat)_2$ (a) and $(CoCp_2)[V(bpy)(Cl_4Cat)_2]$ (b) recorded in dichloromethane solutions.

The formation of $V(bpy)(Cl_4Cat)_2$ from $V(acac)_3$ likely results from oxidation of the V(III) form of the complex. Related V(IV) complexes had been formed by treating $VO(acac)_2$ with 3,5-di-*tert*-butylcatechol and either bipyridine or *o*-phenanthroline. This procedure carried out using tetrachlorocatechol gave polymeric $VO(bpy)(Cl_4Cat)$ as the major product. The reduction potential of $V(bpy)(Cl_4Cat)_2$ shows that a V(III) species would be readily susceptible to reversible oxidation. Since our main interest was in the reduced species, attempts were made to obtain the V(III) complex prior to oxidation.

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[19] Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434.

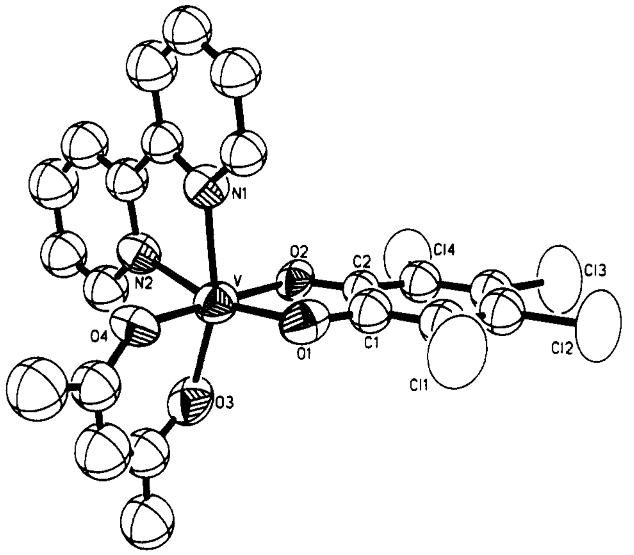

Figure 4. View of the V(bpy)(acac)(Cl_4Cat) molecule.

Table VI. Selected Bond Lengths and Angles for V(bpy)(acac)(Cl_4Cat)

	Lengths (Å)		
V–O1	1.933 (10)	V–O2	1.983 (10)
V–O3	1.958 (11)	V–O4	2.022 (12)
V–N1	2.116 (12)	V–N2	2.141 (12)
O1–C1	1.36 (2)	O2–C2	1.35 (2)
	Angles (deg)		
O1–V–O2	81.4 (4)	O3–V–O4	86.1 (5)
N1–V–N2	74.7 (5)	O1–V–N2	164.2 (5)
O2–V–O4	175.4 (4)	N1–V–O3	161.2 (5)

V(bpy)(acac)(Cl_4Cat). Reactions similar to the one used to form V(bpy)(Cl_4Cat)$_2$ were carried out with more immediate product isolation. The major product obtained by the described procedure was a purple crystalline material identified crystallographically as the dichloromethane solvate of V(bpy)(acac)(Cl_4Cat). A view of the complex molecule is shown in Figure 4, and bond distances and angles are listed in Table VI. Unfortunately, the quality of the structure determination is poor due to the quality of the crystals obtained. However, it is adequate to provide definition of the complex molecule. The complex shows visible transitions at 750, 550, and 450 nm, although rapid decomposition in solution complicated calculation of molar extinction coefficients. Electrochemical characterization indicated that the complex undergoes reversible oxidations at −0.504 (73) and +0.063 (84) V to V(IV) and V(V) forms of the complex and a quasireversible reduction at −1.753 (72) V. The reduction may occur either at the metal to give a V(II) species or at the bipyridine ligand. The magnetic moment measured for the complex in the solid state was 2.75 μ_B, a value typical of octahedral V(III).

The formation of V(bpy)(acac)(Cl_4Cat) in the reaction between V(acac)$_3$, bipyridine, and tetracholrocatechol points to its existence as an intermediate in the reaction that ultimately leads to V(bpy)(Cl_4Cat)$_2$. The potential of the V(III)/V(IV) couple for the complex indicates that it is as strongly reductive as V^{III}(bpy)(Cl_4Cat)$_2^-$.

V(bpy)(Cl_4Cat)$_2^-$. Two synthetic procedures were used to isolate the V(bpy)(Cl_4Cat)$_2^-$ anion. Addition of (PPh_4)Br to solutions that gave V(bpy)(Cl_4Cat)$_2$ resulted in crystallization of the anion as the PPh_4^+ salt. In a second procedure, neutral V(bpy)(Cl_4Cat)$_2$ was chemically reduced with cobaltocene. Both forms of the complex anion were found to undergo air oxidation to give the neutral complex. Electrochemical characterization of ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$] in dichloromethane solution (Figure 5) showed oxidation couples at −0.50 and 0.84 V, similar to those of V(bpy)(Cl_4Cat)$_2$, a reversible reduction at −1.34 V, corresponding to the $CoCp_2$/$CoCp_2^+$ couple, and an additional reduction of the complex anion at −1.904 (100) V. The latter reduction is at a potential associated with V(II)/V(III) couples.[20,21] However, as in the case of V(bpy)(acac)(Cl_4Cat), this may either correspond to reduction of the metal to V(II) or reduction of the bpy ligand. Positive shifts in the potentials of all three redox processes of V(bpy)(Cl_4Cat)$_2^-$ occur in acetonitrile solution. The oxidation potentials move to −0.352 (79) and 0.92 V, while the reduction moves to −1.74 V. The $CoCp_2$/$CoCp_2^+$ couple that appears as an internal reference remains unchanged. Electronic spectra recorded for ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$] in acetonitrile (Figure 3) showed absorptions at 444 (ϵ 8400) and 642 nm (ϵ 3200) for the complex anion and a band at 404 nm (ϵ 283) for the $CoCp_2^+$ cation.

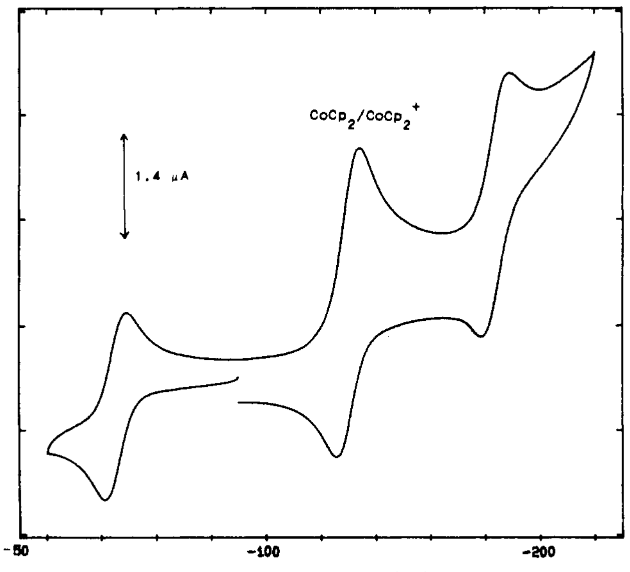

Figure 5. Cyclic voltammogram of ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$] recorded in dichloromethane at a scan rate of 100 mV/s with potentials referenced to the Fc/Fc$^+$ couple. The solution contains a slight excess of $CoCp_2^+$.

Attempted Addition of Bipyridine to ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$]. Parallel solutions of ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$] were prepared under an atmosphere of dry N_2 in acetonitrile. A 10-fold molar excess of bipyridine was added to one of the solutions, and the electronic spectra of both solutions were monitored over a period of 3 weeks. After 9 days, 98% of the original V(bpy)(Cl_4Cat)$_2^-$ remained in solution. Over the period of the next two weeks new spectral bands appeared at 580 and 700 nm, indicating the presence of a decomposition product in both solutions. This complex has been identified by its electronic and EPR spectra as the V(Cl_4Cat)$_3^{2-}$ anion.[22]

An additional solution was prepared containing ($CoCp_2$)[V(bpy)(Cl_4Cat)$_2$] with a 10-fold excess of bipyridine in acetonitrile. This solution was exposed to air, and the resulting spectral changes were monitored. Within a period of 8 min, all of the anionic complex had been converted to neutral V(bpy)(Cl_4Cat)$_2$. Over the following 10 min, the spectrum of V(Cl_4Cat)$_3^{2-}$ appeared and grew in intensity as the spectrum of V(bpy)(Cl_4Cat)$_2$ disappeared.

In none of the V(III) or V(IV) tetrachlorocatecholate complexes was bipyridine observed to displace the catecholate ligands.

Discussion

The V(bpy)(Cl_4Cat)$_2^n$, n = +1, 0, −1, redox series is related to similar complexes of Cr and Fe, M(bpy)(Cl_4Q)$_2^n$, with the

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(20) Auerbach, U.; Della Veolova, B.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1004.

(21) Neves, A.; Ceccato, A. S.; Erthal, S. M. D.; Vencato, I.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1992**, *187*, 119.

(22) (a) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962. (b) Simpson, C. L. Ph.D. Thesis, University of Colorado, 1992.

significant difference that redox chemistry occurs at quinone ligand electronic levels with Cr and Fe while for V the metal is the primary center of redox activity.[15,18] Oxidative and reductive couples of Cr(bpy)(SQ)(Cat) and Fe(bpy)(SQ)(Cat) show dependence upon quinone substituents with corresponding potentials shifted approximately 0.5 V positively for the tetrachloroquinone complexes relative to the 3,5-di-*tert*-butylquinone analogs. An even more pronounced shift occurs for V(bpy)$(Cl_4Cat)_2$ and V(phen)$(DBCat)_2$, although the effects contributing to this shift remain unclear. Both vanadium complexes show strong visible transitions at 740 and 450 nm, and the potential difference between V^{IV}/V^{V} and V^{III}/V^{IV} couples is similar, leading to the conclusion that the frontier orbitals responsible for both the optical spectra and electrochemical activity are primarily metal-localized.

Tunicate Vanadium(III) Coordination Environment. Hawkins has provided strong evidence for the formation of the V(III) cation $[V(bpy)_2Cl]_2O^{2+}$ when the compartment and signet ring cells of the blood of ascidians were treated with saturated seawater solutions of bipyridine.[12] These experiments demonstrate the high concentration of vanadium in these cells and confirm the conclusion that much of the metal is in the form of V(III). Kustin and Nakanishi have investigated coupling between tunichrome and vanadium concentrations and found that the compartment and signet ring cells contain large quantities of vanadium but little free tunichrome.[8] Moreover, high concentrations of free tunichrome exist in the morula cells, cells that also contain high concentrations of vanadium but fail to respond to the bipyridine assay.

Our results have been obtained under conditions that are clearly different from the experimental conditions used in biological tests, but the inability of bipyridine to displace catecholate ligands from vanadium is apparent. With this information, it may be concluded that the V(III) accessed in Hawkins' bipyridine reactions was not present in the form of a catecholate complex and that different coordination environments exist in the three types of cells. Vanadium coordination in the morula cells is likely to the tunichrome catecholate and pyrogallolate functionalities. Coordination in the signet ring and compartment cells occurs through nitrogen and oxygen donor groups that are subject to displacement by bipyridine. This may also address the inconsistency of having a strongly reductive V(III)–catecholate complex in a protic aerobic medium. Unsaturation and conjugation in the tunichrome amide backbone limits flexibility, and it is possible that the catecholate and pyrogallolate coordination sites of a single tunichrome bond with different metal ions. The resulting polymeric structure may provide a protective environment for the nucleophilic V(III) ion. Complexes of V(III) chelated by amine–phenolate ligands have been studied with varying numbers of amine N and phenolate O donor atoms (Table IV).[20,21] As the number of oxygen donors in the coordination sphere decreases, the V(III)/V(IV) potential shifts positively. Neves has reported that the V(III)/V(IV) couple for $V(BBPEN)^+$, containing two phenolate oxygen atoms and four amine nitrogens in the coordination sphere,[21] appears at +0.27 V (vs Fc/Fc^+) in contrast to the catecholate complexes which commonly show V(III)/V(IV) couples near –0.50 V. A coordination environment containing mainly aqua or carboxylate oxygen and amine nitrogen donor atoms would be more consistent with the redox stability and bipyridine accessibility of tunicate V(III) located in the signet ring and compartment cells.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE 90-23636).

Supplementary Material Available: Tables giving crystal data and details of the structure determinations, all atom locations, anisotropic thermal parameters, and bond lengths and angles (20 pages). Ordering information is given on any current masthead page.