Synthesis, Structures, and Spectroscopic Characterization of a Series of *N,N′*-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane Vanadium(III), -(IV), and -(V) Complexes

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Received August 18, 1995[⊗]

Three vanadium-containing complexes, $[(\text{L-N}_4\text{Me}_2)\text{VCl}_2](\text{BPh}_4)$ (**1**), $[(\text{L-N}_4\text{Me}_2)\text{VClO}](\text{ClO}_4)$ (**2**), and $[(\text{L-N}_4\text{Me}_2)\text{VO}_2](\text{BPh}_4)$ (**3**) where L-N_4Me_2 is the tetradentate ligand *N,N′*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane, have been prepared and characterized by X-ray diffraction and electrochemical methods as well as by IR, ^{1}H-NMR, EPR, and electronic absorption spectroscopy. Complex **1** crystallizes in monoclinic space group $P2_1/n$ (No. 14) with $a = 16.940(4)$ Å, $b = 9.902(3)$ Å, $c = 21.936(8)$ Å, $\beta = 108.21(2)°$, $V = 3495(2)$ Å^3, and $Z = 4$, complex **2** in orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 10.163(2)$ Å, $b = 13.351(3)$ Å, $c = 14.762(3)$ Å, $V = 2003(1)$ Å^3 and $Z = 4$, and complex **3** in monoclinic space group $P2_1/c$ (No. 14) with $a = 14.349(3)$ Å, $b = 14.040(5)$ Å, $c = 18.131(10)$ Å, $\beta = 110.62(3)°$, $V = 3419(2)$ Å^3, and $Z = 4$. In all these complexes a distorted cis-octahedral coordination geometry is found with the cis coordination sites occupied either by terminal chloro and/or oxo ligands. Thus, a rather unique series of mononuclear complexes has been established where, for example, in reaction with air consecutive replacements of both chloride ions by oxo donors increases the oxidation state of the six-coordinate vanadium ion from III over IV to V while the residual coordination environment remains preserved. Interestingly, in each complex the electronic properties of the cis donor atom set stabilize only one specific oxidation state of the vanadium ion in order to warrant the isolation of the complex.

Introduction

Currently there is considerable interest in investigating mononuclear vanadium complexes because some haloperoxidases—enzymes that catalyze the peroxide-dependent halogenation of organic substrates—have been shown to contain vanadium in their active sites[1] and also because peroxovanadium(V) complexes have been demonstrated to be suitable oxidizing reagents for a wide variety of organic substrates.[2]

The active site of marine haloperoxidases is thought to consist of a V(V)═O in a distorted octahedral geometry with oxygen and nitrogen atoms as residual donors. From EXAFS measurements[3] it is proposed that the donor atom set around the vanadium consists of one terminal oxide at 1.61 Å, three N/O donors at the rather short distances of 1.72 Å, and two nitrogen donors, presumably histidines, at 2.11 Å. Upon reexamination of the data with new model complexes, it was suggested that the vanadium site might actually be only five-coordinate.[4] A recent structure determination[5] of the haloperoxidase isolated from the fungus *Curvularia inaequalis* indeed assigns a trigonal-bipyramidal coordination geometry to the vanadium ion where the equatorial coordination sites are presumably occupied by an oxide and two hydroxides. At the axial sites a histidine and an exogenous ligand (a hydroxide or an azide, depending on the buffer used for crystallization of the enzyme) are bound to the vanadium ion. A comparison of the sequences of amino acids near the vanadium sites in different haloperoxidases ascribes similar structures to the active sites of the enzymes from a fungi and an algae source.[5] Within this context the exploration of the basic coordination chemistry of vanadium provides valuable insights into the role and the structure−function relationship of the vanadium ion in these enzymes.

Vanadium(V) complexes have been found to act as catalysts in the oxidation of organic substrates by peroxides (e.g., epoxidation of alkenes and hydroxylation of alkanes and aromates).[2,6] Although the mechanisms for these reactions are still obscure and may involve radicals, the reactive species have been identified in stoichiometric reactions as mononuclear peroxovanadium(V) complexes, some of which have been structurally characterized.[2b,6b] Interestingly, in recent times, it has been discovered that peroxovanadium complexes have insulin-mimetic properties.[7]

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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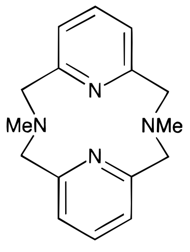
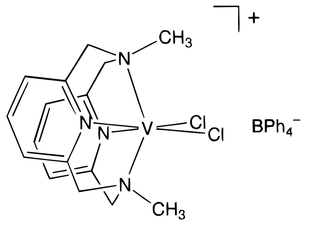
(9) List of abbreviations used: L-N_4Me_2 = *N,N′*-dimethyl-2,11-diaza-[3.3](2,6)pyridinophane; tacn = 1,4,7-trimethyltriazacyclononane; bipy = 2,2′-bipyridine; HB(Me_2pz)$_3$ = hydridotris(3,5-dimethylpyrazolyl)-borate; Me_2pzH = 3,5-dimethylpyrazole; DMF = dimethylformamide; THF = tetrahydrofuran.

S0020-1669(95)01073-1 CCC: $12.00



L-N_4Me_2

In our research we extensively employ derivatives of 2,11-diaza[3.3](2,6)pyridinophane as ligand.[8] This macrocycle has four potential nitrogen donors at its disposal for the complexation of metal ions. Due to its rather small cavity, the 12-membered macrocyclic ring forms preferably cis-octahedral coordination geometries with metal ions. By protecting four of the coordination sites at an octahedral metal ion from nucleophilic reagents, the ligand ensures that any reactivity occurs only at two defined cis coordination sites. In our efforts to develop new oxidation catalysts with this type of ligand, we started to investigate mononuclear vanadium complexes using *N*,*N*′-dimethyl-2,11-diaza[3.3](2,6)pyridinophane (L-N_4Me_2)[9] as ligand. Here we report on the synthesis and characterization of three vanadium complexes (**1**, **2**, and **3**), of which some may serve as useful precursors for later studies with peroxides. In these complexes, the cis coordination sites are occupied by terminal chlorides and/or oxides. Thus, a complete, structurally characterized series of compounds was prepared in which (starting with the dichlorovanadium(III) complex **1**) the chlorides are successively replaced by oxo donors and, concomitantly, the oxidation state of the vanadium ion is raised each time by one unit while the residual coordination environment is retained.



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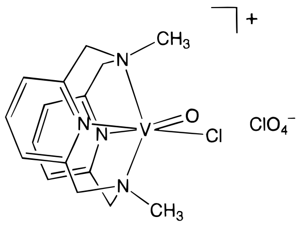

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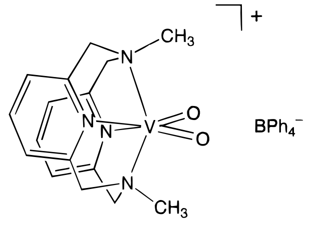

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Experimental Section

Preparation of Compounds. The ligand *N*,*N*′-dimethyl-2,11-diaza[3.3](2,6)pyridinophane (L-N_4Me_2) was synthesized according to published procedures with some slight modifications.[10] Tetraphenylphosphonium dichlorovanadate(V) was prepared as described[11] and purified with dichloromethane. Acetonitrile was dried over CaH_2 and freshly distilled prior to use. All other chemicals were purchased and used without further purification.

[(L-N_4Me_2)VCl_2](BPh_4) (1). Under an atmosphere of pure nitrogen, a solution of L-N_4Me_2 (134 mg, 0.5 mmol) and sodium tetraphenylborate (171 mg, 0.5 mmol) in acetonitrile (25 mL) was added dropwise to acetonitrile (15 mL) containing [$VCl_3(THF)_3$] (187 mg, 0.5 mmol). After heating the reaction mixture to refluxing temperatures, the initial violet precipitate dissolved again and a color change from violet to green occurred. Upon cooling of the reaction mixture to room temperature, the precipitated white salt was removed by filtration and the volume of the solution was reduced to about 10 mL. Ether diffusion into the solution yielded dark green crystals which were separated from the violet coprecipitate sticking to the glass wall. The green product was redissolved in 5 mL of acetonitrile. A second ether diffusion afforded 134 mg (38% yield) of analytically pure product as dark green crystals. Anal. Calcd for $C_{40}H_{40}BCl_2N_4V$: C, 67.72; H, 5.68; N, 7.90. Found: C, 67.51; H, 5.84; N, 7.96. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 259 (sh, 13 800), 273 (sh, 7270), 375 (588), 450 (sh, 79.9), and 635 (72.1) nm. IR (KBr): 1610, 1578, 1480, 1448, 1428, 1167, 1078, 1031, 748, 732, 707, 612 cm^{-1} (strong bands only). Magnetic moment: 2.68 μ_B.

[(L-N_4Me_2)VClO](ClO_4) (2). Under air, L-N_4Me_2 (136 mg, 0.51 mmol) in 96% ethanol (10 mL) was added dropwise to a stirred solution of VCl_3 (80 mg, 0.51 mmol) in 96% ethanol (20 mL). The resulting mixture was refluxed for 15 min and cooled to room temperature before sodium perchlorate (61 mg, 0.50 mmol) was added to the resulting turquoise solution. After refluxing the solution for 10 min, the solvent was completely removed under vacuo. Two consecutive recrystallizations by diffusion of ether into filtered solutions of the residue in acetonitrile (10 mL) afforded 156 mg of product as light-blue crystals (65% yield). Anal. Calcd for $C_{16}H_{20}Cl_2N_4O_5V$: C, 40.87; H, 4.29; N, 11.92. Found: C, 40.88; H, 4.27; N, 11.89. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 257 (7550), 264 (10 800), 356 (45.8), 633 (37.5), and 707 (28.0) nm. IR (KBr): 1610, 1580, 1485, 1449, 1097, 1078, 1027, 982, 968, 879, 815, 624 cm^{-1} (strong bands only). Magnetic moment: 1.73 μ_B.

Warning: Perchlorate salts are potentially explosive and should be handled with care.[12]

[(L-N_4Me_2)VO_2](BPh_4) (3). To avoid contamination by traces of a V(IV)-containing species, the dioxovanadium(V) complex was prepared anaerobically under exclusion of light, using absolute solvents. A solution of L-N_4Me_2 (134 mg, 0.5 mmol) and sodium tetraphenylborate (342 mg, 1.0 mmol) in acetonitrile (40 mL) was added dropwise to stirred acetonitrile (15 mL) containing (PPh_4)[VCl_2O_2] (247 mg, 0.5 mmol). After refluxing the initially turbid orange-colored reaction mixture for 5 min, the solution adopted a yellow color. The precipitate was then removed by filtration before the volume of the solution was reduced to ca. 5 mL in vacuo at 50 °C. Slow cooling of the solution to room temperature resulted in precipitation of most of the produced tetraphenylphosphonium tetraphenylborate. Ether diffusion to the residual solution afforded analytically pure product. The total amount of 260 mg of yellow crystals of **3** corresponds to a yield of 78%. Anal. Calcd for $C_{40}H_{40}BN_4O_2V$: C, 71.65; H, 6.01; N, 8.36. Found: C, 71.52; H, 6.06; N, 8.56. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 253 (11 500), 261 (12 100), 274 (sh, 3780), 341 (376) nm. ^1H NMR (CD_3CN, 200 MHz) δ 3.10 (s, CH_3, 6H), 4.42 ($J_{AB} = 15.9$ Hz, CH_2, 4H), 4.77 ($J_{AB} = 15.9$ Hz, CH_2, 4H), 6.79−7.03 (m, Ph-H, 12H), 7.17 (B-part, $J_{AB_2} = 7.81$ Hz, 3,5-py-H, 4H), 7.20−7.27 (m, Ph-H, 8H), 7.72 (A-part, $J_{AB_2} = 7.81$ Hz, 4-py-H, 2H) ppm. IR (KBr): 1607, 1588, 1477, 1438, 1417, 1379, 1161, 1074, 1028, 939, 914, 903, 896, 875, 865, 792, 761, 744, 733, 706, 605 cm^{-1} (strong bands only).

Physical Methods. ^1H-NMR: Varian Gemini 200 MHz. UV−vis: Varian Cary 5 E. IR: Perkin-Elmer 1700 X FT-IR and Perkin-Elmer 1720 FT-IR. EPR: Bruker ESP 300E. EPR spectra were performed at room temperature and at 140 K on a 1 mM sample in acetonitrile/toluene (v:v = 1:3) solution. The EPR spectra were analyzed with the program SimFonia 1.2 of Bruker. Electrochemistry: PAR Model 270 Research Electrochemistry Software controlled potentiostat/galvanostat Model 273A with the electrochemical cell placed in a glovebox. Electrochemical experiments were performed on 1 mM acetonitrile solutions containing 0.2 M (Bu_4N)ClO_4 as

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Table 1. Summary of Crystal Data, Intensity Collection, and Refinement Parameters for $[(\text{L-N}_4\text{Me}_2)\text{VCl}_2](\text{BPh}_4)$ (**1**), $[(\text{L-N}_4\text{Me}_2)\text{VClO}](\text{ClO}_4)$ (**2**) and $[(\text{L-N}_4\text{Me}_2)\text{VO}_2](\text{BPh}_4)$ (**3**)

data	**1**	**2**	**3**
formula	$C_{40}H_{40}BCl_2N_4V$	$C_{16}H_{20}Cl_2N_4O_5V$	$C_{40}H_{40}BN_4O_2V$
mol wt	709.41	470.20	670.51
crystal dimens, mm	0.3 × 0.4 × 0.5	0.25 × 0.4 × 0.7	0.3 × 0.3 × 0.8
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$ (No.14)	$P2_12_12_1$ (No.19)	$P2_1/c$ (No.14)
Z	4	4	4
a, Å	16.940(4)	10.163(2)	14.349(3)
b, Å	9.902(3)	13.351(3)	14.040(5)
c, Å	21.936(8)	14.762(3)	18.131(10)
β, deg	108.21(2)	(90)	110.62(3)
V, Å^3	3495(2)	2003(1)	3419(2)
d_{calc}, g/cm^3	1.348	1.559	1.303
diffractometer	Hilger & Watts	Syntex $P2_1$	Hilger & Watts
temp, K	153	293	153
λ, Å	0.71073(Mo $K\alpha$)	0.71073(Mo $K\alpha$)	0.71073(Mo$K\alpha$)
μ, cm^{-1}	4.72	7.97	3.32
F(000)	1480	964	1408
scan method	$\omega-2\Theta$	$\Theta-2\Theta$	$\omega-2\Theta$
2Θ limits, deg	$2.5 \le 2\Theta \le 55$	$4 \le 2\Theta \le 50$	$3 \le 2\Theta \le 55$
unique reflcns	8061	3510	7914
reflcns with $F_o > 4\sigma(F_o)$	6120	3024	5672
no. of variables (restraints)	438	303(42)	437
GooF on F^2 [a]	1.057	1.089	1.067
absolute structure parameter		−0.04(4)	
$R(wR^2)$, % [a–c]	4.25 (9.47)	5.02 (11.93)	5.59 (13.66)

[a] For all reflections with $F_o > 4\sigma(F_o)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

supporting electrolyte; a higher than normal electrolyte concentration was applied to minimize solution resistance. All potentials were measured vs a SCE reference electrode at 25 °C. The potentials were not corrected for junction potentials. A Pt-foil electrode was employed as the working electrode. Under these conditions the potential for the ferrocene/ferrocenium ion couple was 0.39 V. Coulometric experiments were performed by using a Pt-gauze electrode. Magnetic susceptibilities: Johnson Matthey magnetic susceptibility balance. The values for the diamagnetic susceptibilities of the ligand $\text{L-N}_4\text{Me}_2$ and of the other components of the complexes were taken from the literature.[8a,13]

Determinations of the Structures of $[(\text{L-N}_4\text{Me}_2)\text{VCl}_2](\text{BPh}_4)$ (1), $[(\text{L-N}_4\text{Me}_2)\text{VClO}](\text{ClO}_4)$ (2), and $[(\text{L-N}_4\text{Me}_2)\text{VO}_2](\text{BPh}_4)$ (3). Single crystals were obtained by slow diffusion of ether into solutions of compounds **1**, **2**, and **3** in acetonitrile. Suitable crystals of **1** and **3** were immersed in oil and then attached to the tips of glass fibers. The glass fibers were subsequently mounted on goniometer heads in a cool nitrogen stream at −120 °C. A crystal of **2** was carefully affixed to the tip of a glass fiber with an adhesive.

Table 1 contains the cell parameters of the crystals and experimental details on the data collections and the structure refinements. Unit cell parameters and the final orientation matrices were obtained from least squares refinement of 25 machine-centered reflections in the range $25° \le 2\Theta \le 28°$ (**1**) or $20° \le 2\Theta \le 25°$ (**2** and **3**). The intensities of three reflections measured every 97 (**1** and **3**) or 200 reflections (**2**) indicated no decay of the crystals during the data collections. The raw data were processed by the programs XDISK[14] or Watshell.[14] The systematic absences uniquely determine the space groups as $P2_1/n$, $P2_12_12_1$, and $P2_1/c$ for **1**, **2**, and **3**, respectively.

The positions of the non-hydrogen atoms were determined by SHELXS 86[14] and by Fourier difference maps using the program SHELXL-93.[14] Atomic scattering factors were taken from a standard source.[15] The structural parameters were refined with the program SHELXL-93, using F^2 of all symmetry-independent reflections except those with very negative F^2-values. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized locations and their isotropic temperature factors were refined. For compound **2**, the perchlorate anion is disordered over two positions. The largest peaks (holes) in the final difference Fourier maps correspond to 0.31 (−0.46) e/Å^3, 0.50 (−0.21) e/Å^3, and 1.44 (−0.63) e/Å^3 for complexes **1**, **2**, and **3**, respectively. The final R factors are given in Table 1. Positional parameters of the complex cations are listed in Tables 2−4. Thermal parameters as well as full lists of distances and angles for all three complexes are provided in the supplementary material.

Results and Discussion

Synthesis of the Complexes. Reaction of $[\text{VCl}_3(\text{THF})_3]$ with the tetraazamacrocyclic ligand $\text{L-N}_4\text{Me}_2$ in absolute acetonitrile under a nitrogen atmosphere and subsequent metathesis with sodium tetraphenylborate affords green crystals of $[(\text{L-N}_4\text{Me}_2)\text{VCl}_2](\text{BPh}_4)$. The IR spectrum of the complex displays typical absorptions of a coordinated $\text{L-N}_4\text{Me}_2$. In addition, the occurrence of the symmetric and the antisymmetric stretching vibrations of the *cis*-VCl_2 group as a rather broad band around 375 cm^{-1} confirms the cis-octahedral geometry of the complex. The magnetic susceptibility measurement reveals a magnetic moment of 2.68 μ_B, which is within the typical range observed for octahedral mononuclear V(III) complexes with a d^2 electron configuration. As expected, due to the spin−orbit coupling in a $^3T_1$ ground state, the magnetic moment deviates from the spin-only value of 2.83 μ_B. The ^{1}H-NMR spectrum of **1** consists of five paramagnetically shifted, broad signals in the range between −20 to 20 ppm, which are attributed to the protons of the coordinated ligand. The appearance of a purple precipitate (presumably a dinuclear μ-chloro or μ-oxo bridged complex) during the synthesis of the mononuclear complex as well as the rather low yield of 38% indicate the formation of side products whose exact identities have not yet been established.

However, when the reaction of vanadium trichloride with the ligand was carried out under air in ethanolic solution, a blue

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Table 2. Fractional Atomic Coordinates (x10^4) and Isotropic Displacement Parameters (Å^2 ×10^3) with esd's for the Non-Hydrogen-Atoms in the Complex Cation of [(L-N_4Me_2)VCl_2](BPh_4) (**1**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$ or U_{iso}
V(1)	1040(1)	833(1)	2176(1)	19(1)
Cl(1)	1817(1)	83(1)	1553(1)	35(1)
Cl(2)	1003(1)	3070(1)	1887(1)	34(1)
N(1)	−160(1)	99(2)	1607(1)	26(1)
N(2)	999(1)	−1085(2)	2557(1)	20(1)
N(3)	1938(1)	989(2)	3117(1)	27(1)
N(4)	302(1)	1281(2)	2746(1)	26(1)
C(1)	−113(1)	−1410(2)	1597(1)	29(1)
C(2)	387(1)	−1928(2)	2243(1)	24(1)
C(3)	263(2)	−3133(2)	2504(1)	36(1)
C(4)	778(2)	−3468(3)	3108(1)	45(1)
C(5)	1391(2)	−2581(3)	3439(1)	37(1)
C(6)	1487(1)	−1387(2)	3150(1)	24(1)
C(7)	2126(1)	−348(2)	3450(1)	33(1)
C(8)	1581(2)	1957(3)	3481(1)	41(1)
C(9)	676(2)	1695(2)	3348(1)	35(1)
C(10)	226(2)	1864(3)	3770(1)	52(1)
C(11)	−606(2)	1563(3)	3567(2)	57(1)
C(12)	−978(2)	1094(3)	2954(2)	50(1)
C(13)	−503(1)	971(2)	2549(1)	33(1)
C(14)	−831(1)	562(3)	1861(1)	47(1)
C(15)	−354(2)	567(3)	926(1)	42(1)
C(16)	2733(2)	1564(3)	3070(1)	42(1)

^{a} The equivalent isotropic thermal parameter U_{eq} (Å^2) is defined as $U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}_i.\mathbf{a}_j$.

Table 3. Fractional Atomic Coordinates (×10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) with esd's for the Non-Hydrogen-Atoms in the Complex Cation of [(L-N_4Me_2)VClO](ClO_4) (**2**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$ or U_{iso}
V(1)	8654(1)	3075(1)	2937(1)	37(1)
Cl(1)	8981(1)	2356(1)	4366(1)	61(1)
O(1)	9418(3)	2280(2)	2291(2)	57(1)
N(1)	10106(3)	4280(3)	3042(3)	45(1)
N(2)	8021(3)	4065(2)	1934(2)	38(1)
N(3)	6565(3)	2674(2)	2824(2)	40(1)
N(4)	7620(3)	4254(3)	3690(2)	37(1)
C(1)	10121(5)	4776(4)	2126(3)	52(1)
C(2)	8770(5)	4871(3)	1766(3)	43(1)
C(3)	8253(5)	5673(4)	1311(3)	52(1)
C(4)	6957(6)	5653(4)	1034(3)	57(1)
C(5)	6205(5)	4823(4)	1224(3)	52(1)
C(6)	6753(4)	4036(3)	1679(3)	40(1)
C(7)	6094(4)	3057(3)	1927(3)	48(1)
C(8)	5802(4)	3150(4)	3576(3)	52(1)
C(9)	6315(5)	4174(3)	3808(3)	43(1)
C(10)	5593(5)	4968(4)	4127(4)	59(1)
C(11)	6243(6)	5859(4)	4304(4)	64(2)
C(12)	7572(6)	5941(4)	4173(4)	56(1)
C(13)	8254(5)	5100(3)	3866(3)	42(1)
C(14)	9719(5)	5028(4)	3762(3)	50(1)
C(15)	11443(5)	3895(4)	3252(4)	66(2)
C(16)	6348(5)	1569(3)	2848(4)	61(1)

^{a} The equivalent isotropic thermal parameter U_{eq} (Å^2) is defined as $U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j$.

complex of stoichiometry [(L-N_4Me_2)VClO](ClO_4) was formed in 65% yield, after addition of sodium perchlorate. IR spectroscopy confirms coordination of the macrocyclic ligand. Compared to the spectrum of **1**, the rather narrow band at 380 cm^{-1}, corresponding to a V−Cl stretching vibration, indicates coordination of only one chloride. Further, two intensive IR bands are observed at 982 and 968 cm^{-1} for the vanadyl(IV) complex. On the basis of the finding that for six-coordinate vanadyl(IV) complexes a V═O stretching frequency is generally observed around 950 cm^{-1} while for five-coordinate vanadyl(IV) complexes it is found around 980 cm^{-1},[16] the more intense IR band at 968 cm^{-1} is tentatively attributed to the V═O stretching vibration. The magnetic moment of 1.73 μ_B corresponds to the spin-only value of a d^1 electron configuration. This is typical for vanadyl(IV) complexes where the strong π-donor capability of the oxo donor lifts the degeneracy of the t_{2g}-orbitals, thereby prohibiting any strong spin−orbit coupling.

Table 4. Fractional Atomic Coordinates (×10^4) and Isotropic Displacement Parameters (Å^2 x 10^3) with esd's for the Non-Hydrogen-Atoms in the Complex Cation of [(L-N_4Me_2)VO_2](BPh_4) (**3**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$ or U_{iso}
V(1)	822(1)	1918(1)	2148(1)	20(1)
O(1)	1110(2)	1892(2)	3106(1)	33(1)
O(2)	324(2)	885(1)	1817(1)	30(1)
N(1)	−450(2)	2908(2)	1900(1)	19(1)
N(2)	1485(2)	3341(2)	2259(1)	21(1)
N(3)	2245(2)	1703(2)	1964(1)	22(1)
N(4)	553(2)	2426(2)	949(1)	18(1)
C(1)	−63(2)	3811(2)	2348(2)	27(1)
C(2)	924(2)	4088(2)	2290(2)	23(1)
C(3)	1272(2)	5015(2)	2309(2)	30(1)
C(4)	2225(2)	5143(2)	2298(2)	34(1)
C(5)	2797(2)	4364(2)	2255(2)	30(1)
C(6)	2399(2)	3457(2)	2235(1)	22(1)
C(7)	2941(2)	2543(2)	2243(2)	26(1)
C(8)	2016(2)	1540(2)	1099(2)	25(1)
C(9)	1234(2)	2229(2)	620(1)	19(1)
C(10)	1161(2)	2618(2)	−98(2)	25(1)
C(11)	394(2)	3258(2)	−456(2)	27(1)
C(12)	−293(2)	3470(2)	−100(2)	24(1)
C(13)	−194(2)	3027(2)	609(1)	18(1)
C(14)	−923(2)	3115(2)	1031(2)	23(1)
C(15)	−1245(2)	2531(2)	2178(2)	27(1)
C(16)	2747(2)	830(2)	2394(2)	33(1)

^{a} The equivalent isotropic thermal parameter U_{eq} (Å^2) is defined as $U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j$.

The dioxovanadium(V) complex [(L-N_4Me_2)VO_2](BPh_4) was obtained in a 78% yield by the addition of (PPh_4)[VCl_2O_2] to acetonitrile containing the ligand L-N_4Me_2 and 2 equiv of sodium tetraphenylborate. The reaction has to be carried out under exclusion of light and moisture or substantial production of a green byproduct occurs, which cannot be removed from the product by repeated recrystallization. EPR spectroscopy attributes the contamination to some vanadyl(IV) species.

^{1}H-NMR spectroscopy of the pure dioxovanadium(V) complex shows that, as expected, the compound is diamagnetic. Upon coordination, all NMR signals of the ligand protons are shifted to lower fields. But the most distinctive feature of the NMR spectrum is the appearance of an AB-coupling pattern for the diastereotopic methylene protons on the ligand (instead of the singlet observed for the free ligand) as a consequence of the fact that the rapid inversions at the amine nitrogen atoms are revoked by the coordination of the ligand to the metal ion. This observation further demonstrates that, in solution, the ligand remains coordinated to the vanadium ion at all times. IR spectroscopy also confirms coordination of the ligand. The absence of any characteristic V−Cl stretching vibrations in the far-IR region and the observation of two VO_2-stretching vibrations at 914 and 903 cm^{-1} are consistent with the formulation of **3** as a *cis*-dioxovanadium(V) complex.

The complex [(L-N_4Me_2)VCl_2]$^+$ can be converted to [(L-N_4Me_2)VClO]$^+$ with a 58% yield by treating a solution of **1** in acetonitrile with aqueous ethanol under air. An analogous way has been previously pursued in the preparation of the neutral mononuclear vanadyl complex [(tacn)VX_2O] (with X = Cl, F)

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(16) (a) Bonadies, J. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4088. (b) Li, X.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1988**, *27*, 4657.

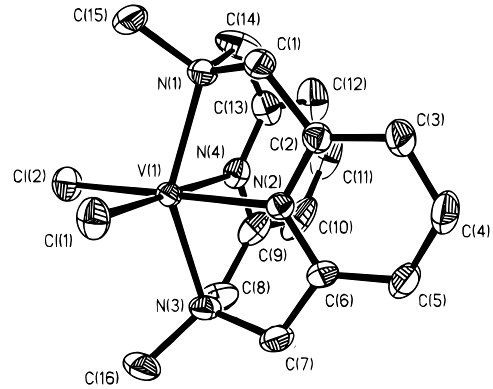

Figure 1. Structure of $[(L\text{-}N_4Me_2)VCl_2]^+$ showing thermal ellipsoids at 50% probability and the atom numbering scheme.

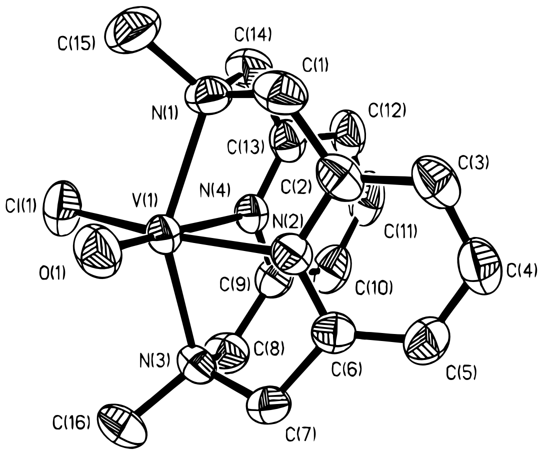

Figure 2. Structure of $[(L\text{-}N_4Me_2)VClO]^+$ showing thermal ellipsoids at 50% probability and the atom numbering scheme.

by oxidation of $[(tacn)VX_3]$ with air in aqueous methanol solution.[17] Although the vanadyl(IV) complex is quite stable in most solvents under air, it can be oxidized in a 63% yield to the dioxovanadium(V) complex by molecular oxygen in the presence of aqueous tetrahydrofuran. A similar observation has been made for the complex $[(bipy)_2VClO]Cl$.[18]

Structures of $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$ (1), $[(L\text{-}N_4Me_2)\text{-}VClO](ClO_4)$ (2), and $[(L\text{-}N_4Me_2)VO_2](BPh_4)$ (3). Structure determinations were carried out on single crystals of $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$, $[(L\text{-}N_4Me_2)VClO](ClO_4)$, and $[(L\text{-}N_4Me_2)\text{-}VO_2](BPh_4)$. Perspective views of the complex cations with the atomic numbering schemes are displayed in Figures 1−3. A comparison of some selected distances and angles is contained in Table 5. The overall coordination geometries of all complexes are best described by distorted octahedrons. While complexes **1** and **3** approach an overall C_{2v} symmetry, the symmetry of complex **2** is reduced to approximately C_s. As in some previously reported complexes containing $L\text{-}N_4Me_2$,[8,19] the tetradentate ligand is folded along the $N_{amine}-N_{amine}$ axis, thus leaving two cis coordination sites available for complexation by the chloro and/or oxo-ligands. The most obvious distortion from an ideal octahedral coordination geometry is the substantial deviation of the $N_{amine}\text{-}V\text{-}N_{amine}$ angle from ideal 180° to 147° (**1** and **2**) and 143° (**3**).

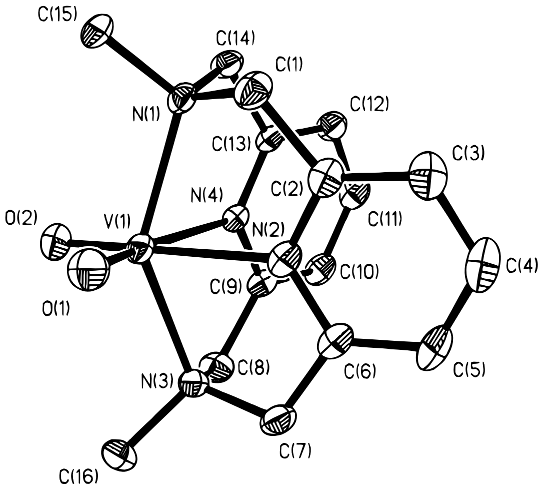

Figure 3. Structure of $[(L\text{-}N_4Me_2)VO_2]^+$ showing thermal ellipsoids at 50% probability and the atom numbering scheme.

In complex **1**, the average V-Cl distance of 2.298 ± 0.001 Å is similar to those obtained in other octahedral vanadium(III) chloride complexes.[20,21] As in other metal chloride complexes with $L\text{-}N_4Me_2$ as ligand,[8,19] the axial $V\text{-}N_{amine}$ bonds with an average length of 2.153 ± 0.001 Å are longer than the equatorial $V\text{-}N_{py}$ bonds which average to 2.079 ± 0.006 Å. However, the difference between the axial and the equatorial metal-nitrogen bond lengths is much less pronounced in complex **1**.

In $[(L\text{-}N_4Me_2)VClO]^+$ the V-O bond distance of 1.624 Å is consistent with a double bond between a six-coordinate vanadium(IV) and a terminal oxo function.[18,21−23] The lengthening of the V-Cl bond from 2.298 Å to 2.341 Å despite the higher oxidation state of the vanadium ion can be explained by the fact that a weakly π-bonding Cl^- and a stronger π-donor O^{2-} compete for the same d-orbital. In general, the V-Cl bond lengths in *cis*-chlorooxovanadium(IV) complexes are somewhat larger than those found in vanadium(III) complexes containing a *cis*-VCl_2 unit.[18,21−23]

Substitution of one Cl^- by O^{2-} with concomitant oxidation of the vanadium also leads to some quite interesting changes in the coordination of the macrocyclic ligand. While the length of $V-N_{py}$ bond trans to the chloride stays approximately the

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[17] (a) Köppen, M.; Fresen, G.; Wieghardt, K.; Llusar, R. M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1988**, *27*, 721. (b) Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1991**, *46B*, 1077.

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

[19] (a) Fronczek, F. R. ; Mamo, A.; Pappalardo, S. *Inorg. Chem.* **1989**, *28*, 1419. (b) Sakaba, H.; Kabuto, C.; Horino, H.; Arai, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1822.

[20] The V−Cl distances in mononuclear octahedral complexes containing the *cis*-$V^{III}Cl_2$ unit range from 2.269 to 2.361 Å with a mean at 2.323 Å. (a) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379. (b) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G.; Martin, J. L.; Smith, P. D. *Inorg. Chem.* **1984**, *23*, 4589. (c) Cotton, F. A.; Duraj, S. A.; Powell, G. L.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *113*, 81. (d) Bultitude, J.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2253. (e) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2646. (f) Kynast, U.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1988**, *17*, 53. (g) Henderson, R. A.; Hills, A.; Hughes, D. L.; Lowe, D. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1755. (h) Cotton, F. A.; Lu, J.; Ren, T. *Inorg. Chim. Acta* **1994**, *215*, 47. (i) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1992**, *31*, 141. (j) Sorensen, K. L.; Ziller, J. W.; Doherty, N. M. *Acta Crystallogr., Sect. C* **1994**, *50*, 407.

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[22] Collison, D.; Eardley, D. R.; Mabbs, F. E.; Powell, A. K.; Turner, S. S. *Inorg. Chem.* **1993**, *32*, 664.

[23] The V−Cl and V═O distances in mononuclear octahedral complexes containing the *cis*-$V^{IV}ClO$ unit range from 2.292 to 2.400 Å and from 1.584 to 1.651 Å, with means at 2.347 and 1.599 Å, respectively. (a) Zah-Letho, J.; Samuel, E.; Dromzee, Y.; Jeannin, Y. *Inorg. Chim. Acta* **1987**, *126*, 35. (b) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013. (c) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1991**, 1414. (d) Kabanos, T. A.; Keramidas, A. D.; Papaioannou, A.; Terzis, A. *Inorg. Chem.* **1994**, *33*, 845.

Table 5. Selected Distances and Angles in $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$ (**1**), $[(L\text{-}N_4Me_2)VClO](ClO_4)$ (**2**), and $[(L\text{-}N_4Me_2)VO_2](BPh_4)$ (**3**)

	1	2	3
V(1)−N(1)	2.152(2)	2.189(4)	2.211(2)
V(1)−N(2)	2.084(2)	2.087(4)	2.191(2)
V(1)−N(3)	2.153(2)	2.196(4)	2.201(2)
V(1)−N(4)	2.073(2)	2.195(3)	2.189(2)
V(1)−Cl(1)	2.2969(8)	2.341(2)	
V(1)−Cl(2)	2.2990(9)		
V(1)−O(1)		1.624(3)	1.639(2)
V(1)−O(2)			1.634(2)
N(1)−V(1)−N(2)	77.38(7)	78.0(1)	75.30(8)
N(1)−V(1)−N(3)	146.80(7)	146.8(1)	143.02(8)
N(1)−V(1)−N(4)	77.57(7)	76.1(1)	75.48(8)
N(1)−V(1)−Cl(1)	99.13(6)	98.2(1)	
N(1)−V(1)−Cl(2)	103.09(5)		
N(1)−V(1)−O(1)		101.5(2)	96.36(10)
N(1)−V(1)−O(2)			105.10(9)
N(2)−V(1)−N(3)	77.47(7)	78.6(1)	75.13(8)
N(2)−V(1)−N(4)	81.47(7)	76.0(1)	73.34(8)
N(2)−V(1)−Cl(1)	92.31(5)	160.6(1)	
N(2)−V(1)−Cl(2)	170.63(5)		
N(2)−V(1)−O(1)		98.3(2)	89.08(10)
N(2)−V(1)−O(2)			164.18(9)
N(3)−V(1)−N(4)	77.58(8)	75.6(1)	75.15(8)
N(3)−V(1)−Cl(1)	103.19(6)	96.1(1)	
N(3)−V(1)−Cl(2)	98.33(5)		
N(3)−V(1)−O(1)		105.0(2)	104.85(10)
N(3)−V(1)−O(2)			97.55(10)
N(4)−V(1)−Cl(1)	173.45(6)	84.6(1)	
N(4)−V(1)−Cl(2)	89.46(5)		
N(4)−V(1)−O(1)		174.1(2)	161.93(10)
N(4)−V(1)−O(2)			91.32(9)
Cl(1)−V(1)−Cl(2)	96.83(3)		
Cl(1)−V(1)−O(1)		101.1(1)	
O(1)−V(1)−O(2)			106.48(11)

same, the $V-N_{py}$ bond trans to O^{2-} is remarkably elongated to 2.195 Å. This trans influence is a well-known effect found in complexes containing the strong π donor O^{2-} as ligand. In order to accommodate the larger $V-N_{py}$ bond, the vanadium ion in **2** protrudes more out of the macrocyclic cavity than in **1**, resulting in slightly larger $V-N_{amine}$ distances and a decreased $N_{py}-V-N_{py}$ angle. In general, the steric rigidity and the small ring size of the macrocyclic ligand account for the observation that, in all complexes with $L\text{-}N_4Me_2$ as ligand, the metal ion does not lie on the intersecting line of the least-squares planes of the two pyridine rings and that, therefore, the angle between both pyridine planes is normally considerably less than the $N_{py}-M-N_{py}$ angle.[8] In complex **2**, the asymmetry of the $V-N_{py}$ bonds introduces some additional strain onto the coordinated macrocycle. Thus, within this series of compounds, the angle between the pyridine planes reaches its minimum with 49.0° in complex **2** and the displacement of the vanadium ion from the least-squares planes of the pyridine rings amounts to 0.492 ± 0.076 Å, compared to 0.249 ± 0.006 Å and 0.209 ± 0.078 Å in complexes **1** and **3**, respectively.

In $[(L\text{-}N_4Me_2)VO_2]^+$, the V−O bond lengths average to 1.637 ± 0.003 Å and are within the range commonly found in *cis*-dioxovanadium(V) complexes with octahedral coordination geometries.[24,25] The slight increase of the average V−O bond despite the higher nuclear charge on the vanadium ion derives from the fact that in the *cis*-dioxo compound both coordinated oxo groups compete for the same vacant d_{xy}-orbital and, therefore, the V−O bond order is slightly reduced in comparison with the previously discussed vanadyl(IV) complex. This decrease in bond strength is also demonstrated by the decrease in the V=O stretching vibration frequency from 968 cm^{-1} in the vanadyl complex to 914 and 903 cm^{-1} in the *cis*-dioxovanadium(V) complex. A similar reduction of the V=O bond strength has been observed for other *cis*-dioxovanadium(V) complexes, which distinguish themselves from the corresponding vanadyl(IV) complexes only by the fact that one oxo function is replaced by a weak π-donor while the residual coordination environment around the central ion is preserved.[18,25]

The $V-N_{py}$ bonds trans to both V=O groups are, with 2.190 ± 0.001 Å, as long as the corresponding trans $V-N_{py}$ bond in **2**, again providing evidence for the strong trans influence of V=O groups. In comparison with compound **2**, the average $V-N_{amine}$ bond length of 2.206 ± 0.005 Å changes only slightly. The increase from 96.8° (**1**) to 101.1° (**2**) to 106.5° (**3**) for the angle included by the bondings between the vanadium and the cis coordinating ligands reflects the stronger electron repulsion between the shorter V=O bond and the other ligand bonding. Of all three compounds presented here, the central metal ion protrudes to the greatest extent out of the macrocyclic cavity in the dioxovanadium(V) complex, as is manifested in the small $N_{py}-V-N_{py}$ and $N_{amine}-V-N_{amine}$ angles. It is worthwhile to point out that in complex **3** the axial $V-N_{amine}$ bonds are nearly as large as the equatorial $V-N_{py}$ bonds. Considering that the $M-N_{py}$ bond determines for the most part the coordination mode of the macrocycle,[8] this finding serves as evidence for the adaptability of this sterically rigid macrocycle toward individual complexing conditions given by the size and charge of the metal ion as well as by the electronic and steric factors of the residual ligand donors trans to the pyridine nitrogens.

Such a series of vanadium complexes which differ only in the oxidation state of the vanadium ion and the donor composition at two coordination sites is quite rare. With bipy as ligand, a rather similar series has been obtained in which, however, only the structures of $[(bipy)_2VClO]^+$ and $[(bipy)_2VO_2]^+$ were established.[18,26] In all other instances, only the vanadium(III) and the vanadyl(IV) equivalents were obtained.[21,22,25] For example, with the anionic tridentate ligand $(HB(Me_2pz)_3)^-$ only the complexes $[\{HB(Me_2pz)_3\}VCl_2(DMF)]$ and $[\{HB(Me_2pz)_3\}VClO(DMF)]$, but not the corresponding dioxovanadium(V) complex, were reported.[21] On the other hand, in the pair of compounds $[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)]$ and $[\{HB(Me_2pz)_3\}VClO(Me_2pzH)]$, the protonation of the pyrazolyl ligand varies in addition to the replacement of one chloride by an oxide.[21,22]

Electronic Absorption and Electron Paramagnetic Resonance Spectra. The electronic absorption spectra of the three complexes in acetonitrile are displayed in Figure 4. Assuming an octahedral ligand field description for complex **1**, the absorption bands at 635 and 450 nm are assigned to the transitions $^3T_1(F) \rightarrow {}^3T_2(F)$ and $^3T_1(F) \rightarrow {}^3T_1(P)$, respectively, based on their low intensities. The third band $^3T_1(F) \rightarrow {}^3A_2(F)$ lies in the UV region and is obscured by intensive CT bands.

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(24) The V=O distances in mononuclear octahedral complexes containing the *cis*-V^VO_2 unit range from 1.613 to 1.670 Å with a mean at 1.636 Å. (a) Scheidt, W. R.; Tsai, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867. (b) Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3873. (c) Scheidt, W. R.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3878. (d) Drew, R. E.; Einstein, F. W. B.; Gransden, S. E. *Can. J. Chem.* **1974**, *52*, 2184. (e) Isobe, K.; Ooi, S.; Nakamura, Y.; Kawaguchi, S.; Kuroya, H. *Chem. Lett.* **1975**, 35. (f) Jeannin, Y.; Launay, J. P.; Sedjadi, M. A. S. *J. Coord. Chem.* **1981**, *11*, 27. (g) Giacomelli, A.; Floriani, C.; de S. Duarte, A. O.; Chiesi-Villa,A.; Guastini, C. *Inorg. Chem.* **1982**, *21*, 3310. (h) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168. (i) Stomberg, R. *Acta Chem. Scand., Ser. A* **1986**, *40*, 168. (j) Neves, A.; Horner, M.; Fenner, H.; Strähle, J. *Acta Crystallogr., Sect. C* **1993**, *49*, 1737.

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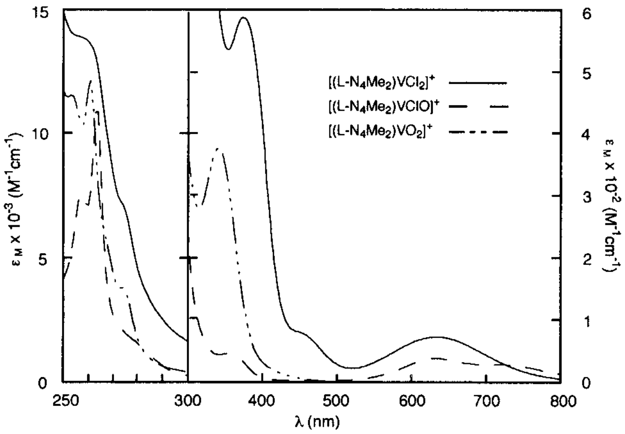

Figure 4. Electronic absorption spectra of $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$ (**1**), $[(L\text{-}N_4Me_2)VClO](ClO_4)$ (**2**), and $[(L\text{-}N_4Me_2)VO_2](BPh_4)$ (**3**) in acetonitrile solutions.

From the position of the $^3T_1(F) \rightarrow {}^3T_2(F)$ absorption band,[27] the ligand field parameter 10 Dq is estimated to be 17 300 cm^{-1}, which is surprisingly larger than the one observed for the cis-octahedral complex $[(bipy)_2VCl_2]^+$.[26] In agreement with the spectra of the uncoordinated ligand[8a] and with those of both other vanadium complexes, an intense absorption is found around 260 nm, which is attributed to a $\pi \rightarrow \pi^*$ transition. The other two absorptions at 375 and 273 nm are tentatively assigned to CT bands.

The visible region of the electronic absorption spectrum of compound **2** is comprised of three relatively weak absorptions at 707, 633, and 356 nm, which are, according to Ballhausen and Gray,[28] attributed to the d−d transitions $d_{xy} \rightarrow (d_{xz},d_{yz})$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{z^2}$, respectively, assuming approximate tetragonal geometry with the V=O bond aligned along the *z*-axis. As previously mentioned, the value of the magnetic moment of the complex also indicates a nondegenerate ground state. The value of 10 Dq = 15 800 cm^{-1} can be obtained directly from the second d−d transition. This value is, as expected, lower than those observed for the complexes $[(bipy)_2VClO]^+$ (17 400 cm^{-1})[18] and $[(HB(Me_2pz)_3)VClO(Me_2pzH)]$ (16 700 cm^{-1})[22] with similar cis-octahedral VN_4ClO coordination environments where, however, in contrast to **2**, all nitrogen donors have π-acceptor capabilities. X-band electron paramagnetic resonance spectra were obtained for the complex in acetonitrile/toluene (v/v = 1:3) at room temperature and at 140 K. The *g* and A^V values were determined by simulation of the spectra. At room temperature the solution spectrum displays eight lines due to the coupling of the $S = {}^1/_2$ electron spin with the vanadium nuclear spin ($I = {}^7/_2$). The isotropic $\langle g \rangle$ and $\langle A^V \rangle$ values were found to be 1.975 and 90.75 $\times 10^{-4}$ cm^{-1}, respectively. The frozen solution renders a nearly axial EPR signal. From $g_{\parallel} = 1.955 < g_{\perp} = 1.983$ of the anisotropic spectrum and from the lack of any observable superhyperfine coupling to the nuclear spin of the nitrogen atoms, it can be concluded that the unpaired electron is localized in the d_{xy}-orbital.[29] The somewhat lower $g_{\parallel}$ value compared to those obtained for $[(bipy)_2VClO]^+$ is consistent with the inferior π-acceptor capabilities of $L\text{-}N_4Me_2$ compared to bipy.[18] The anisotropic coupling constants $A^V_{\parallel}$ and $A^V_{\perp}$ were determined to be 160 $\times 10^{-4}$ and 55 $\times 10^{-4}$ cm^{-1}. These values, as well as that for $\langle A^V \rangle$, are in the common range for vanadyl(IV) complexes with N_4ClO environments.[18,22]

As expected for d^0 metal ions, there are no d−d bands in the visible region of the electronic absorption spectrum of the dioxovanadium(V) complex, while the UV region is dominated by CT bands at 341 and 274 nm and the two $\pi \rightarrow \pi^*$ bands at 261 and 253 nm, which are also found at slightly shifted wavelengths in the other two complexes.

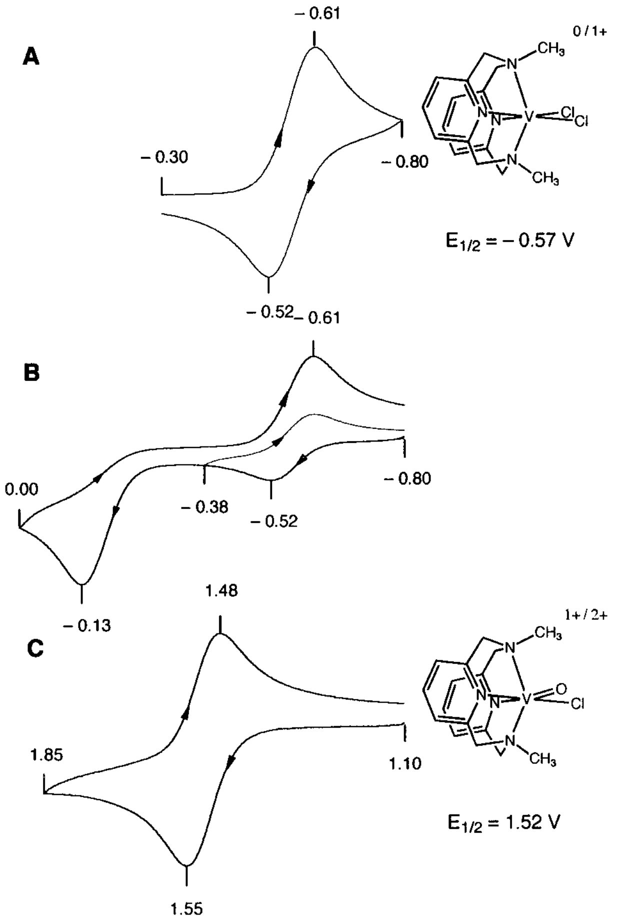

Figure 5. Cyclic voltammograms (A) of $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$ (**1**) (200 mV/s), (B) of the product obtained by reducing $[(L\text{-}N_4Me_2)VCl_2](BPh_4)$ at −0.77 V (200 mV/s), and (C) of $[(L\text{-}N_4Me_2)VClO](ClO_4)$ (**2**) (50 mV/s) at a Pt-foil electrode in acetonitrile solutions at 25 °C; peak potentials and half-wave potentials vs SCE are indicated.

Electrochemical Properties. The redox chemistry of the complexes in acetonitrile solutions was investigated by cyclic voltammetry and by electrolysis. The cyclic voltammograms are presented in Figure 5.

The vanadium(III) complex **1** can be reduced at −0.57 V vs SCE. The independence of the cathodic peak current $i_{p,c}$ from $v^{1/2}$ shows that the electron transfer is diffusion controlled. At high scan rates, e.g., v = 200 mV/s, the separation of the peak potentials $\Delta E_p \approx 90$ mV and the ratio of the peak currents, $i_{p,a}/i_{p,c} \approx 0.9$, indicate a somewhat quasi-reversible electron transfer step. However, lowering the scan rates is accompanied by a decrease of $i_{p,a}/i_{p,c}$ to about 0.45 at v = 5 mV/s. Potential controlled electrolysis at −0.75 V results in the passage of 1.03e$^-$ per molecule. Upon reoxidation at −0.35 V, about 90% of the initially transferred charge is collected. In addition to the quasi-reversible redox response at −0.57 V, which is vastly diminished compared to the size of the original reductive current of the oxidized species, the cyclic voltammogram of the deep-blue reduced species (Figure 5) reveals a further irreversible oxidation process at −0.13 V. As a result of the oxidation at −0.13 V, complex **1** is formed again. As illustrated by reaction 1, the electrochemical results are interpreted to mean that complex **1** is reduced in a quasi-reversible one-electron reduction

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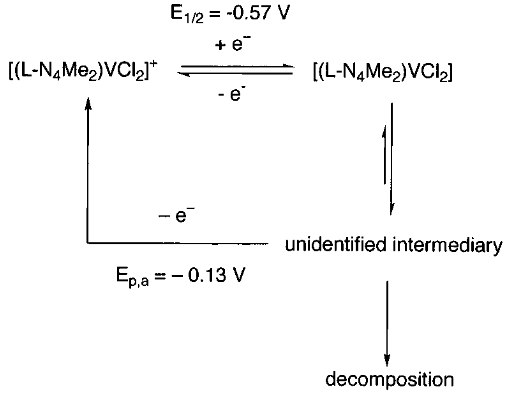
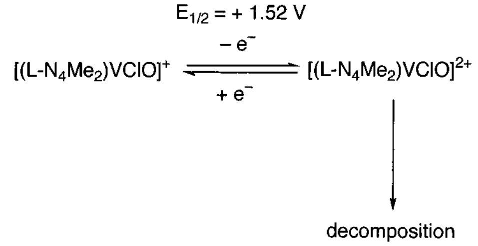
(27) Ballhausen, C. J. *Z. Phys. Chem., Neue Folge* **1957**, *11*, 205.
(28) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111.
(29) Kivelson, D.; Lee, S.-K. *J. Chem. Phys.* **1964**, *41*, 1896.

step to [(L-N_4Me_2)VCl_2], which equilibrates with some not identified species with an irreversible oxidation potential at −0.13 V.



(1)



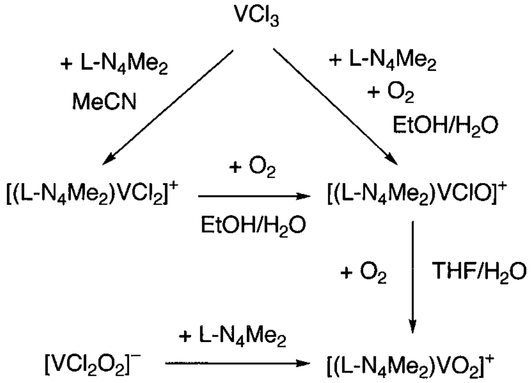
(2)

The vanadyl(IV) complex can be oxidized by one electron at the rather high potential of 1.52 V vs SCE. Also in this redox reaction, since $\Delta E_p = 70$ mV and $i_{p,c}/i_{p,a} \approx 1$ at a scan rate of 50 mV/s, cyclic voltammetry assigns quasi-reversibility to the electron transfer step. While $i_{p,a}/v^{1/2}$ is approximately constant over the whole range of scan rates, the ratio of peak currents is reduced to 0.70 at 5 mV/s. A coulometric oxidation at 1.72 V reveals a small, but constant, current after the passage of 1*F*. When the oxidation of the complex was stopped after the exact flow of 1e⁻ per molecule, there was no reductive current observed upon re-reduction at 1.32 V, indicating, as shown in reaction 2, that the immediate oxidation product, [(L-N_4Me_2)VClO]$^{2+}$, is not stable on a coulometric time scale (20–30 min) but irreversibly reacts or decomposes to some unknown product(s). It is interesting to note that a possible intermediate in the reaction mechanism of vanadium-containing haloperoxidases might consist of a vanadium(V) ion coordinated by an oxide and a halide. The instability of [(L-N_4Me_2)VClO]$^{2+}$ serves as evidence that additional negatively charged ligand donors, preferably with π-donor properties, are needed to stabilize a vanadium(V) species with such a ligand donor set. The effect of an additional charge is demonstrated by the shift of 160 mV to a lower redox potential for the mononuclear complex [{HB(Me_2pz)$_3$}VClO(Me_2pzH)].[22] But even here, the N_4ClO coordination environment does not seem to support a stable vanadium(V) ion. The introduction of anionic oxygen donors like alkoxides decreases even further the redox potential, thus finally permitting isolation of the vanadium(V) complex [{HB(Me_2pz)$_3$}VClO(OBu^t)].[4]

The cyclic voltammogram of the dioxovanadium(V) complex **3** (not shown) does not display any reversible redox reactions. Upon reduction, a peak potential was observed at −1.36 V.

Summary. Novel complexes of the tetraazamacrocyclic ligand L-N_4Me_2 with vanadium have been prepared and characterized by X-ray crystallography and other physical methods. The reactions carried out in this investigation are summarized in Scheme 1. The compounds represent a series of mononuclear complexes containing six-coordinate vanadium in the oxidation states III, IV, and V, respectively, where two chloride ions at two cis-coordination sites are successively replaced by oxo donors with retainment of the residual donor environment. This series of complexes provides us with the rather unique opportunity to examine the influence which the electronic and steric properties of two cis coordinating ligands exert on the structure and stability of the vanadium complexes. The electrochemical results demonstrate quite impressively how the electronic properties of the cis donors stabilize just one specific oxidation state of the vanadium ion in a given donor environment.

Scheme 1



In contrast to the 3,5-dimethyl-substituted tris(pyrazolyl)-borate, which decomposes to some extent in the reaction with vanadium trichloride,[21,22] L-N_4Me_2 is quite stable and is therefore well suited for further studies on the basic coordination chemistry of vanadium. Preliminary studies utilizing the vanadyl(IV) and the dioxovanadium(V) complexes as oxo-transfer reagents have shown that compound **2** does not react with triphenylphosphine under anaerobic conditions, while **3** produces approximately 0.5 equiv of the corresponding phosphinoxide. With respect to this reaction, the relatively easy successive interconversion of complex **1** via **2** to compound **3** by air might prove itself to be very helpful in the development of catalytically proceeding reactions with oxygen as the terminal oxidizing reagent. However, since in this reaction the tetranuclear complex [{(L-N_4Me_2)VO(μ-O)}$_3$VO]$^{3+}$ is formed as the main product, it seems that the reaction of **3** with phosphine does not occur by a simple oxo transfer but instead by a more complicated, possibly radical-involving mechanism. The further investigation of this complex and the continuing exploration of the basic coordination chemistry of vanadium, particularly the reactivity of the complexes with peroxides, will be reported elsewhere.

Acknowledgment. We gratefully acknowledge financial assistance by the Deutsche Forschungsgemeinschaft and by the University of Hamburg.

Supporting Information Available: Crystallographic data for the complexes [(L-N_4Me_2)VCl_2](BPh$_4$), [(L-N_4Me_2)VClO](ClO$_4$), and [(L-N_4Me_2)VO_2](BPh$_4$); details of data collections and tabulations of positional and thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions; Figure S1, X-band EPR spectra of [(L-N_4Me_2)VClO](ClO$_4$) (**2**) in acetonitrile/toluene (v/v = 1:3) solution (a) at room temperature and (b) as frozen glass at 140 K (28 pages). Ordering information is given on any current masthead page.

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