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Synthesis, Characterization, and Molecular Structures of a Series of [(3,5-Dimethylpyrazolyl)borato]vanadium(III) and -(IV) Complexes

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Reaction of VCl_3 or vanadyl bis(acetylacetonate) with tris(3,5–dimethylpyrazolyl)borate yields a series of vanadium(III) and -(IV) complexes. Among these are the following: $\{HB(Me_2pz)_3\}VCl_2(DMF)(H_2O)$ (I), $\{HB(Me_2pz)_3\}VCl_2(DMF)$ (II), $\{HB(Me_2pz)_3\}VOCl(DMF)$ (III), $\{HB(Me_2pz)_3\}VO(acac)$ (IV), and $\{HB(Me_2pz)_3\}VOCl_2$ (V). The vanadium(III) complexes can be air-oxidized to the respective oxovanadium(IV) species. The vanadium(IV) complexes III and IV undergo reversible electrochemical oxidation to diamagnetic vanadium(V) materials. Synthesis of vanadium(III) complexes using solvents other than DMF leads to extensive decomposition of the (pyrazolyl)borate ligand and isolation of two decomposition products: $K[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)]$ (VI) and $[(Me_2pz)_2VOCl_2]_2\cdot THF$ (VII). The structures of II, III, V, VI, and VII have been determined by X-ray crystallography: IIb, monoclinic $P2_1/c$, $a = 9.535$ (17) Å, $b = 20.43$ (3) Å, $c = 16.959$ (14) Å, $\beta = 104.59$ (6)°, $Z = 4$; III, monoclinic $P2_1/n$, $a = 11.077$ (2) Å, $b = 16.095$ (2) Å, $c = 14.108$ (5) Å, $\beta = 100.40$ (3)°, $Z = 4$; V, monoclinic, $P2_1/c$, $a = 13.518$ (4) Å, $b = 11.064$ (5) Å, $c = 14.817$ (6) Å, $\beta = 112.71$ (4)°, $Z = 4$; VI, monoclinic, $C2/c$, $a = 20.584$ (6) Å, $b = 10.723$ (3) Å, $c = 24.601$ (7) Å, $\beta = 96.15$ (2)°, $Z = 8$; VII, orthorhombic, $C222_1$, $a = 12.484$ (4) Å, $b = 22.996$ (14) Å, $c = 12.471$ (5) Å, $Z = 4$. The metal is octahedral and the tris(pyrazolyl)borate molecule functions as a facially coordinating tridentate ligand in all structures except V. In V the ligand is bidentate and the vanadium adopts a square-pyramidal geometry. The solvent-dependent change in coordination mode of the ligand is discussed.

Introduction

Although the presence of vanadium in biological systems (e.g. Amavadin from the mushroom *Aminata muscaria*[1] or the vanadium–tunichrome system in the blood cells of ascidians[2]) is well established, only two vanadoenzymes are known.[3,4] The most unusual of these are the V(V)-dependent bromoperoxidases isolated from several species of marine algae, which catalyze the reaction

$$RH + H_2O_2 + X^- \rightarrow RX + H_2O + OH^-$$

Little is presently known about the structure of the vanadium-containing active site although a variety of physical methods suggest a primarily O or N,O donor set.[5-8]

The study of model complexes with biologically relevant ligands represents another viable means with which to outline the structural, redox, and mechanistic possibilities available to vanadium in biomolecules such as the bromoperoxidases. Previously, we have investigated the coordination chemistry of vanadium with phenolate-containing ligands, which could mimic tyrosine coordination.[9-12] We have now turned our attention to vanadium complexes of the tris(pyrazolyl)borate ligands, which can in many ways mimic histidine nitrogen ligation.[13,14]

In addition to their similarity to the imidazole group, the tris(pyrazolyl)borato ligands have a number of attractive features as a system with which to study the reactivity of vanadium. These include the following. (1) They have the ability to occupy three cis coordination sites on the metal while leaving open another three cis coordination sites for attachment to other ligands. These open sites, which are capable of binding small molecules, are important for any study on the reactivity and catalytic behavior of vanadium. (2) They have the ability to prepare sterically demanding (i.e. the 3,5-dimethyl, 3-phenyl, or 3-*tert*-butyl derivatives) complexes that can prevent dimerization pathways for inactivation. Sterically demanding ligands have proven to be very successful at stabilizing a number of previously unstable complexes.[15,16] (3) The ligands are easily synthesized. (4) The ligands appear able to stabilize metals in a wide variety of oxidation states.

Despite the widespread use of tris(pyrazolyl)borates in transition-metal chemistry,[17,18] little prior work has been done with vanadium. To our knowledge only two vanadium tris(pyrazolyl)borate complexes have been discussed in the literature. These are the vanadium(IV) complex $HB(pz)_3VCl_3$[19] and the vanadium(III) complex $HB(pz)_3VCl_2(THF)$.[20] No reaction chemistry or structural information, and only very limited characterization (elemental analysis), have been reported. Vanadium(V) species appear to be unknown. Vanadium(III) and -(IV) complexes of the topologically similar ligands the 1,4,7-triazacyclononanes have been studied by Wieghardt and co-workers.[21,22] In this paper, we report the synthesis and characterization of a series of vanadium(III) and -(IV) complexes with the tris(3,5-dimethylpyrazolyl)borato ligand and provide the first X-ray structural characterization for these compounds.

Experimental Section

Materials. Unless otherwise stated, reactions were carried out under an atmosphere of pure dry argon or nitrogen by utilizing standard

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Schlenk techniques. Solvents were dried and distilled under a blanket of inert gas before use. Potassium hydridotris(3,5-dimethylpyrazolyl)borate was prepared as previously described.[23] The purity of the ligand was confirmed by proton NMR spectroscopy. Vanadyl bis(acetylacetonate) was synthesized by a literature procedure.[24] Anhydrous vanadium trichloride, hydrated vanadyl sulfate, and $VOCl_3$ were obtained from the Aldrich Chemical Co. and used as received.

Synthesis. [{HB(Me$_2$pz)$_3$}VCl$_2$(DMF)(H$_2$O)] (I). To 2.0 g of potassium hydridotris(3,5-dimethylpyrazolyl)borate dissolved in DMF was added 0.93 g of anhydrous vanadium trichloride. The slurry was stirred overnight, by which time all the VCl_3 had dissolved and an intense violet solution was obtained. The solution was filtered through Celite to remove KCl, and DMF was removed under vacuum. The resulting solid was very hygroscopic, and the material used for analysis appeared to contain one water molecule and one coordinated DMF molecule.[25] Anal. Calcd for $C_{18}H_{31}N_7BVCl_2O_2$: C, 42.4; H, 6.1; N, 19.2; V, 10.0; Cl, 13.7. Found: C, 42.2; H, 6.1; N, 17.6; V, 10.2; Cl, 13.3.

{HB(Me$_2$pz)$_3$}VCl$_2$(DMF)·C$_6$H$_6$ (IIa). [{HB(Me$_2$pz)$_3$}VCl$_2$(DMF)(H$_2$O)] was dissolved in benzene under argon to produce a violet solution. Upon standing, the solution deposited a quantity of green crystals. The crystals were filtered off, washed with a small quantity of benzene, and dried under vacuum. Anal. Calcd for $C_{24}H_{34}N_7BVCl_2O$: C, 50.7; H, 6.0; N, 17.2; Cl, 12.3; V, 8.9. Found: C, 50.3; H, 6.1; N, 17.5; Cl, 11.9; V, 8.3.

{HB(Me$_2$pz)$_3$}VOCl(DMF) (III). To 10 g of K[HB(Me$_2$pz)$_3$] in 200 mL of dry DMF was added an equimolar quantity of VCl_3 (4.7 g). After the mixture was stirred overnight to yield a deep purple solution, it was exposed to the air and stirred for an additional 12 h. The resulting deep green solution was extracted with CH_2Cl_2/H_2O, and the organic layer was dried over anhydrous sodium sulfate. Bright green crystals formed overnight from a concentrated methylene chloride solution layered with ether. The crystals were washed with hot H_2O, methanol, and finally ether and then air-dried, yielding 3.8 g, 30%. An alternative synthesis of III involved reaction of K[HB(Me$_2$pz)$_3$] with VCl_3 in DMF to yield purple I. Compound I was then oxidized with 1 equivalent of *tert*-butyl hydroperoxide (3.0 M solution in 2,2,4-trimethylpentane). Addition of the peroxide caused an immediate color change to deep green. The solution was allowed to stir for 2 h, and DMF was removed under vacuum. The green solid was dissolved in methylene chloride, and the resulting solution was overlayered with hexane. The solution was left open to the air for 12 h. From this solution blue crystals were obtained. These were collected, washed with hexane, and dried under vacuum. Anal. Calcd for $C_{18}H_{29}N_7BVClO_2$: C, 45.7; H, 6.3; N, 20.7; Cl, 7.5; V, 10.7. Found C, 45.1; H, 6.1; N, 20.2; Cl, 8.0; V, 11.1. Although the color of this product varied from that produced by air oxidation, the IR spectra, electrochemical properties, and analyses of the two materials were identical.

{HB(Me$_2$pz)$_3$}VO(acac) (IV). A 20-g sample of K[HB(Me$_2$pz)$_3$] was refluxed with an equimolar amount of VO(acac)$_2$ in methanol. The initially blue-green solution gradually darkened to a deep green and precipitated a large quantity of light-colored solid. After 3-4 h of reflux, the solution was filtered while hot and the solid product washed extensively with methanol, yielding 13.6 g, 45%. The pale blue solid could be recrystallized from a hot saturated solution in acetonitrile. Anal. Calcd for $C_{20}H_{29}N_6BVO_3$: C, 51.8; H, 6.3; N, 18.1. Found: C, 52.1; H, 6.2; N, 18.2.

The following materials were obtained in small amounts from reactions of K[HB(Me$_2$pz)$_3$] and VCl_3 using THF as a solvent rather than DMF. The products were characterized by single-crystal X-ray diffraction and, where possible, elemental analysis.

{HB(Me$_2$pz)$_3$}VOCl$_2$ (V). Reaction of VCl_3 with K[HB(Me$_2$pz)$_3$] overnight in THF followed by chromatography on silica gel resulted in the transient formation of a violet band on the column. The violet color rapidly faded, and a green band eluted from the column with CH_2Cl_2/THF. The green solution was evaporated to dryness, the residue was dissolved in dry CH_2Cl_2, and the resulting solution was overlayered with hexane. The solution immediately became cloudy with a white precipitate. Upon standing in the freezer for several weeks, the solution deposited a small quantity of well-formed green crystals along with considerable amounts of the white solid (identified by NMR spectroscopy to be a mixture of uncoordinated ligand and free 3,5-dimethylpyrazole). The green crystals were subjected to X-ray diffraction analysis.

K[{HB(Me$_2$pz)$_3$}VCl$_2$(Me$_2$pz)] (VI). If the crude anaerobic reaction mixture used to prepare V is overlayered directly with hexane and cooled in a freezer, without silica gel chromatography, a new green crystalline solid can be isolated. The product was identified by X-ray crystallography. Anal. Calcd for $C_{20}H_{29}N_8VBCl_2K\cdot{}^1/_2THF$. C, 44.8; H, 5.6; N, 20.1; V, 9.4. Found: C, 44.6; H, 6.1; N, 20.0; V, 9.2.

[(Me$_2$pz)$_2$VOCl$_2$]$_2$·solvent (VII). If the green reaction mixture above was allowed to crystallize slowly in the presence of air, it produced dark blue crystals, which were subjected to X-ray diffraction analysis. These crystals proved to be the THF adduct of a decomposition product, [(Me$_2$pz)$_2$VOCl$_2$]$_2$. Crystals separated from the solvent and air-dried lost crystallinity as they converted into the hydrate. Anal. Calcd for $C_{20}H_{28}N_8V_2Cl_4O_2\cdot 6H_2O$: C, 27.6; H, 6.0; N, 12.9; V, 11.7. Found: C, 27.1; H, 5.2; N, 12.4; V, 11.6.

Physical Methods. Infrared spectra were obtained on either a Nicolet 6000 FT-IR or a PE 683 instrument as KBr pellets. Room-temperature solid-state susceptibilities were measured by using a Johnson-Matthey MSB-1 susceptibility balance. Solution data were obtained via the Evans method on a Bruker 270 MHz FT-NMR instrument.[26] Electron paramagnetic resonance spectroscopy employed either a Varian E-4 or an EM500 spectrometer. Spectra were measured in the indicated solvents with the use of quartz tubes at room temperature and/or at 77 K. UV-visible spectra were obtained either on a Perkin-Elmer 553 or a Varian DMS 100 spectrophotometer. Analyses were performed by Schwarzkopf Microanalytical Laboratories, Robertson Microanalytical Laboratories, or they were obtained locally by using a PE 240C elemental analyzer.

Collection and Analysis of X-ray Data. Data crystals of II, III, V, VI, and VII were mounted in Lindeman capillaries and transferred to either a Nicolet R3mv or an Enraf-Nonius CAD4 diffractometer. Preliminary diffractometer data and axial photography led to unit cell choices. Following accurate centering of 24 relatively high angle reflections, intensity data were collected on II, III, V, VI, and VII at room temperature as previously described.[27] Crystal data and data collection parameters are summarized in Table I. Since absorption coefficients were small and none of the crystals showed significant deterioration during data collection, no decay or absorption corrections were applied to the data.

Solution and Refinement of the Structures. Data were reduced and the models refined by using either the SHELX 86 program package provided with the Nicolet R3mv or the SDP-plus suite of programs on the Enraf-Nonius CAD4. Structures were solved by standard Patterson or direct-methods procedures and refined by full-matrix least-squares techniques as previously described.[27] Parameters used in the solution and refinement of the structures are summarized in Table I. Hydrogen atoms were included as fixed contributions in idealized positions for II, VI, and VII. Hydrogen atoms were not located in III or V, but their contributions were included in the refinements. Final atomic parameters are found in Tables II–VI. Anisotropic thermal parameters, idealized hydrogen atom parameters, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Vanadium(III) Complexes. Reaction at room temperature of VCl_3 and K[HB(pz*)$_3$], where pz* = 3,5-dimethylpyrazolyl, in degassed DMF yields a deep purple solution, λ_{max} = 489 nm. The magnitude of the extinction coefficient ($\epsilon > 10^3$) indicates that this band must be due to some type of charge-transfer interaction, the nature of which we have not investigated. The stoichiometry as established by elemental analysis is LVCl$_2$(sol)$_2$, where sol = DMF or H_2O. Mass spectrometry on the 3,5-dimethyl derivative shows the presence of DMF and a major high-mass peak in both EI and CI modes at 418 amu, which corresponds to the unsolvated LVCl$_2$. This information, coupled with the ready solubility of the complexes in nonpolar solvents and their facile ionization in the mass spectrometer, suggests that both chlorides in I are coordinated and are not counterions. Since V(III) is expected to be six-coordinate overall,[28] two formulations would be reasonable:

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(25) A similar violet complex was prepared by refluxing equimolar amounts of potassium tris(3-phenylpyrazolyl)borate with VCl_3 in THF overnight. After evaporation of the THF, the solid was dissolved in dichloromethane and the solution filtered through Celite to remove KCl. Evaporation of the filtrate left a hygroscopic purple solid. Anal. Calcd for $C_{27}N_6H_{26}BVCl_2O_2$: C, 55.2; H, 4.4; N, 14.3. Found: C, 55.7; H, 5.0; N, 13.8. The analogous tris(3-*tert*-butylpyrazolyl)borato complex was prepared similarly.

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Table I. Summary of Crystallographic Data and Data Collection

parameter	IIb	III	V	VI	VII
formula	$C_{30}H_{41}BN_7OCl_2V$	$C_{18}H_{29}BN_7O_2ClV$	$C_{15}H_{22}BN_6OCl_2V$	$C_{20}H_{29}BN_8Cl_2KV$	$C_{24}H_{40}N_8O_3Cl_4V_2$
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$C2/c$	$C222_1$
temp, K	21	24	21	21	21
a, Å	9.535 (7)	11.077 (2)	13.518 (4)	20.584 (6)	12.484 (4)
b, Å	20.43 (3)	16.095 (2)	11.064 (5)	10.732 (3)	22.996 (14)
c, Å	16.959 (14)	14.108 (5)	14.817 (9)	24.601 (7)	12.471 (5)
β, deg	104.59 (6)	100.40 (3)	112.71 (4)	96.15 (2)	90.00
V, Å^3	3197 (6)	2474 (5)	2045 (6)	5403 (3)	3580 (3)
d_{calcd}, g cm^{-3}	1.347	1.269	1.410	1.363	1.360
Z	4	4	4	8	4
fw	648.3	472.7	435.0	554.3	732.4
cryst size, mm	0.22 × 0.25 × 0.28	0.35 × 0.45 × 0.15	0.25 × 0.30 × 0.24	0.15 × 0.20 × 0.22	0.15 × 0.20 × 0.25
μ, mm^{-1}	0.503	0.520	0.820	0.732	1.68
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)				
scan type	θ–2θ				
data collection	$\pm h,+k,+l$ $3.0 < 2\theta < 55.0°$	$+h,+k,\pm l$ $3.0 < 2\theta < 50.0°$	$\pm h,+k,+l$ $3.0 < 2\theta < 50.0°$	$\pm h,+k,+l$ $3.0 < 2\theta < 45.0°$	$+h,+k,+l$ $3.0 < 2\theta < 50.0°$
no. of unique data	5750	4102	2626	3561	1794
no. of data, $I - 3\sigma(I)$	3996	2350	2291	1810	1210
data to parameter ratio	12:1	9:1	10:1	6:1	7:1
R_1[a]	0.069	0.062	0.053	0.086	0.072
R_2[b]	0.077	0.091	0.061	0.065	0.069
largest peak,[c] e/Å^3	0.48	0.55	0.63	0.56	0.98
Δ/σ[d]	0.535	0.310	0.032	0.007	0.010

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $R_2 = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$. [c] Largest peak in the final difference Fourier map. [d] Largest shift (Δ) to error (σ) ratio in the final least-squares cycle.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[\{HB(Me_2pz)_3\}VCl_2]\cdot 2C_6H_6$

	x	*y*	*z*	*U*(eq)[a]
V(1)	4705 (1)	−1887 (1)	1804 (1)	35 (1)
Cl(1)	6844 (1)	−1791 (1)	1369 (1)	53 (1)
Cl(2)	4173 (2)	−2975 (1)	1414 (1)	55 (1)
N(1)	5715 (4)	−1796 (2)	3640 (2)	34 (1)
N(2)	5909 (4)	−2162 (2)	2987 (2)	37 (1)
N(3)	2844 (4)	−1849 (2)	2282 (2)	36 (1)
N(4)	3042 (4)	−1647 (2)	3085 (2)	36 (1)
N(5)	4705 (4)	−737 (2)	2962 (2)	37 (1)
N(6)	4891 (4)	−886 (2)	2192 (2)	37 (1)
N(7)	3003 (5)	−1577 (2)	−728 (3)	47 (2)
O(1)	3499 (4)	−1600 (2)	655 (2)	47 (1)
B(1)	4476 (6)	−1297 (3)	3523 (3)	37 (2)
C(1)	7004 (5)	−2589 (3)	3292 (3)	44 (2)
C(2)	7513 (6)	−3084 (3)	2777 (3)	56 (2)
C(3)	7511 (5)	−2490 (3)	4129 (3)	49 (2)
C(5)	6812 (7)	−1673 (3)	5146 (3)	60 (2)
C(6)	1780 (6)	−1698 (3)	3306 (3)	50 (2)
C(7)	4999 (6)	−297 (2)	1834 (3)	43 (2)
C(8)	1634 (7)	−1513 (3)	4147 (4)	70 (3)
C(9)	3804 (6)	−1717 (3)	−9 (3)	45 (2)
C(10)	765 (6)	−1949 (3)	2652 (3)	55 (2)
C(11)	5242 (8)	−238 (3)	991 (3)	67 (3)
C(12)	4875 (6)	204 (3)	2359 (3)	55 (1)
C(13)	6695 (5)	−1991 (3)	4333 (3)	43 (2)
C(14)	4688 (6)	−86 (3)	3062 (3)	45 (2)
C(15)	4516 (9)	233 (3)	3828 (4)	77 (3)
C(16)	801 (6)	−2297 (3)	1181 (4)	64 (2)
C(17)	3434 (7)	−1711 (3)	−1481 (3)	61 (2)
C(18)	1438 (5)	−2030 (3)	2021 (3)	45 (2)
C(19)	1615 (7)	−1289 (4)	−804 (4)	107 (4)
C(41)	−772	−308	2770	184 (10)
C(42)	−74 (17)	241 (7)	2790 (7)	178 (9)
C(43)	−13 (16)	708 (6)	3323 (8)	148 (7)
C(44)	−646 (21)	615 (9)	3898 (11)	221 (13)
C(45)	−1376 (18)	69 (11)	3932 (13)	233 (15)
C(46)	−1444 (14)	−377 (9)	3333 (12)	195 (11)
C(61)	787 (29)	−178 (12)	741 (10)	176 (12)
C(62)	1254 (15)	291 (13)	323 (17)	186 (11)
C(63)	−483 (29)	−473 (8)	431 (18)	178 (12)

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

Table III. Atomic Coordinates (×10^4) for $\{HB(Me_2pz)_3\}VOCl(DMF)$

	x	*y*	*z*
V(1)	2171 (1)	1731 (7)	4418 (8)
C6(1)	2985 (2)	3023 (1)	4070 (1)
O(1)	1637 (5)	2004 (3)	5392 (3)
O(2)	3851 (4)	1335 (3)	5114 (3)
N(1)	2859 (5)	1250 (3)	3052 (4)
N(2)	2002 (5)	863 (3)	2366 (4)
N(3)	1604 (5)	479 (3)	4399 (4)
N(4)	1014 (5)	106 (3)	3564 (4)
N(5)	501 (5)	1957 (3)	3460 (4)
N(6)	29 (5)	1390 (3)	2774 (4)
N(7)	5690 (5)	1531 (4)	6086 (4)
C(1)	3880 (6)	1333 (5)	2675 (5)
C(2)	3695 (7)	1009 (5)	1731 (6)
C(3)	2501 (8)	712 (5)	1563 (5)
C(4)	1688 (6)	100 (4)	5113 (5)
C(5)	1138 (7)	844 (5)	4721 (6)
C(6)	720 (6)	693 (4)	3732 (5)
C(7)	−323 (7)	2569 (5)	3417 (5)
C(8)	−1343 (7)	2412 (5)	2718 (6)
C(9)	−1079 (6)	1650 (5)	2321 (5)
C(11)	5043 (6)	1708 (5)	3203 (6)
C(16)	4689 (6)	1811 (4)	5556 (5)
C(17)	5897 (8)	644 (5)	6266 (7)
C(18)	6669 (8)	2110 (6)	6503 (6)
C(31)	1747 (9)	312 (6)	665 (6)
C(41)	2295 (7)	76 (5)	6141 (5)
C(61)	132 (7)	−1276 (5)	2971 (6)
C(71)	−108 (9)	3333 (6)	4092 (7)
C(91)	−1884 (7)	1169 (6)	1524 (6)
B(1)	747 (8)	601 (5)	2601 (6)

(a) $[LVCl_2(sol)]\cdot sol$ where L is functioning in a typical tridentate mode or (b) $LVCl_2(sol)_2$ where L must be only bidentate with one dangling pyrazole arm. Several pieces of evidence suggest that the actual formulation is best described by b. First, when the purple material is dissolved in benzene and allowed to stand, it leads to the crystallization of a new light *green* V(III) complex (vide infra) which X-ray has been shown to be $LVCl_2(sol)\cdot sol$. This eliminates that formulation for the purple complex. Second, the infrared spectra of all the well-characterized vanadium complexes of the (3,5-dimethylpyrazolyl)borate ligand, where it functions in a tridentate fashion, show a single sharp band at ~1542 cm^{-1} in the region for an aromatic C–N stretch in the coordinated pyrazole ring. The one crystallographically characterized vanadium complex where the ligand is bidentate (vide infra) shows two infrared bands in this region, one at 1570 cm^{-1}

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $\{HB(Me_2pz)_3\}VOCl_2$

	x	*y*	*z*	*U*(eq)[a]
V(1)	8015 (1)	2127 (1)	3370 (1)	34 (1)
Cl(1)	6747 (1)	2272 (1)	4096 (1)	57 (1)
Cl(2)	7350 (1)	3899 (1)	2509 (1)	52 (1)
O(1)	9128 (3)	2452 (3)	4202 (2)	50 (1)
N(1)	7953 (3)	237 (3)	3514 (3)	37 (2)
N(4)	8538 (3)	1684 (3)	2253 (3)	31 (1)
N(3)	8108 (3)	760 (3)	1594 (3)	32 (1)
N(2)	7614 (3)	−525 (3)	2740 (3)	39 (2)
C(1)	9332 (4)	2177 (4)	2048 (3)	36 (2)
C(3)	8644 (4)	696 (4)	974 (3)	37 (2)
B(1)	7229 (5)	−39 (5)	1681 (4)	39 (2)
C(2)	9433 (4)	1578 (5)	1268 (3)	41 (2)
C(4)	8259 (4)	−441 (5)	4328 (4)	50 (2)
C(6)	7696 (5)	−1691 (5)	3057 (5)	54 (3)
C(31)	8358 (5)	−168 (5)	147 (4)	54 (2)
C(5)	8116 (5)	−1649 (5)	4071 (5)	58 (3)
C(11)	9969 (5)	3228 (6)	2607 (4)	56 (2)
C(61)	7383 (7)	−2771 (5)	2397 (5)	76 (4)
C(41)	8711 (6)	82 (6)	5341 (4)	69 (3)
N(5)	6051 (3)	1780 (4)	880 (3)	45 (2)
N(6)	6235 (3)	820 (4)	1515 (3)	41 (2)
C(7)	5100 (4)	2306 (6)	737 (4)	56 (2)
C(91)	5235 (5)	−235 (7)	2399 (5)	77 (3)
C(9)	5363 (4)	740 (5)	1746 (4)	52 (2)
C(8)	4644 (5)	1630 (6)	1283 (4)	61 (3)
C(71)	4755 (6)	3432 (7)	144 (5)	82 (3)

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

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $K[\{HB(Me_2Pz)_3\}VCl_2(Me_2pz)]$

	x	*y*	*z*	*U*(eq)[a]
V(1)	1208 (1)	2907 (2)	1399 (1)	34 (1)
Cl(1)	187 (1)	2805 (3)	1743 (1)	50 (1)
Cl(2)	1330 (2)	734 (3)	1449 (2)	52 (1)
N(1)	1164 (5)	4882 (9)	1364 (5)	42 (4)
N(2)	1377 (4)	5448 (9)	908 (4)	37 (4)
C(11)	2182 (6)	3698 (12)	2476 (5)	41 (5)
C(12)	2250 (6)	3380 (12)	3028 (5)	49 (6)
C(13)	1753 (6)	2609 (12)	3113 (5)	42 (5)
N(3)	2111 (5)	3071 (9)	1066 (4)	41 (4)
N(4)	2145 (4)	3844 (9)	627 (4)	36 (4)
C(21)	1395 (5)	6689 (13)	995 (6)	40 (5)
C(22)	1161 (6)	6942 (12)	1483 (6)	52 (6)
C(23)	1045 (6)	2800 (12)	1713 (5)	41 (5)
N(5)	781 (4)	2905 (10)	584 (4)	42 (4)
N(6)	967 (5)	3825 (10)	237 (4)	42 (4)
C(41)	579 (7)	3728 (14)	−243 (5)	50 (6)
C(42)	173 (6)	2732 (14)	−207 (6)	56 (6)
C(43)	292 (6)	2233 (14)	305 (6)	52 (6)
N(7)	1664 (4)	3086 (9)	2219 (4)	37 (4)
N(8)	1420 (4)	2434 (9)	2620 (4)	46 (4)
C(31)	2752 (6)	3799 (12)	454 (5)	43 (5)
C(32)	3121 (6)	2992 (12)	790 (5)	46 (5)
C(33)	2720 (6)	2547 (10)	1165 (5)	40 (5)
C(1)	1571 (6)	1954 (13)	3615 (5)	75 (6)
C(2)	2576 (6)	4601 (11)	2208 (5)	64 (6)
C(7)	643 (6)	4642 (13)	−697 (5)	73 (7)
C(3)	779 (6)	5574 (12)	2241 (5)	61 (6)
C(4)	1601 (6)	7580 (11)	580 (5)	67 (6)
C(5)	2948 (6)	4516 (12)	−18 (5)	65 (6)
C(6)	2899 (6)	1647 (11)	1618 (5)	62 (6)
C(8)	−47 (6)	1163 (13)	543 (5)	72 (6)
B(1)	1553 (7)	4681 (14)	419 (6)	48 (6)
K(1)	4503 (3)	3934 (7)	2050 (4)	185 (5)
K(2)	5100 (25)	4779 (24)	2344 (19)	142 (23)

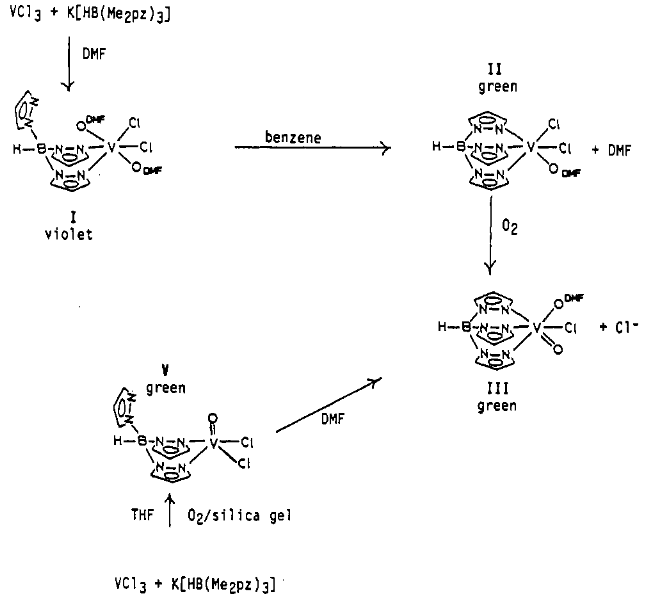
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(Me_2pz)_2VOCl_2]_2 \cdot THF$

	x	*y*	*z*	*U*(eq)[a]
V(1)	0	813 (1)	7500	32 (1)
Cl(1)	0	2338 (1)	9393 (2)	41 (1)
V(2)	0	2518 (1)	7500	33 (1)
O(1)	0	1513 (4)	7500	30 (3)
Cl(4)	−1052 (3)	744 (2)	9067 (3)	42 (1)
O(2)	0	3210 (5)	7500	56 (5)
O(60)	0	−135 (5)	7500	41 (4)
C(61)	−24 (17)	−503 (5)	6540 (10)	55 (5)
C(62)	−236 (14)	−1099 (6)	6926 (13)	62 (6)
N(21)	−1686 (8)	2384 (4)	7500	39 (3)
N(12)	1510 (8)	1195 (5)	9191 (8)	31 (3)
N(11)	1411 (8)	775 (5)	8462 (9)	36 (4)
N(22)	−2136 (8)	1957 (5)	8089 (9)	37 (4)
C(11)	2468 (12)	1205 (7)	9686 (11)	46 (5)
C(13)	2344 (13)	494 (7)	8481 (12)	52 (6)
C(21)	−3202 (12)	1912 (7)	7959 (12)	47 (5)
C(23)	−2502 (12)	2632 (6)	6985 (11)	38 (4)
C(1)	2776 (13)	1637 (7)	10498 (13)	61 (6)
C(22)	−3463 (10)	2340 (7)	7258 (11)	44 (5)
C(4)	−2344 (13)	3120 (7)	6246 (13)	62 (7)
C(2)	2626 (13)	−26 (7)	7778 (16)	72 (8)
C(12)	3024 (12)	739 (7)	9261 (13)	61 (6)
C(3)	−3829 (11)	1458 (6)	8538 (13)	56 (6)

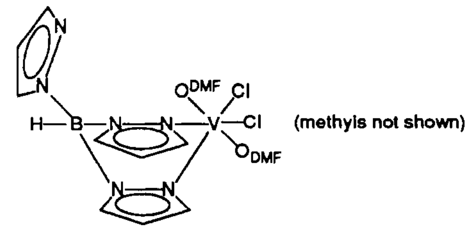
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I[a]



[a] For clarity the methyl groups are not shown. In DMF solution, the H_2O in I is replaced by a second DMF.

for the uncoordinated arm and one at 1542 cm^{-1} for the coordinated rings in an ca. 1:3 ratio. The purple species also displays two bands, 1574 and 1542 cm^{-1}, in a 1:3 ratio, strongly suggesting that the ligand is bidentate with a dangling pyrazole arm. Thus the structure can be represented by



Further support for this formulation comes from the observation that attempted synthesis of I in a less coordinating solvent than DMF does not lead to the purple bidentate complex but rather goes directly to the tridentate species, II. Interestingly, the very sterically crowded (3-phenylpyrazolyl)- and (3-*tert*-butyl-

Table VII. Selected Properties of the Complexes Prepared in This Study[a]

complex	color	ν_{B-H}, cm^{-1}	$\nu_{V=O}$, cm^{-1}	$E°$(vs SCE), V	μ_{eff}, μ_B	λ, nm	ε, L/(mol cm)	g_0	A_0, G
				V(III) Species					
I	violet	2557	na	...	2.3	485	1700	na	na
II	green	2540	na	...	2.2	630	30	na	na
V	green	2549	na	...	...	...	...	na	na
				V(IV) Species					
III	green-blue	2545	965	1.43	1.67	776	53	1.9854	103.9
						610	19		
IV	green	2500	957	1.18	1.70	774	56	1.9817	99.2
						562	11		
VI	blue	na	1027	...	...	...	...	...	...

[a] Key: na, not applicable; ..., not measured.

pyrazolyl)borates appear to form only the bidentate complexes even in noncoordinating solvents.

When I is dissolved in nonpolar solvents such as benzene and the solutions are allowed to stand, green crystals of II separate (Scheme I). These crystals, which have a magnetic moment of 2.2 μ_B, have been subjected to single-crystal X-ray diffraction analysis. The presence of the coordinated DMF in the bulk material was confirmed by the IR band at 1630 cm^{-1}. The formation of II from I in nonpolar solvents apparently results from the dissociation of one of the coordinated solvent molecules and the shift from a bidentate to tridentate mode of coordination of the (pyrazolyl)borate ligand. Both I and II are modestly air sensitive in the solid state and undergo rapid oxidation to vanadium(IV) in solution. The anomalously low magnetic moment (expected ~2.7 μ_B) suggests that some oxidation has occurred in the bulk sample. The alternative explanation of antiferromagnetic coupling between vanadium(III) centers such as seen in the oxo-bridged dimer reported by Wieghardt[21] seems unlikely if the X-ray structure, which reveals discrete mononuclear species, is representative of the bulk material. Selected physical properties of these complexes are summarized in Table VII.

Vanadium(IV) Complexes. Vanadium(IV) complexes of the tris(pyrazolyl)borates can be prepared in one of two basic ways: either by oxidation of the V(III) species or by direct synthesis using V(IV) starting material.

As an example of the oxidation method, a DMF or THF solution of either I or II, stirred in the air overnight, results in the oxidation of the vanadium(III) to an oxovanadium(IV) center, as demonstrated by the appearance of characteristic EPR, UV-vis, and infrared spectra (Table VII). Crystallization from methylene chloride/hexane resulted in blue crystals of $\{HB(Me_2pz)_3\}VOCl(DMF)$ (III), suitable for X-ray diffraction analysis. A direct synthesis of a V(IV) complex could be achieved by refluxing vanadyl bis(acetylacetonate) with $K[HB(Me_2pz)_3]$ in methanol. The product $\{HB(Me_2pz)_3\}VO(acac)$ precipitates from the solution as a light blue solid, which can be recrystallized from hot acetonitrile to yield pure IV. The EPR, UV-vis, and IR spectra of IV are all consistent with an oxovanadium(IV) complex that retains one coordinated acetylacetonate ($\nu_{C=O}$ = 1580 cm^{-1}), presumably bound in a bidentate fashion, forming an octahedral metal ion. Conversion of the N_3O_2Cl donor set in III to the N_3O_3 ligand environment in IV leads to a lowering of the V=O stretch by ~10 cm^{-1} and shift in the λ_{max} of the optical spectra from 610 to 562 nm. Both III and IV undergo one-electron quasireversible oxidations in DMF, as determined by cyclic voltammetry (i.e., $i_{pa}/i_{pc} \approx 1$ and ΔE_p values are near those for one-electron standards in DMF). Compound IV is about 0.2 V easier to oxidize than III. This may reflect the fact that the oxophilic vanadium(V) center which is produced by the oxidation is better stabilized by the acetylacetonate in IV than the DMF and chloride in III.

In addition to the complexes outlined above, it was possible to prepare and characterize small quantities of a V(IV) species where the (pyrazolyl)borate ligand is bidentate rather than tridentate. Thus, when a THF solution is exposed to air, chromatographed on silica gel, and then cooled, bright green crystals of $\{HB(Me_2pz)_3\}VOCl_2$ (V) appear. The green crystals of V were subjected to single-crystal X-ray diffraction analysis. The structure revealed that the tris(pyrazolyl)borato ligand adopts an unusual bidentate mode of coordination with one dangling 3,5-dimethylpyrazolyl ring. Such structures have been reported for other metals.[29-31] Charge considerations indicate that the dangling pyrazole must be protonated.

The strong preference of the vanadyl unit to adopt a square-pyramidal geometry may be responsible for the bidentate binding of the ligand to the vanadium. The facial geometry imposed by simultaneous coordination of all three rings is incompatible with a square-pyramidal geometry, and the ligand adopts a bidentate mode in relatively uncoordinating solvents such as THF. In strongly coordinating solvents such as DMF, however, an octahedral geometry is enforced, which allows the ligand to be tridentate, as seen with IV. Alternatively, the formation of HCl from reaction of VCl_3 with traces of moisture in the THF could result in protonation of one of the pyrazolyl rings, which would reduce its tendency to coordinate. In a weakly basic solvent such as DMF, any HCl formed could be neutralized by the solvent and hence all three pyrazole rings would coordinate the vanadium.

Decomposition Products. DMF appears to be the solvent of choice for the synthesis of all materials that use VCl_3 as a vanadium source, due to an apparently extreme sensitivity of the 3-substituted (pyrazolyl)borate ligand to acid-catalyzed decomposition. Synthesis in solvents other than DMF, such as THF or dichloromethane, invariably yield complex mixtures of products. These reactions are also complicated by the appearance of unidentified white organic precipitates that contaminate the vanadium-containing products and necessitate their mechanical separation. The result is that yields are low and the products are often impure. Nevertheless we have been able to identify, primarily by X-ray crystallography, several vanadium-containing materials from these mixtures.

From the initially green solution produced by reaction of VCl_3 and the 3,5-dimethyl ligand in THF can be isolated green crystals of $K[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)]$, and as solutions age further and oxidize, deep blue crystals of $[VOCl_2(Me_2pz)_2]_2\cdot THF$ are formed. The free 3,5-dimethylpyrazole in these species clearly arises from ligand degradation. This apparent sensitivity to decomposition on the part of the substituted ligand has been previously reported for its reactions with Nb and Ta.[32] The Ti(III) analogue of $K[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)]$ has also recently been structurally characterized and is also thought to arise from a decomposition pathway.[33]

Several potential pathways for these decompositions have been advanced. These include hydrolysis of the B-N bond by traces of water[34] in the solvents used or the abstraction of the oxophilic boron by oxygenated solvents.[33] Our results are more consistent

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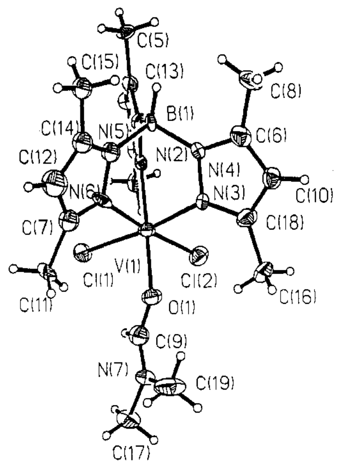

Figure 1. Structure of $\{HB(Me_2pz)_3\}VCl_2(DMF)$ showing 40% probability thermal ellipsoids and the atom-labeling scheme.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $[\{HB(Me_2pz)_3\}VCl_2(DMF)]\cdot 2C_6H_6$

V(1)–Cl(1)	2.345 (4)	V(1)–Cl(2)	2.339 (4)
V(1)–N(2)	2.120 (5)	V(1)–N(3)	2.130 (5)
V(1)–N(6)	2.141 (5)	V(1)–O(1)	2.082 (5)
Cl(1)–V(1)–Cl(2)	97.8 (1)	Cl(1)–V(1)–N(2)	90.8 (2)
Cl(2)–V(1)–N(2)	92.5 (1)	Cl(1)–V(1)–N(3)	172.2 (1)
Cl(1)–V(1)–N(6)	90.2 (2)	Cl(2)–V(1)–N(6)	82.1 (2)
Cl(1)–V(1)–O(1)	90.0 (1)	Cl(2)–V(1)–O(1)	88.4 (1)
N(2)–V(1)–O(1)	178.7 (2)	N(3)–V(1)–O(1)	91.7 (2)
N(6)–V(1)–O(1)	90.2 (2)		

Table IX. Selected Bond Lengths (Å) and Angles (deg) for $[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)_3]^-$

V(1)–Cl(1)	2.349 (4)	V(1)–Cl(2)	2.347 (4)
V(1)–N(1)	2.123 (10)	V(1)–N(3)	2.117 (10)
V(1)–N(5)	2.100 (9)	V(1)–N(7)	2.140 (9)
Cl(1)–V(1)–Cl(2)	91.8 (1)	Cl(1)–V(1)–N(1)	91.4 (3)
Cl(2)–V(1)–N(1)	176.2 (3)	Cl(1)–V(1)–N(3)	177.3 (3)
Cl(2)–V(1)–N(3)	90.5 (3)	N(1)–V(1)–N(3)	86.4 (4)
Cl(1)–V(1)–N(5)	92.6 (3)	Cl(2)–V(1)–N(5)	94.6 (3)
N(1)–V(1)–N(5)	87.2 (4)	N(3)–V(1)–N(5)	85.7 (4)
Cl(1)–V(1)–N(7)	89.1 (3)	Cl(2)–V(1)–N(7)	90.4 (3)
N(1)–V(1)–N(7)	87.7 (4)	N(3)–V(1)–N(7)	92.4 (4)
N(5)–V(1)–N(7)	174.7 (4)		

with the acid lability of the B–N bond as suggested by Bradley, Hursthouse, et al.[32] Since DMF undoubtedly contains some water and yet high yields of I, II, and IV are obtained in this solvent, it would appear that water is not the problem. However, in the presence of a strong Lewis acid such as VCl_3, traces of water will form HCl, which, if not neutralized by a basic solvent such as DMF, could lead to B–N bond cleavage. When a vanadyl bis(acetylacetonate) is used as a vanadium source rather than VCl_3, high-yield syntheses can be obtained even in protic solvents.

Description of Structures. $LVCl_2(DMF)\cdot 2C_6H_6$ (IIb). Figure 1 shows the atom-labeling scheme for the neutral $LVCl_2(DMF)$ molecule. The two benzene solvent molecules are not shown. Selected bond lengths and angles are summarized in Table VIII. The vanadium(III) is capped by a facial, tridentate tris(pyrazolyl)borato ion in which the two chlorides and the oxygen of the coordinated DMF complete the roughly octahedral coordination sphere. The N–V–N angles are all slightly less than the idealized 90° (averaging ~86°) as a result of the "bite" of the facially coordinating ligand. However, the bite angle is significantly larger for the (3,5-dimethylpyrazolyl)borato ligand than for the analogous 1,4,7-trimethyl-1,4,7-triazacyclononane ligand reported by Wieghardt (N–V–N ~ 80°).[22] The vanadium–nitrogen bonds in II are all ~2.13 Å and are slightly shorter than those seen for the neutral triazacyclononane (V–N ~ 2.16 Å). The remaining V–Cl and $V–O_{DMF}$ bonds are in the range expected for octahedral V(III).

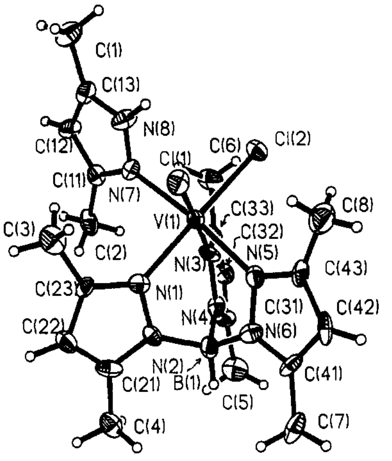

Figure 2. Structure of the anion $[\{HB(Me_2pz)_3\}VCl_2(Me_2pz)]^-$ of VI showing 40% probability thermal ellipsoids and the atom-labeling scheme.

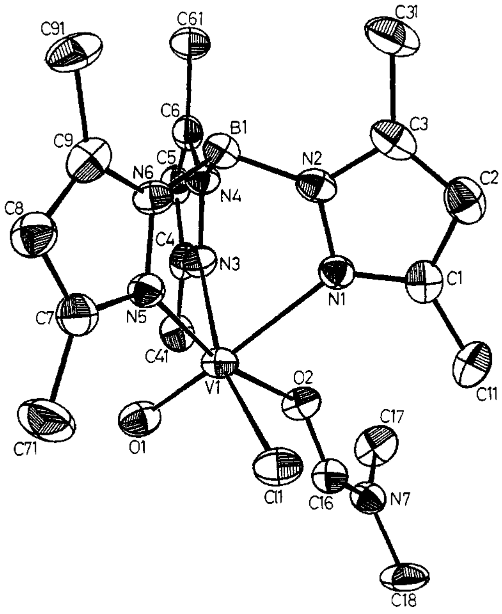

Figure 3. Structure of $\{HB(Me_2pz)_3\}VOCl(DMF)$ showing 30% probability thermal ellipsoids and the atom-labeling scheme.

Table X. Selected Bond Lengths (Å) and Angles (deg) for $\{HB(Me_2pz)_3\}VOCl(DMF)$

V(1)–Cl(1)	2.354 (2)	V(1)–N(1)	2.329 (6)
V(1)–O(1)	1.649 (5)	V(1)–N(3)	2.110 (5)
V(1)–O(2)	2.043 (4)	V(1)–N(5)	2.117 (5)
Cl(1)–V(1)–O(1)	98.5 (2)	O(1)–V(1)–N(5)	94.8 (2)
Cl(1)–V(1)–O(2)	91.5 (1)	O(2)–V(1)–N(1)	83.6 (2)
Cl(1)–V(1)–N(1)	85.7 (1)	O(2)–V(1)–N(3)	87.2 (2)
Cl(1)–V(1)–N(3)	165.0 (2)	O(2)–V(1)–N(5)	167.4 (2)
Cl(1)–V(1)–N(5)	92.2 (2)	N(1)–V(1)–N(3)	79.2 (2)
O(1)–V(1)–O(2)	96.7 (2)	N(1)–V(1)–N(5)	84.7 (2)
O(1)–V(1)–N(1)	175.8 (2)	N(3)–V(1)–N(5)	86.1 (2)
O(1)–V(1)–N(3)	96.6 (2)		

$K[LVCl_2(Me_2pz)]$ (VI). Compound VI is also a monomeric V(III) species. The overall structure of the $LVCl_2(Me_2pz)$ anion and the atom-labeling scheme are depicted in Figure 2. Relevant bond lengths and angles are found in Table IX. Overall, the structure differs little from compound II except as expected for replacement of the neutral DMF by the anionic 3,5-dimethylpyrazolide ion. The overall geometry is more nearly a perfect octahedron with the greatest deviation from ideal angles being ±4°. That the coordinated free pyrazole is bound as a deprotonated pyrazolide anion is indicated by the overall charge on the complex and the totally delocalized electronic structure revealed in the ring. A neutral protonated pyrazole would be expected to

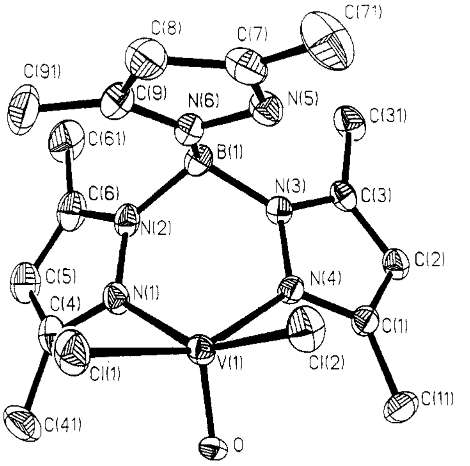

Figure 4. Structure of $\{HB(Me_2pz)_3\}VOCl_2$ showing 40% probability thermal ellipsoids and the atom-labeling scheme.

Table XI. Selected Bond Lengths (Å) and Angles (deg) for $\{HB(Me_2pz)_3\}VOCl_2$

V(1)–Cl(1)	2.356 (1)	V(1)–Cl(2)	2.323 (1)
V(1)–O(1)	1.575 (3)	V(1)–N(1)	2.107 (4)
V(1)–N(4)	2.093 (3)		
Cl(2)–V(1)–Cl(1)	89.8 (1)	O(1)–V(1)–Cl(1)	105.6 (1)
O(1)–V(1)–Cl(2)	106.7 (2)	N(1)–V(1)–Cl(1)	87.5 (1)
N(1)–V(1)–Cl(2)	150.6 (1)	N(1)–V(1)–O(1)	102.2 (2)
N(4)–V(1)–Cl(1)	154.8 (1)	N(4)–V(1)–Cl(2)	86.6 (1)
N(4)–V(1)–O(1)	99.3 (2)	N(4)–V(1)–N(1)	83.5 (1)

have a more localized structure with alternating C–C bond lengths. Unfortunately, the overall quality of the structure is diminished by the badly disordered potassium cation. The disorder was treated as a two-site model with optimized occupancies of 0.82 in site 1 and 0.18 in site 2.

LVOCl(DMF) (IV). The structure of IV is illustrated in Figure 3. The pertinent bond lengths and angles are summarized in Table X. This mononuclear V(IV) complex displays a facially coordinated tridentate (pyrazolyl)borate with a chloride ion, an oxygen from a coordinated DMF solvent, and the expected oxo group leading to an overall octahedral geometry. The vanadyl oxygen to vanadium bond length of 1.65 Å is somewhat longer than one might expect (six-coordinate V═O bond ≈ 1.62 Å). The vanadium–nitrogen bond to the (pyrazolyl)borate ring trans to the oxo group is, as expected, considerably (2.33 vs. ~2.12 Å) longer than the other vanadium–nitrogen bonds and is a reflection of the strong trans effect of the oxo group. The other bond distances and angles are unremarkable. The V(IV)–N distances are only marginally, if at all, shorter than the corresponding V(III) distances, despite the expected reduction in ionic radius (0.64 vs 0.53 Å).[35] This suggests that the oxophilic V(IV) center prefers hard oxygen donors to the softer pyrazole nitrogens.

$LVOCl_2$ (V). The most unusual complex isolated in this study is the vanadium(IV) species V. The structure of this complex is shown in Figure 4. Bond lengths and angles are reported in Table XI. Surprisingly, the vanadium is only five-coordinate in V and the ligand does not adopt the expected facial tridentate geometry but is instead bound to the vanadyl ion in a bidentate fashion. The coordination sphere of the vanadium(IV) is completed by two chlorides and an oxo group. The coordination geometry is nicely square pyramidal with cis chlorides and the vanadium located 0.52 Å out of the best least-squares plane defined by N(1), N(4), Cl(1), and Cl(2) and toward the oxo group. The plane of the uncoordinated pyrazolyl ring is twisted so that it is approximately perpendicular to the planes of the two coordinated rings. The vanadium–oxygen bond of 1.57 Å is in the range expected for five-coordinate vanadium(IV). The V–Cl bonds (2.34 Å) and V–N bonds (2.10 Å) are nearly the same as those seen in the six-coordinate IV.

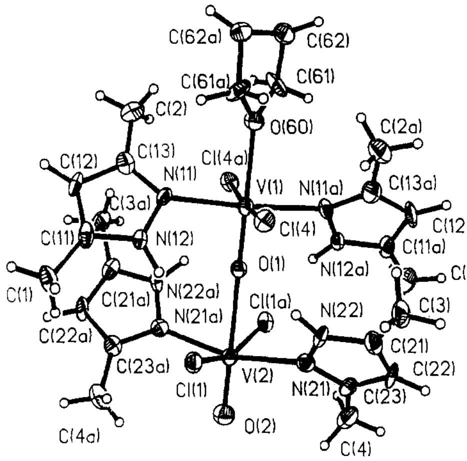

Figure 5. Structure of $[(Me_2pz)_2VOCl_2]_2{\cdot}THF$ showing 40% probability thermal ellipsoids and the atom-labeling scheme.

Table XII. Selected Bond Lengths (Å) and Angles (deg) for $[(Me_2pz)VOCl_2]_2{\cdot}THF$

V(1)–O(1)	1.609 (10)	V(1)–Cl(4)	2.361 (4)
V(1)–O(60)	2.181 (12)	V(1)–N(11)	2.132 (11)
Cl(1)–V(2)	2.396 (3)	V(2)–O(1)	2.311 (10)
V(2)–O(2)	1.591 (13)	V(2)–N(21)	2.127 (11)
Cl(4)–V(1)–O(1)	93.8 (1)	O(60)–V(1)–O(1)	180.0 (1)
O(60)–V(1)–Cl(4)	86.2 (1)	N(11)–V(1)–O(1)	92.3 (3)
N(11)–V(1)–Cl(4)	89.5 (3)	N(11)–V(1)–O(60)	87.7 (3)
O(1)–V(2)–Cl(1)	80.9 (1)	O(2)–V(2)–Cl(1)	99.9 (1)
O(2)–V(2)–O(1)	180.0 (1)	N(21)–V(2)–Cl(1)	88.5 (1)
N(21)–V(2)–O(1)	81.7 (3)	N(21)–V(2)–O(2)	98.3 (3)

$[(Me_2pz)_2VOCl_2]_2{\cdot}THF$ (VII). Deep blue compound VII is a dinuclear V(IV) complex formed from decomposition of the starting tris(pyrazolyl)borate ligand during reaction with VCl_3 in THF. The structure and atom-labeling scheme are shown in Figure 5. Table XII gives relevant bond lengths and angles. Each vanadium is formally six-coordinate and bonded to two trans neutral 3,5-dimethylpyrazole rings and two trans chlorides. The two vanadium centers are connected by an asymmetric oxo bridge through O(1). Since the molecule displays a crystallographically imposed 2-fold rotation axis through V(1), V(2), O(1), O(2), and O(60), the bridge is constrained to be strictly linear. The asymmetry in the bridge, (V(2)–O(1) = 2.31 Å; V(1)–O(1) = 1.61 Å) suggests that the complex can be regarded as two weakly interacting five-coordinate oxovanadium(IV) species. The nonbridging V(2)–O(2) bond of 1.59 Å is about that expected for a nearly five-coordinate V(IV) center. The V(1) atom is capped by a THF oxygen (V(1)–O(60) = 2.18 Å), giving both metals pseudooctahedral symmetry. For steric reasons, the two V^{IV}-$(Me_2pz)_2Cl_2$ fragments are staggered relative to each other. Interestingly, while the V═O bond lengths (1.59 and 1.61 Å) are only slightly elongated with respect to their expected five-coordinate values by the axial ligation, the V═O stretch in the IR spectrum is shifted by over 50 cm^{-1} to ~1000 cm^{-1}.

Comparison of the Structures of Vanadium, Molybdenum, and Titanium Tris(pyrazolyl)borates. Among the early-transition-metal complexes of the tris(pyrazolyl)borate[36-40] ligand, most data are available for those of Mo. Dozens of Mo complexes have been

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structurally characterized, while only two Ti complexes are known. Structures of molybdenum (pyrazolyl)borates, include complexes of Mo(II), -(III), -(IV), -(V), -(VI), and -(VII). They show the expected general trend of shorter Mo–N bond distances with increasing oxidation state, ranging from ~2.21 Å for Mo(II) to ~2.16 Å for Mo(VII). The Ti complexes, both reported as Ti(III), have M–N values averaging 2.18 Å. The V(III)–N bond lengths observed in II and VI average 2.12 Å, and the V(IV)–N bond lengths in III and V, 2.11 Å. Since the M(III) ionic radii for Mo, Ti, and V are expected to be roughly similar (0.65, 0.67, and 0.64 Å, respectively),[35] a comparison of the structures with this oxidation state suggests that the vanadium is bound somewhat more tightly to the ligand than either Ti or Mo although these differences are small.

It is interesting to compare directly the analogous $\{HB(Me_2pz)_3\}MCl_2(Me_2pz)$ structures for V(III) and Ti(III). These two complexes differ only by the fact that the V(III) complex is cationic and isolated as the potassium salt, whereas the Ti(III) species is neutral.[33] This implies that the free pyrazole is bound as a pyrazolide anion in the V(III) complex and as a neutral protonated pyrazole with the Ti. The X-ray structure reveals that the coordinated pyrazolide in the V(III) complex has a totally delocalized structure, as was expected. A neutral protonated pyrazole should have a localized structure with alternating C–C bond lengths. Indeed, the Ti(III) complex shows evidence of some electronic localization, which is consistent with its formulation as a coordinated neutral molecule.

Summary. Vanadium(III) and -(IV) complexes of the 3,5-dimethyl-substituted tris(pyrazolyl)borate ligand have been prepared and characterized by X-ray crystallography. The ligand is found to exhibit both bi- and tridentate coordination modes that are solvent dependent. These complexes may be useful as models for vanadium–histidine binding in metalloproteins. Study of the substitution chemistry of these complexes, particularly with peroxides, is underway and will be reported elsewhere.

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Supplementary Material Available: Tables of bond lengths, bond angles, H atom coordinates and isotropic displacement parameters, and anisotropic displacement parameters (20 pages); listings of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Vanadium(V) and -(IV) Hydroxamate Complexes. X-ray Crystal Structures of Oxochlorobis(benzohydroxamato)vanadium(V) and Oxoisopropoxo(*N*,*N*′-dihydroxy-*N*,*N*′-diisopropylheptanediamido)vanadium(V)

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Although hydroxamic acids have been used for many years in colorimetric analyses of vanadium, the full characterization of the complexes formed has not been accomplished. In this study a number of vanadyl dihydroxamate complexes are described. Two vanadium(V) complexes, oxochlorobis(benzohydroxamato)vanadium(V) ($VOCl(bz)_2$) and oxoisopropoxo(*N*,*N*′-dihydroxy-*N*,*N*′-diisopropylheptanediamido)vanadium(V) (VO(OiPr)L), are structurally characterized by X-ray crystallography, and both have pseudooctahedral coordination sites in which the second monodentate group is cis to the oxo oxygen. Large, opaque, purple-black crystals of $VOCl(bz)_2$ were found to conform to monoclinic space group $P2_1/n$, with $a = 11.1054$ (15) Å, $b = 10.853$ (16) Å, $c = 18.3508$ (22) Å, and $\beta = 94.92$ (1)°. The measured (1.40 g cm^{-3}) and calculated (1.40 g cm^{-3}) densities are consistent with 4 molecules of $VOCl(bz)_2$/unit cell. Least-squares refinement of the structure converged with conventional (and weighted) R indices (on $|F_o|$) of 3.43% (4.76%) with the use of 2795 reflections with $F_o^2 > 3\sigma(F_o^2)$. Crystals of VO(OiPr)L were obtained as orange-red hexagonal prisms; they conform to space group $P2_1/c$, with $a = 8.2170$ (10) Å, $b = 15.7946$ (15) Å, $c = 16.2124$ (19) Å, and $\beta = 97.48$ (1)°. The measured (1.28 g cm^{-3}) and calculated (1.28 g cm^{-3}) densities indicate 2 molecules of the centrosymmetric dimer $[VO(OiPr)L]_2$/unit cell. Least-squares refinement of the structure converged with conventional (and weighted) R indices of 5.05% (6.19%) with use of 1489 reflections with $F_o^2 > 3\sigma(F_o^2)$. These are the first X-ray crystallographically determined structures of any vanadium hydroxamate complexes. It is found that under some experimental conditions tris(hydroxamato)vanadium(IV) complexes are formed, resulting from the highly unusual dissociation of the vanadyl V=O bond; these undergo reversible electrochemical reduction to the corresponding vanadium(III) complexes. Both dihydroxamic acid and monohydroxamic acid ligand complexes are characterized, and their vis/UV spectra and other physical properties are described.

Introduction

Hydroxamic acids form highly colored complexes with vanadium(V) or -(IV) under a wide variety of conditions and have been used extensively as analytical reagents for the detection of this metal.[1-8] Nevertheless, very little is known about the structure of the complexes that are formed. The most commonly used analytical procedure is the extraction of vanadium(V) by hydroxamic acids from aqueous HCl into an organic phase (usually chloroform), and spectrophotometric detection of the intensely purple-black species ($\lambda_{max} = 510$–575 nm, $\epsilon = 3.9$–6.9×10^3 cm^{-1} M^{-1}) which form. Although this reaction has been used analytically for over 30 years,[8] it was not until relatively recently that the colored species was identified as oxochlorobis(hydroxamato)vanadium(V), when Pande and Tandon succeeded in isolating oxochlorobis(*N*-phenylbenzohydroxamato)vanadium(V).[9] This and similar compounds are formed under highly acidic conditions (3–8 N HCl), where some potentially interfering metals (such as iron) do not form hydroxamate complexes.[4] Selectivity can be further enhanced by varying the functionalities attached to the hydroxamate moieties.[4] Because of this selectivity, and the fact

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