Inorg. Chem. **2002**, *41*, 2243–2249

Inorganic Chemistry Article

Mononuclear and Mixed-Valence Binuclear Oxovanadium Complexes with Benzimidazole-Derived Chelating Agents

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Received September 4, 2001

Oxovanadium complexes with H_2bzimpy (2,6-bis[benzimidazol-2′-yl]pyridine) and Me_2bzimpy (2,6-bis[*N*′-methylbenzimidazol-2′-yl]pyridine), and H_3ntb (tris[benzimidazol-2′-yl-methyl]amine) and Me_3ntb (tris[*N*′-methylbenzimidazol-2′-yl-methyl]amine) have been synthesized. Dioxovanadium(V) and oxovanadium(IV) complexes prepared from H_2bzimpy and Me_2bzimpy are $[V^VO_2(Hbzimpy)]\cdot1.25H_2O$ (**1**), $[V^VO_2(Me_2bzimpy)](ClO_4)\cdot H_2O$ (**3**), $[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2\cdot2H_2O$ (**2**), and $[V^{IV}O(Me_2bzimpy)(H_2O)_2](CF_3SO_3)_2$ (**4**). H_3ntb and Me_3ntb afforded oxovanadium(IV) complexes, $[V^{IV}O(Hntb)]\cdot2MeOH$ (**5**), $[V^{IV}O(H_3ntb)Cl]Cl\cdot H_2O$ (**7**), $[V^{IV}O(Me_3ntb)SO_4]\cdot H_2O$ (**9**), $[V^{IV}O(Me_3ntb)Cl]Cl\cdot H_2O$ (**10**), and mixed-valence complexes, $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^VO(H_3ntb)](CF_3SO_3)_3\cdot2H_2O$ (**8**) and $[(Me_3ntb)V^{IV}O(\mu\text{-}O)V^VO(Me_3ntb)](CF_3SO_3)_3\cdot3H_2O$ (**11**). Crystal structures of **2**, **7**, and **11** are reported. The mixed-valence complexes, **8** and **11**, show 15-line isotropic ESR spectra in fluid solutions at room temperature. These compounds also exhibit an intervalence transfer band around 1015 nm which is essentially independent of solvent, so these compounds are stable, mixed-valence species where the single unpaired electron is delocalized over the two vanadium centers at ambient temperature. With respect to one-electron reduction, the dioxovanadium(V) complexes are redox-potential equivalent with their monooxovanadium(IV) counterparts.

Introduction

The discoveries of vanadium-containing enzymes and of activities of vanadium in biological systems have led to increased interest in the coordination chemistry of vanadium.[1–3] Vanadium is a bioessential element found in high concentrations in ascidians,[4] in some mushrooms,[5] and in polychæte worms,[6] but its role is still not well understood. Two families of vanadium-containing enzymes, nitrogenases[7,8] and haloperoxidases,[9] have been isolated and characterized. The most important physiological effect produced by vanadium is an insulin-mimetic property.[10,11] A recent report[12] reveals the structure of an azide derivative of the chloroperoxidase from the fungus *Curvularia inæqualis*, wherein the vanadium(V) center is bound to three oxygen donors and an azide, while a histidine imidazole acts as the sole protein-derived ligand. The involvement of vanadoenzymes in both reductive ($N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$) and oxidative ($RH + H_2O_2 + HX \rightarrow RX + 2H_2O$) transformations signifies the importance of the +3, +4, and +5 oxidation states. The synthesis as well as characterization of low molecular weight complexes with these biologically important oxidation states of vanadium will help in making further progress in the elucidation of the biological roles of vanadium. In this paper, we report the chemistry of oxovanadium (+4, +5, +4/+5) complexes derived from two classes of benzimidazole-containing ligands: (i) H_2bzimpy (2,6-bis[benzimidazol-2′-yl]pyridine),

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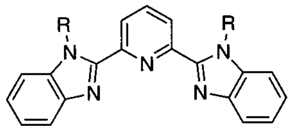
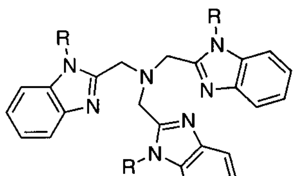
10.1021/ic010945x CCC: $22.00
Published on Web 03/23/2002

Me_2bzimpy (2,6-bis[*N*′-methylbenzimidazol-2′-yl]pyridine) and (ii) H_3ntb (tris[benzimidazol-2′-yl-methyl]amine), Me_3ntb (tris[*N*′-methylbenzimidazol-2′-yl-methyl]amine). Benzimidazoles have attracted attention as histidine-imidazole mimics,[13] while tripodal ligands such as H_3ntb have emerged as a growing and important class of biomimetic chelating agents over the past few years.[14,15]



R = H, H_2bzimpy
R = Me, Me_2bzimpy



R = H, H_3ntb
R = Me, Me_3ntb

Experimental Section

Reagents from commercial sources were used as received. The syntheses of H_2bzimpy, Me_2bzimpy,[16,17] H_3ntb,[18] and Me_3ntb[19] were as reported previously. Acetonitrile and *N*,*N*-dimethylformamide (DMF) were purified by distillation off P_4O_{10} (under N_2) or CaH_2 (under vacuum), respectively. Elemental analyses were performed by Robertson Microlit Inc. (Madison, NJ).

$VO(CF_3SO_3)_2$. An aqueous solution of $Ba(CF_3SO_3)_2$, generated in situ from CF_3SO_3H and excess $BaCO_3$, was allowed to react with an equivalent amount of $VOSO_4{\cdot}2H_2O$. Stoichiometry was judged turbidimetrically, and the precipitated $BaSO_4$ was filtered off. This $VO(CF_3SO_3)_2$ solution was standardized by referring its absorbance to that of a $VOSO_4{\cdot}2H_2O$ solution ($\epsilon = 13.8$ M^{-1} cm^{-1} at 780 nm).

[V^VO_2(Hbzimpy)]·1.25H_2O (1). Solid vanadyl acetylacetonate (Aldrich) $VO(acac)_2$ (0.265 g, 1 mmol) was added to a stirred solution of H_2bzimpy (0.311 g, 1 mmol) in 40 mL of warm MeOH. The initial green color changed to yellow in ~15 min, and a yellow precipitate formed. After 3 h, the solid was filtered off, washed with MeOH, recrystallized from a large volume of CH_2Cl_2, and air-dried to yield 0.17 g (40%) of yellow microcrystals. Anal. Calcd for $C_{19}H_{14.5}N_5O_{3.25}V$: C, 54.9; H, 3.5; N, 16.8. Found: C, 54.8; H, 3.4; N, 16.6. MS(FAB): *m*/*z* = 394 ([VO_2(Hbzimpy) + H]$^+$).

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[$V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2{\cdot}2H_2O$ (2). A mixture of H_2bzimpy (0.311 g, 1 mmol) and $VO(CF_3SO_3)_2$ (1 mmol) in 50 mL of MeOH was refluxed overnight. The resulting bright green solution was rotary evaporated to dryness. The solid residue was recrystallized from acetonitrile−toluene (5:1) by slow evaporation on a steam bath. Yield: 0.45 g green crystals (60%). Anal. Calcd for $C_{21}H_{21}N_5F_6O_{11}S_2V$: C, 33.7; H, 2.8; N, 9.4. Found: C, 33.8; H, 2.6; N, 9.5. MS(FAB): *m*/*z* = 527 ([VO(H_2bzimpy)($CF_3SO_3)_2]^+$).

[$V^VO_2(Me_2bzimpy)](ClO_4){\cdot}H_2O$ (3). Solid $VO(acac)_2$ (0.265 g, 1 mmol) was added to a stirred solution of Me_2bzimpy (0.34 g, 1 mmol) in 50 mL of MeOH. A yellow color developed in ~5 min. After 1 h, solid $NaClO_4$ (2 g) was added. Stirring continued overnight, and the resulting yellow precipitate was filtered off and recrystallized from a large volume of MeOH. Yield: 0.1 g (40%). Anal. Calcd for $C_{21}H_{19}N_5ClO_7V$: C, 46.7; H, 3.5; N, 13.0. Found: C, 46.9; H, 3.3; N, 13.0. MS(FAB): *m*/*z* = 422 ([VO_2(Me_2bzimpy)]$^+$).

[$V^{IV}O(Me_2bzimpy)(H_2O)_2](CF_3SO_3)_2$ (4). This compound was synthesized in 65% yield from $VO(CF_3SO_3)_2$ and Me_2bzimpy using a procedure similar to that for **2**. The solvent used for recrystallization was CH_3NO_2−MeOH (2:1). Anal. Calcd for $C_{23}H_{21}N_5F_6O_9S_2V$: C, 37.3; H, 2.9; N, 9.5. Found: C, 37.0; H, 2.9; N, 9.7. MS(FAB): *m*/*z* = 555 ([VO(Me_2bzimpy)(CF_3SO_3)]$^+$).

[V^{IV}O(Hntb)]·2MeOH (5). $VO(acac)_2$ (0.265 g, 1 mmol) and H_3ntb (0.407 g, 1 mmol) were refluxed for 3 h in 150 mL of MeOH. The violet crystalline precipitate was filtered off, washed with hot MeOH, and dried under vacuum over $CaCl_2$. Yield: 0.375 g (70%). Anal. Calcd for $C_{26}H_{27}N_7O_3V$: C, 58.2; H, 5.0; N, 18.3. Found: C, 57.9; H, 4.9; N, 18.2. MS(FAB): *m*/*z* = 473 ([VO(Hntb) + H]$^+$).

[$V^{IV}O(H_3ntb)(H_2O)](ClO_4)_2{\cdot}0.5H_2O{\cdot}0.33CH_3COCH_3$ (6). A solution of $VOSO_4{\cdot}2H_2O$ (0.2 g, 1 mmol) in 50 mL of MeOH was added to a MeOH solution (30 mL) of $Ba(ClO_4)_2{\cdot}3H_2O$ (0.4 g, 1 mmol) and H_3ntb (0.407 g, 1 mmol). After overnight stirring, the reaction mixture was rotary evaporated to dryness. The solid was extracted with ~50 mL of MeOH and filtered to separate any precipitated $BaSO_4$, along with some green solid. The blue filtrate was evaporated to dryness, and the solid mass was dissolved in acetone. Diethyl ether diffusion to this blue acetone solution led to the formation of large blue crystals, which were filtered off, washed with ether, and dried over $CaCl_2$ in vacuo. The crystals rapidly effloresce on drying. Yield: 0.25 g (35%). Anal. Calcd for $C_{25}H_{26}N_7Cl_2O_{10.83}V$: C, 41.7; H, 3.6; N, 13.6. Found: C, 41.8; H, 3.4; N, 13.5. MS(FAB): *m*/*z* = 573 ([VO(H_3ntb)(ClO_4)]$^+$).

[$V^{IV}O(H_3ntb)Cl]Cl{\cdot}H_2O$ (7). To a stirred solution of H_3ntb (0.407 g, 1 mmol) in 70 mL of absolute EtOH was added $VOCl_3$ (0.173 g, 1 mmol). The initially pale yellow solution turned blue on overnight reflux, and blue crystals were deposited on slow evaporation at 50 °C. These were filtered off and dried in vacuo over $CaCl_2$. The crystals lose their luster upon desiccation. Yield: 0.26 g (45%). Anal. Calcd for $C_{24}H_{23}N_7Cl_2O_2V$: C, 51.2; H, 4.1; N, 17.4. Found: C, 51.3; H, 4.1; N, 17.2. MS(FAB): *m*/*z* = 509 ([VO(H_3ntb)Cl]$^+$).

[(H_3ntb)V^{IV}O(μ-O)V^VO(H_3ntb)]($CF_3SO_3)_3{\cdot}2H_2O$ (8). A solution of H_3ntb (0.407 g, 1 mmol) and $VO(CF_3SO_3)_2$ (1 mmol) in 50 mL of MeOH was stirred for 2 days. The resulting dark green solution was rotary evaporated to dryness and the residue recrystallized twice from acetonitrile−toluene to give brown crystals. Yield: 0.25 g (35%). Anal. Calcd for $C_{51}H_{46}N_{14}F_9O_{14}S_3V_2$: C, 42.3; H, 3.2; N, 13.5. Found: C, 42.0; H, 3.3; N, 13.6. MS(FAB): *m*/*z* = 1262 ([$(VO)_2(O)(H_3ntb)_2(CF_3SO_3)_2]^+$).

[$V^{IV}O(Me_3ntb)SO_4$]·H_2O (9). A solution of $VOSO_4·2H_2O$ (0.2 g, 1 mmol) in 30 mL of MeOH was added dropwise to a stirred solution of Me_3ntb (0.447 g, 1 mmol) in 40 mL of MeOH. A blue precipitate formed in ~5 min. After 1 h, the solid was filtered off, washed with MeOH, and air-dried. Yield: 0.5 g (80%). Anal. Calcd for $C_{27}H_{29}N_7O_6SV$: C, 51.4; H, 4.6; N, 15.6. Found: C, 51.7; H, 4.4; N, 15.6. MS(FAB): $m/z = 613$ ([VO(Me_3ntb)SO_4 + H]$^+$).

[$V^{IV}O(Me_3ntb)Cl$]Cl·H_2O (10). This compound was synthesized in 40% yield from Me_3ntb and $VOCl_3$ using a procedure similar to that for **7** and recrystallized from MeOH. Anal. Calcd for $C_{27}H_{29}N_7Cl_2O_2V$: C, 53.6; H, 4.8; N, 16.2. Found: C, 53.6; H, 4.9; N, 16.0. MS(FAB): $m/z = 551$ ([VO(Me_3ntb)Cl]$^+$).

[(Me_3ntb)$V^{IV}O$(μ-O)V^VO(Me_3ntb)](CF_3SO_3)$_3$·$3H_2O$ (11). This compound was synthesized in 40% yield from Me_3ntb and VO(CF_3SO_3)$_2$ using a procedure similar to that for **8**. Anal. Calcd for $C_{57}H_{60}N_{14}F_9O_{15}S_3V_2$: C, 44.2; H, 3.9; N, 12.6. Found: C, 44.1; H, 3.7; N, 12.5. MS(FAB): $m/z = 1345$ ([(VO)$_2$(O)(Me_3ntb)$_2$(CF_3SO_3)$_2$]$^+$).

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1610 FT-IR using KBr disks. ESR spectra were obtained with a Varian E-12 X-band spectrometer calibrated near $g = 2$ with diphenylpicrylhydrazyl radical. g-Values are ±0.005; isotropic g-values are designated as g_o. Magnetic susceptibilities were determined at ambient temperature using a Johnson-Matthey Mark-II susceptometer. Electronic spectra are from a Perkin-Elmer 330 spectrophotometer, equipped with an integrating sphere for diffuse reflectance or from a Perkin-Elmer Lambda-2B spectrophotometer. Mass spectra were obtained either on a ZABHF or Finnigan-4500 mass spectrometer operating in FAB or CI mode. Electrochemical measurements were made at 25 °C in deoxygenated CH_3CN or DMF solutions using a BAS 100A electrochemical analyzer. The three-electrode assembly comprised the working electrode, a Ag^+(0.01 M, 0.1 M NEt_4ClO_4, CH_3CN)/Ag reference electrode, and a Pt auxiliary electrode. The working electrodes were Pt disk, beads, or wires for voltammetry at scan rates from 20 to 2000 mV s^{-1}, and a Pt disk for rotating electrode (rde) polarography (wherein $E_{1/2}$ is defined as the potential at which $i = i_L/2$ [20]). The supporting electrolyte was 0.1−0.2 M NEt_4ClO_4, and solutions for voltammetry and polarography were ~1 mM in complex.

X-ray Crystallography. Single crystals of [$V^{IV}O(H_2bzimpy)(H_2O)_2$]($CF_3SO_3$)$_2$·$2H_2O$ (**2**), [$V^{IV}O(H_3ntb)Cl$]Cl·H_2O (**7**), and [(H_3ntb)$V^{IV}O$(μ-O)V^VO(H_3ntb)](CF_3SO_3)$_3$·$2H_2O$ (**8**) were obtained from DMF, acetonitrile/toluene, EtOH and acetonitrile, respectively. The crystals of **7** and **8** effloresce, so the ones used for X-ray crystallographic study were sealed in capillary tubes with mother liquor.

All measurements were made as previously described[21] on a Siemens P4S diffractometer with graphite-monochromated Mo Kα radiation. Pertinent crystallographic data are summarized in Table 1. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of setting angles of 25 reflections. The intensities of three standard reflections measured after every 150 reflections showed no greater fluctuations than expected from Poisson statistics. Lorentz polarization and absorption corrections were applied. A total of 2235, 6526, and 7760 reflections were collected for [$V^{IV}O(H_2bzimpy)(H_2O)_2$]($CF_3SO_3$)$_2$·$2H_2O$ (**2**), [$V^{IV}O(H_3ntb)Cl$]Cl·H_2O (**7**), and [(H_3ntb)$V^{IV}O$(μ-O)V^VO(H_3ntb)](CF_3SO_3)$_3$·$2H_2O$ (**8**), respectively, of which 2235 ($R_{int} = 0.0000$), 6093 ($R_{int} = 0.0325$), and 7406 ($R_{int} = 0.0632$) were unique; equivalent reflections were averaged. The structures were solved by direct methods and refined by full-matrix least-squares methods.[22] Hydrogen atoms were included in structure factor calculations in idealized positions.

Table 1. Crystallographic Data for [$V^{IV}O(H_2bzimpy)(H_2O)_2$]($CF_3SO_3$)$_2$·$3H_2O$ (**2**), [$V^{IV}O(H_3ntb)Cl$]Cl·H_2O (**7**), and [(H_3ntb)$V^{IV}O$(μ-O)V^VO(H_3ntb)](CF_3SO_3)$_3$·$4H_2O$ (**8**)

	2	**7**	**8**
formula	$C_{21}H_{21}F_6N_5O_{11}S_2V$	$C_{24}H_{27}Cl_2N_7O_4V$	$C_{51}H_{50}F_9N_{14}O_{16}S_3V$
fw	748.49	599.37	1484.09
cryst syst	orthorhombic	triclinic	monoclinic
cryst size, mm^3	0.36 × 0.68 × 0.56	0.12 × 0.30 × 0.24	0.16 × 0.54 × 0.24
space group	*Fdd*2	$P\bar{1}$	$P2_1/m$
a, Å	31.271(3)	7.981(2)	11.505(2)
b, Å	12.934(2)	9.842(2)	21.376(4)
c, Å	14.625(2)	18.473(4)	13.547(2)
α, deg	90	74.864(12)	90
β, deg	90	78.91(2)	109.274(14)
γ, deg	90	79.277(14)	90
V, Å^3	5915.4(11)	1360.3(6)	3145.1(10)
Z	8	2	2
D_{calcd}, g cm^{-3}	1.681	1.463	1.567
F(000)	3032	618	1494
μ, cm^{-1}	5.79	6.05	4.98
λ (Mo Kα), Å	0.71073	0.71073	0.71073
T, K	293	293	293
R;[a] R_w[b]	0.0425, 0.1035	0.0632, 0.1428	0.0942, 0.2245

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

Results and Discussion

Synthesis. The reaction between H_2bzimpy and $V^{IV}O$(acac)$_2$ in MeOH yields the molecular dioxovanadium(V) complex, [V^VO_2(Hbzimpy)]·$1.25H_2O$ (**1**), wherein the ligand is singly deprotonated from a benzimidazole's pyrrolic N. In the case of Me_2bzimpy, a similar reaction generates a cationic dioxovanadium(V) complex, the absence of ionizable protons in the ligand necessitating the addition of excess ClO_4^- to precipitate the cationic complex as [V^VO_2(Me_2bzimpy)](ClO_4)·H_2O (**3**). The infrared spectra of **1** and **3** show two V=O stretches at 890 and 965 cm^{-1} in each.[23,24] Oxovanadium(IV) complexes of H_2bzimpy and Me_2bzimpy, [$V^{IV}O(H_2bzimpy)(H_2O)_2$]($CF_3SO_3$)$_2$·$2H_2O$ (**2**) and [$V^{IV}O(Me_2bzimpy)(H_2O)_2$]($CF_3SO_3$)$_2$ (**4**), are obtained by reacting the ligands with VO(CF_3SO_3)$_2$. Interestingly, even prolonged reflux of the reaction mixture does not yield any oxovanadium(V) complexes, while, by contrast, the reaction of **2** or **4** with imidazole simply yields the corresponding dioxovanadium(V) complexes, without the incorporation of imidazole into the molecule. This suggests that, in the reactions yielding the vanadium(V) compounds **1** and **3**, basicity in the medium (via acetylacetonate) is a relevant factor in the oxidation to V^VO.

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Table 2. Electronic and IR[a] Spectral Data for Complexes

compound	IR (cm^{-1})	UV−vis λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[V^VO_2(Hbzimpy)]\cdot1.25H_2O$ (**1**)[b]	890, 965 [ν(V=O)]	392 sh (16000), 320 (23000)
$[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2\cdot2H_2O$ (**2**)[c]	985 [ν(V=O)], 1250 (br) [$\nu(CF_3SO_3)$]	754 (50), 493 (70), 363 sh (15000), 321 (28000), 230 sh (27000)
$[V^VO_2(Me_2bzimpy)](ClO_4)\cdot H_2O$ (**3**)[b]	890, 960 [ν(V=O)], 1100 (br) [$\nu(ClO_4)$]	380 sh (13000), 368 sh (4000), 322 (35000)
$[V^{IV}O(Me_2bzimpy)(H_2O)_2](CF_3SO_3)_2$ (**4**)[c]	980 [ν(V=O)], 1250 (br) [$\nu(CF_3SO_3)$]	764 (53), 581 (28), 398 sh (16000), 320 (26000), 299 (22000), 216 sh (45000)
$[V^{IV}O(Hntb)]\cdot2MeOH$ (**5**)[d]	985 [ν(V=O)]	772, 555, 362 sh
$[V^{IV}O(H_3ntb)(H_2O)](ClO_4)_2\cdot0.5H_2O\cdot0.33Me_2CO$ (**6**)[e]	990 [ν(V=O)], 1710 [ν(C=O)]	754 (75), 535 sh (22), 403 sh (85), 302 sh (2500)
$[V^{IV}O(H_3ntb)Cl]Cl\cdot H_2O$ (**7**)[c]	990 [ν(V=O)]	752 (61), 569 sh (19), 426 sh (15), 279 sh (23000), 266 sh (22000), 239 sh (16500)
$[(H_3ntb)V^{IV}O(\mu\text{-}O)V^VO(H_3ntb)](CF_3SO_3)_3\cdot2H_2O$ (**8**)[c]	985 [ν(V=O)], 760 [ν(V−O−V)], 1250 (br) [$\nu(CF_3SO_3)$]	1014 (1659), 829 sh (1000), 715 sh (790), 386 (3200), 279 sh (37000), 266 sh (34000), 240 sh (25000)
$[V^{IV}O(Me_3ntb)SO_4]\cdot H_2O$ (**9**)[d]	950 [ν(V=O)], 1180, 1140, 610, 660 [$\nu(SO_4)$]	780, 568, 362 sh
$[V^{IV}O(Me_3ntb)Cl]Cl\cdot H_2O$ (**10**)[c]	990 [ν(V=O)]	756 (67), 548 sh (25), 417 sh (26), 280 sh (24000), 266 sh (21000), 241 sh (17000)
$[(Me_3ntb)V^{IV}O(\mu\text{-}O)V^VO(Me_3ntb)](CF_3SO_3)_3\cdot3H_2O$ (**11**)[c]	995 [ν(V=O)], 770 [ν(V−O−V)], 1250 (br) [$\nu(CF_3SO_3)$]	1013 (2170), 842 sh (1300), 693 sh (870), 419 sh (4400), 380 sh (4800), 280 sh (34000), 266 sh (20000), 247 sh (10000)

[a] In KBr pellets. [b] In DMF. [c] In MeOH. [d] In $MgCO_3$ (solid). [e] In CH_3CN.

H_3ntb forms a molecular oxovanadium(IV) complex, $[V^{IV}O(Hntb)]\cdot2MeOH$ (**5**), when refluxed with $VO(acac)_2$ in MeOH. This complex, in which the ligand is doubly deprotonated, is only poorly soluble in DMF. A soluble complex, $[V^{IV}O(H_3ntb)(H_2O)](ClO_4)_2\cdot0.5H_2O\cdot0.33CH_3COCH_3$ (**6**), where the benzimidazole protons are not dissociated, is obtained via initially forming a sulfato complex. Treatment of the reaction mixture with $Ba(ClO_4)_2\cdot3H_2O$ replaces the sulfate by perchlorates. It should be noted that a small amount of a brown compound, possibly a mixed-valence $V^{IV}V^V$ complex, is also formed along with **6**. A blue insoluble sulfato compound, $[V^{IV}O(Me_3ntb)SO_4]\cdot H_2O$ (**9**), is obtained from the reaction of Me_3ntb and $VOSO_4\cdot2H_2O$. Sulfate coordination to vanadium in **9** is evident in the infrared spectrum from the splitting of $\nu_3(SO_4)$ into two components (1180, 1140 cm^{-1}) as well as $\nu_4(SO_4)$ (610, 660 cm^{-1}).[25,26] Reaction of $VO(acac)_2$ and Me_3ntb did not produce a cleanly isolable product, and attempts to prepare oxovanadium(V) complexes of H_3ntb or Me_3ntb using $VOCl_3$ were unsuccessful. Instead, the chloride-coordinated oxovanadium(IV) complexes, $[V^{IV}O(H_3ntb)Cl]Cl\cdot H_2O$ (**7**) and $[V^{IV}O(Me_3ntb)Cl]Cl\cdot H_2O$ (**10**), were obtained. Although mononuclear oxovanadium(V) complexes of H_3ntb and Me_3ntb could not be isolated, reaction of these ligands with $VO(CF_3SO_3)_2$ yields the oxo-bridged mixed-valence $V^{IV}V^V$ complexes, $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^VO(H_3ntb)](CF_3SO_3)_3\cdot2H_2O$ (**8**) and $[(Me_3ntb)V^{IV}O(\mu\text{-}O)V^VO(Me_3ntb)](CF_3SO_3)_3\cdot3H_2O$ (**11**), in ∼40% yield. The IR spectra of **8** and **11** show V=O stretches at 985 and 990 cm^{-1}, respectively.[27]

Electronic Spectra. The electronic absorption spectra of the complexes are summarized in Table 2. The oxovanadium(IV) complexes of H_2bzimpy and Me_2bzimpy, **2** and **4**, respectively, exhibit two d−d transitions of moderate intensity. For vanadium(IV) complexes, it is generally regarded that the unpaired electron is in a d_{xy} orbital and transitions occur to $[d_{xy}, d_{yz}]$ (ν_1), $d_{x^2-y^2}$ (ν_2), and d_{z^2} (ν_3) with increasing energies.[28] The ν_3 band usually lies in the charge-transfer region, and so, in **2** and **4**, ν_1 and ν_2 are observed distinctly, whereas the ν_3 transition indeed appears to be obscured by charge-transfer transitions. Solution spectra of the oxovanadium(IV) complexes of H_3ntb and Me_3ntb, **6**, **7**, and **10**, show all three d−d transitions. Because of the insoluble nature of the tripodal oxo complexes **5** and **9** in common organic solvents, solution spectra could not be obtained, but the solid-state reflectance spectra of these two complexes also exhibit three d−d transitions. The data given in Table 2 indicate that although the energy of ν_1 is practically the same for **2**−**7**, **9**, and **10**, the ν_2-band energy varies in the order **2** > **6** > **10** > **5** > **9** ≈ **7** > **4**. Nonetheless, at this point, we cannot establish any clear correlation between the ν_2-band energy and another molecular parameter.

The electronic spectra of $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^VO(H_3ntb)](CF_3SO_3)_3\cdot2H_2O$ (**8**) and $[(Me_3ntb)V^{IV}O(\mu\text{-}O)V^VO(Me_3ntb)](CF_3SO_3)_3\cdot3H_2O$ (**11**) exhibit intense absorption in the near-IR region around 1015 nm. This absorption, which is absent from the oxovanadium(IV) complexes, is assigned to the intervalence transfer (IT) transition observed in some of the known mixed-valence vanadium complexes.[29−35] The band's position is insensitive to variations in the solvent (MeOH,

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Table 3. ESR Data for the Complexes[a]

compound	$g_{\|}$	$10^4\|A_{\|}\|$	$g_{\perp}$	$10^4\|A_{\perp}\|$	g_{iso}	$\|A_{iso}\|$	g_{av}
$[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2 \cdot 2H_2O$ (**2**)[b]	1.943	190	1.972	59	1.985	99	
	1.944	180	1.981	69			
$[V^{IV}O(Me_2bzimpy)(H_2O)_2](CF_3SO_3)_2$ (**4**)[c]	1.939	180	1.979	66	1.988	97	
	1.943	170	1.981	62			
$[V^{IV}O(Hntb)] \cdot 2MeOH$ (**5**)[d]							1.982
$[V^{IV}O(H_3ntb)(H_2O)](ClO_4)_2 \cdot 0.5H_2O \cdot 0.33Me_2CO$ (**6**)[e]	1.951	170	1.977	63	1.971	92	
$[V^{IV}O(H_3ntb)Cl]Cl \cdot H_2O$ (**7**)[f]	1.955	165	1.978	55	1.965	90	
$[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)](CF_3SO_3)_3 \cdot 2H_2O$ (**8**)[g]					1.957	46	
$[V^{IV}O(Me_3ntb)SO_4] \cdot H_2O$ (**9**)[d]							1.998
$[V^{IV}O(Me_3ntb)Cl]Cl \cdot H_2O$ (**10**)[f]	1.945	165	1.983	55	1.969	94	
$[(Me_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(Me_3ntb)](CF_3SO_3)_3 \cdot 3H_2O$ (**11**)[h]					1.965	47	

[a] Values for $g_{\|}$, $A_{\|}$, $g_{\perp}$, $A_{\perp}$, g_{av} from cryogenic glass at 77 K; g_{iso}, A_{iso} from fluid solution at 298 K and A in cm^{-1}, simulations performed on a Macintosh G3 platform using software routines by Addison, A. W.; Cain, M. Drexel University, 1992, as derived from Lozos, G. P.; Hoffman, B. M.; Fronz, G. C. *QCPE* **1974**, *11*, 265. [b] Cryogenic glass in DMF and fluid solution in CH_3CN. [c] DMF. [d] Polycrystalline. [e] 2-Methoxyethanol. [f] DMF−MeOH. [g] CH_3CN/DMF. [h] CH_3CN.

CH_3CN, DMF), suggesting that these mixed-valence complexes fall into class-III of the Robin and Day classification.[36]

ESR and Electrochemical Studies. The X-band ESR data are summarized in Table 3. The spectra of the oxovanadium(IV) complexes **2**, **4**, **6**, **7**, and **10** were recorded in fluid solutions at ambient temperature as well as in cryogenic glasses at 77 K. ESR spectra of the ntb-chelates **5** and **9** were recorded only in their polycrystalline state because of their insolubility in common organic solvents. The complexes assigned as vanadium(V) (**1** and **3**) are ESR-silent. The eight-line fluid solution spectra of the oxovanadium(IV) compounds are accounted for by a single $S = {}^1/_2$ species in which the unpaired electron in a d_{xy} orbital is coupled to the nuclear spin of the vanadium nucleus ($I = {}^7/_2$). Their cryogenic glass spectra are characterized by two overlapping sets of eight lines corresponding to the g-anisotropy of an axial system. The ESR data show that the $g_{\|}$ values for the bzimpy-containing complexes are lower than for the ntb-containing ones, whereas the $A_{\|}$ values show the opposite trend. This is generally observed for vanadium(IV), the numbers and types of the equatorial donors being directly correlated with the g- and A-values,[37] benzimidazole-N and pyridine-N having similar contributions.[38] For instance, the values $g_{\|} = 1.954$, $A_{\|} = 166$, $g_{\perp} = 1.982$, and $A_{\perp} = 59$ predicted on these bases[39] for the $(N_{arom})_3Cl$ equator in **7** are quite close to the values observed in DMF/MeOH. For the $[V^{IV}O(H_2bzimpy)(H_2O)_2]^{2+}$ salt **2** (Figure 1) and its Me_2bzimpy analogue **4**, additional lines in the cryogenic spectra indicate

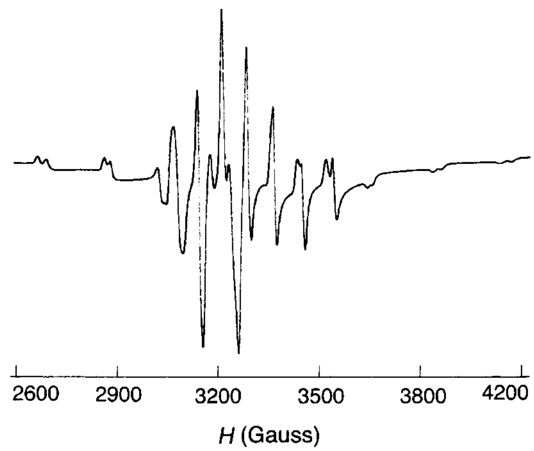

Figure 1. First-derivative cryogenic ESR spectrum of $[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2 \cdot 2H_2O$ (**2**) in DMF at 77 K.

the presence of two species. The similarity between water ($g_o = 1.985$, $A_o = 113 \times 10^{-4}$ cm^{-1}) and DMF ($g_o = 1.983$, $A_o = 109 \times 10^{-4}$ cm^{-1}) as solvents for oxovanadium(IV) sulfate gainsays the second species as arising from displacement of coordinated water by solvent DMF, though the differences in $g_{\|}$ and $A_{\|}$ are consistent with the possibility of a V═O versus V−OH_2 tautomerism (N_3O vs N_2O_2) in solution.

The mixed-valence oxovanadium(IV/V) complexes show 15-line isotropic spectra in fluid solutions at room temperature (Figure 2), indicating that the single unpaired electron is delocalized over the two vanadium centers on the ESR time scale. These resonances for the H_3ntb complex **8** ($g_{iso} = 1.957$ and $A_{iso} = 46$ cm^{-1}) and its Me_3ntb analogue **11** ($g_{iso} = 1.965$ and $A_{iso} = 47$ cm^{-1}) are comparable with those reported for the mixed-valence complex $[V_2(tmpa)_2(O)_3](ClO_4)_3$.[29] This mixed-valence nature is also clearly evidenced by the dimer paramagnetism: $\chi T = 0.45 \pm 0.1$ cm^3 mol^{-1} for **8** ($\mu = 1.9 \pm 0.3$ μ_B per dimer at 294 K). Unambiguous assignment of the cryogenic glass spectra for the V^{IV}−O−V^{V} systems has proved evasive.

Cyclic voltammograms of bzimpy chelates **1**−**4** and H_3ntb chelate **6** show irreversible redox processes. These are observed for (scan rate 100 mV s^{-1}) **1** (in DMF, $E_{p,c} = -1.53$ V), **2** (in DMF, $E_{p,c} = -1.47$ V), **3** (in MeCN, $E_{p,c} = -1.59$ V), **4** (in MeCN, $E_{p,a} = 1.33$ V, $E_{p,c} = -1.42$ V), and **6** (in

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(39) Zah-Letho, J.; Samuel, E.; Livage, J. *Inorg. Chem*. **1988**, *27*, 2233. These ESR parameters for Cl_4 equators on V(IV) are not completely independent of the axial ligands.

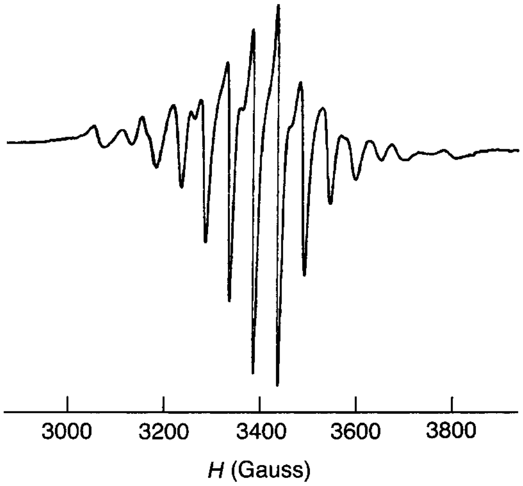

Figure 2. First-derivative ESR spectrum of dinuclear $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)](CF_3SO_3)_3{\cdot}2H_2O$ (**8**) in MeCN−DMF at ambient temperature.

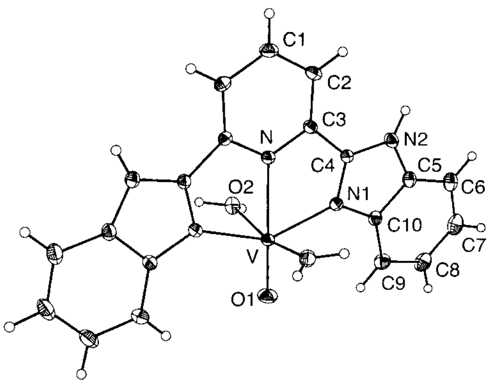

Figure 3. ORTEP representation (50% probability ellipsoids) of $[V^{IV}O(H_2bzimpy)(H_2O)_2]^{2+}$ in $[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2{\cdot}2H_2O$ (**2**).

MeCN, $E_{p,a} = +1.36$ V, $E_{p,c} = -1.43$ V). It is noteworthy that all the experimentally observed reductions occurred at ca. −1.5 V (ca. −1.2 V vs SCE), regardless of whether the electroactive species is V^{IV} or V^{V}. This difference in oxidation state is compensated by the presence of the additional oxo ligand in the V^{V} systems; that is, the dioxovanadium(V) and monooxovanadium(IV) complexes are redox-potential equivalent. The mixed-valence complexes **8** and **11** show reversible cyclic voltammograms in MeCN. The potentials for these mixed-valence complexes at 100 mV s^{-1} are given in parentheses for **8** ($E_{1/2}$(ox) = +1.13 V, $E_{1/2}$(red) = −0.41 V) and **11** ($E_{1/2}$(ox) = +1.12 V, $E_{1/2}$(red) = −0.41 V). Reversible electron transfer for the redox processes $V^{IV}V^{V} \rightarrow V^{V}V^{V}$ and $V^{IV}V^{V} \rightarrow V^{IV}V^{IV}$ is of course implied by the observed electron delocalization over both vanadium centers. These data, along with the ESR spectra in fluid solutions and electronic spectra imply that the mixed-valence compounds persist in the solution phase.

Description of Crystal Structures. ORTEP diagrams of the complex cations $[V^{IV}O(H_2bzimpy)(H_2O)_2]^{2+}$ in **2**, $[V^{IV}O(H_3ntb)Cl]^{+}$ in **7**, and $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)]^{3+}$ from **8** are shown in Figures 3−5, respectively. Selected bond distances and angles are listed in Table 4.

The H_2bzimpy-ligated vanadium(IV) cation of **2** has a six-coordinate vanadium atom with an N_3O_3 coordination en-

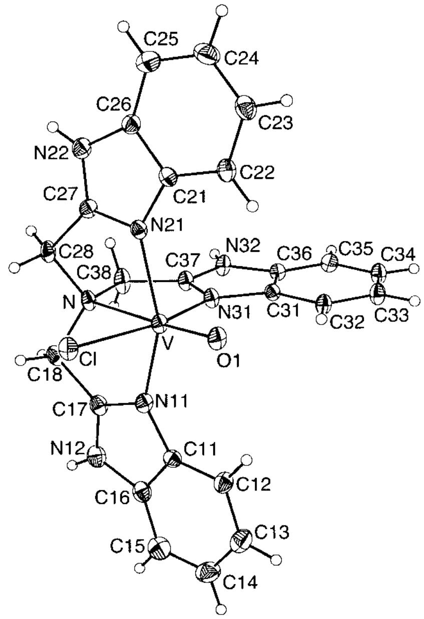

Figure 4. ORTEP representation (50% probability ellipsoids) of $[V^{IV}O(H_3ntb)Cl]^{+}$ in $[V^{IV}O(H_3ntb)Cl]Cl{\cdot}H_2O$ (**7**).

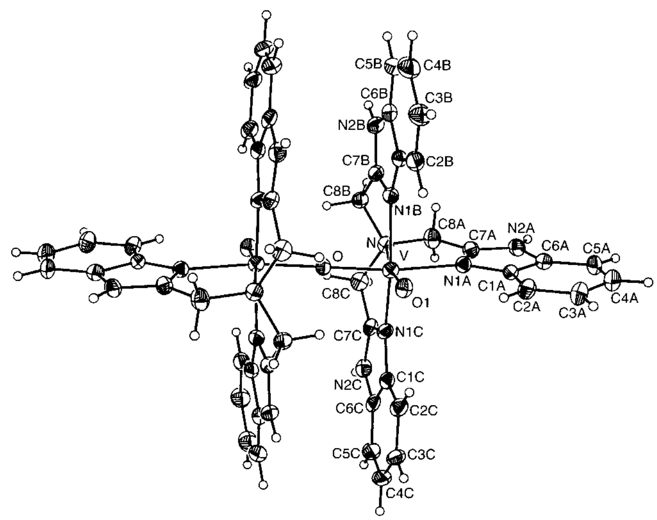

Figure 5. ORTEP representation (50% probability ellipsoids) of the dinuclear $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)]^{3+}$ cation in $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)](CF_3SO_3)_3{\cdot}2H_2O$ (**8**).

vironment. The oxygens come from the oxo group and two water molecules, whereas the nitrogens belong to the obligatorily meridianal H_2bzimpy ligand. The short V−O(1) bond distance (1.59 Å) is typical of V^{IV}=O which indicates considerable π-bond character. The V−OH_2 distances (V−O(2) = 2.053 Å) are somewhat longer than those reported for $[VO(S\text{-peida})(H_2O)]$[34] (2.018 Å) and for $[VO(Hhida)(H_2O)]$[40] (2.021 Å). The geometry around the vanadium atom is distorted octahedral. In the plane comprising N(1)−O(2)−N(1#1)−O(2#1) atoms, the donor atoms lie within 0.190 Å of the least-squares plane, and V is displaced toward the vanadyl oxygen by 0.445 Å. The cisoid angles in this plane lie between 88.3° and 87.4°, whereas the transoid angles lie between 145.1° and 180°. If we consider

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds **2**, **7**, and **8**

$[V^{IV}O(H_2bzimpy)(H_2O)_2](CF_3SO_3)_2 \cdot 2H_2O$ (**2**)			
V−O(1)	1.590(5)	V−O(2)	2.053(3)
V−N	2.244(4)	V−N(1)	2.117(3)
O(1)−V−N	180.0	N(1)−V−N(1#1)	145.1(2)
O(2)−V−O(2#1)	165.8(2)	N(1)−V−O(2)	88.31(12)
N(1)−V−O(2#1)	87.43(13)	O(2)−V−N(1#1)	87.44(13)
N(1#1)−V−O(2#1)	88.31(12)	O(1)−V−N(1)	107.44(8)
O(1)−V−O(2)	97.12(9)	O(1)−V−N(1#1)	107.44(8)
O(1)−V−O(2#1)	97.12(9)		
$[V^{IV}O(H_3ntb)Cl]Cl \cdot H_2O$ (**7**)			
V−O(1)	1.593(3)	V−N	2.417(4)
V−N(11)	2.058(4)	V−N(21)	2.066(4)
V−N(31)	2.078(4)	V−Cl	2.353(2)
N(21)−V−N(11)	147.72(14)	N−V−O(1)	172.6(2)
N(31)−V−Cl	162.29(10)	N−V −N(31)	75.15(13)
N−V−Cl	87.14(10)	N(31)−V−O(1)	97.5(2)
O(1)−V−Cl	100.25(13)	N(21)−V−N(31)	85.6(2)
N(21)−V−N	73.28(14)	N(21)−V−Cl	89.28(11)
N(21)−V−O(1)	107.1(2)	N(11)−V−N	74.47(14)
N(11)−V−N(31)	87.5(2)	N(11)−V−O(1)	105.1(2)
N(11)−V−Cl	87.88(12)		
$[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)](CF_3SO_3)_3 \cdot 2H_2O$ (**8**)			
V−O(1)	1.594(5)	V−O	1.8412(11)
V−N	2.430(5)	V−N(1A)	2.111(5)
V−N(1B)	2.048(6)	V−N(1C)	2.043(6)
O(1)−V−N	170.5(2)	N(1B)−V−N(1C)	149.6(2)
N(1A)−V−O	159.9(2)	N(1A)−V−N(1B)	86.6(2)
N(1A)−V−N(1C)	87.9(2)	N(1B)−V−O	87.3(2)
N(1C)−V−O	87.7(2)	O(1)−V−N(1A)	95.9(2)
O(1)−V−N(1B)	105.1(2)	O(1)−V−N(1C)	105.3(2)
O(1)−V−O	104.2(2)	N−V−N(1A)	74.7(2)
N−V−N(1B)	74.6(2)	N−V−N(1C)	75.1(2)
N−V−O	85.23(14)	V−O−V′	179.99(1)

the equatorial plane for the distorted octahedron as N(1)−N−N(1#1)−O(1), the H_2bzimpy−oxo plane, then these four donor atoms and the V form a perfect plane. The cisoid angles in this plane lie between 72.6° and 107.4°.

The structure of the H_3ntb chloro cation **7** shows that the vanadium atom possesses a distorted octahedral geometry with an N_4OCl donor set, the molecule being devoid of symmetry. Relative to the mean equatorial plane comprising the N(11)−N(31)−N(21)−Cl atoms, the vanadium atom is displaced toward the vanadyl oxygen (O(1)) by 0.457 Å. The bond distances are comparable to those listed for **2**. N(benzimidazole)−V bond distances are similar to other reported benzimidazole-containing oxovanadium complexes.[41] Figure 4 also illustrates that the H_3ntb ligand flexes quite adequately to accommodate the tetragonal or pseudo-octahedral coordination at vanadium, although it is seen to impose trigonal stereochemistry in other cases.[41,42] At the same time, the fact that H_3ntb forms a set of five-membered chelate rings leads to N−V−N angles (73.3°−87.5°) which are reduced from the normal octahedron 90° values.

Crystals of H_3ntb complex **8** contain binuclear $[(H_3ntb)V^{IV}O(\mu\text{-}O)V^{V}O(H_3ntb)]^+$ units. The bridging oxygen atom in the binuclear cation is part of an obligatorily antilinear[30] V−O−V system as a result of its occupying the crystallographic inversion center that relates the two halves of the complex cation. In each half of the binuclear unit, an H_3ntb acts as a tetradentate ligand with a terminal and a bridging oxo ligand completing the distorted octahedral coordination sphere. For the equatorial plane defined by NN(1A)O(1)O (leaving two benzimidazoles axial), the donor atoms lie within 0.0046 Å of the least-squares plane, and the V atom is displaced toward O(1) by 0.0103 Å. Bond distances between the vanadium atom and the vanadyl oxygen atom (1.594 Å) and between the bridging oxo group and the vanadium atom (1.841 Å) are comparable with those of other mixed-valence oxo-bridged V^{IV}/V^{V} complexes.[29,30,32,40]

Acknowledgment. We thank Drexel University for support and Dr. J. P. Glusker of Fox Chase Cancer Center for kind assistance with some crystallographic calculations.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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