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Alkoxo Bound Monooxo- and Dioxovanadium(V) Complexes: Synthesis, Characterization, X-ray Crystal Structures, and Solution Reactivity Studies

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A large variety of oxovanadium(V) complexes, mononuclear VO_2^+ and VO^{3+} in addition to the dinuclear VO^{3+}, of the structural type $(VOL)_2$, $(VOHL)_2$, VOLHQ, $K(VO_2HL)$, $K(VO_2H_2L)$, or (salampr) (VO_2L) {where L = Schiff base ligand possessing alkoxo group(s); HQ = 8-hydroxyquinoline; salampr = cation of reduced Schiff base derived from salicylaldehyde and 2-amino-2-methylpropan-1-ol}, bound to alkoxo, phenolate and imine groups have been synthesized in high yields and characterized by several spectral and analytical methods, including single crystal X-ray studies. While the mononuclear VO_2^+ complexes have been synthesized at alkaline pH, the dinuclear VO^{3+} complexes have been synthesized under neutral conditions using alkoxo rich Schiff base ligands. The X-ray structures indicate that the cis-dioxo complexes showed longer $V-O_{alkoxo}$ bond lengths compared to the monooxo counterparts. The plot of $V-O_{phen}$ bond distances of several VO^{3+} complexes vs the lmct showed a near linear correlation with a negative slope. The cyclic voltammograms revealed a reversible V(V)/V(IV) couple with the reduction potentials increasing to more negative ones as the number of alkoxo groups bound to V increases from 1 to 2. Moreover, the cis-dioxo VO_2^+ complexes are easier to reduce than their monooxo counterparts. The solution stability of these complexes was studied in the presence of added water (1:4, water: solvent), where no decomposition was observed, unlike other Schiff base complexes of V. The conversion of the dioxo complexes to their monooxo counterparts in the presence of catalytic amounts of acid is also demonstrated. The reactivity of alkoxo bound V(V) complexes is also reported. X-ray parameters are as follows. H_4L^3: monoclinic space group, $P2_1/c$; $a = 10.480(3)$, $b = 8.719(6)$, $c = 12.954(8)$ Å; $\beta = 101.67(4)°$; $V = 1126(1)$ Å^3; $Z = 4$; $R = 0.060$, $R_w = 0.058$. Complex **1**: monoclinic space group, $P2_1/n$; $a = 12.988(1)$, $b = 9.306(2)$, $c = 19.730(3)$ Å; $\beta = 99.94(1)°$; $V = 2348.9(7)$ Å^3; $Z = 4$; $R = 0.031$, $R_w = 0.027$. Complex **2**: monoclinic space group, $P2_1/n$; $a = 12.282(3)$, $b = 11.664(2)$, $c = 12.971(4)$ Å; $\beta = 97.89(2)°$; $V = 1840.5(8)$ Å; $Z = 4$; $R = 0.035$, $R_w = 0.038$. Complex **5**: monoclinic space group, $P2_1/c$; $a = 17.274(2)$, $b = 6.384(2)$, $c = 16.122(2)$ Å; $\beta = 116.67(1)°$; $V = 1588.7(7)$ Å^3; $Z = 4$; $R = 0.039$, $R_w = 0.043$. Complex **8**: monoclinic space group, $P2_1/c$; $a = 11.991(1)$, $b = 11.696(4)$, $c = 12.564(3)$ Å; $\beta = 110.47(1)°$; $V = 1650.8(8)$ Å^3; $Z = 2$; $R = 0.045$, $R_w = 0.049$.

Introduction

The discovery that vanadium is involved in the bacterial nitrogen fixation (*nitrogenases*),[1] in the halogenation of organic substrates (*haloperoxidases*),[2] as low molecular weight complex (*amavadin*)[3] isolated from *Aminata muscaria*, and in *tunichromes*[4] led to renewed interest in the chemistry of model compounds with varying N/O coordination sites. Recent X-ray determination of the azide modified vanadium enzyme (*chloroperoxidase*) at 2.1 Å resolution reveals that azide coordinates directly to the metal center, resulting in a structure with three non-protein oxygens and an ϵ_2-N of histidine as a ligand.[5] *cis*-Dioxovanadium(V), VO_2^+, complexes have been reported as functional mimics of vanadium−bromoperoxidase[6] and also as structural models for vanadium(V)−transferrin.[7] Interest in vanadium(V) bound alkoxides has increased in the recent past in view of the short V−O distance observed from EXAFS at 1.72 Å for vanadium−bromoperoxidase that may arise from a vanadyl ester bond.[8]

Vanadium exists in acidic solutions as VO_2^+ and in highly alkaline medium as tetrahedral VO_4^{3-}.[9] While VO_2^+ is common, the presence of VO^{3+} is also known.[10] There is a report in the literature on the formation of VO^{3+} and VO_2^+ using the same ligand, under different experimental conditions but without any X-ray structure.[11] Though dibasic tridentate ligands prefer

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(1) Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature (London)* **1986**, *322*, 388.

(2) (a) Vilter, H. *Phytochemistry* **1984**, *23*, 1387. (b) Wever, R.; de Boer, E.; Plat, H.; Krenn, B. E. *FEBS Lett.* **1987**, *216*, 1.

(3) Kneifel, H.; Bayer, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

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

(5) (a) Messerschmidt, A.; Wever, R. *J. Inorg. Biochem*, **1995**, *59*, 580. (b) Messerschmidt, A.; Wever, R. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 392.

(6) (a) Clague, M. J.; Keder, N. L.; Butler, A. *Inorg. Chem.* **1993**, *32*, 4754. (b) Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1995**, *117*, 3475.

(7) Butler, A.; Danzitz, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 1864.

(8) Arber, J. M.; de Boer, E.; Garner, C. D.; Hasnain, S. S.; Wever, R. *Biochemistry* **1989**, *28*, 7968.

(9) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; 1980.

(10) (a) Chakravarty, J.; Dutta, S.; Chandra, S. K.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 4249. (b) Mondal, S.; Dutta, S.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1115. (c) Chakravarty, J.; Dutta, S.; Dey, A.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1994**, 557.

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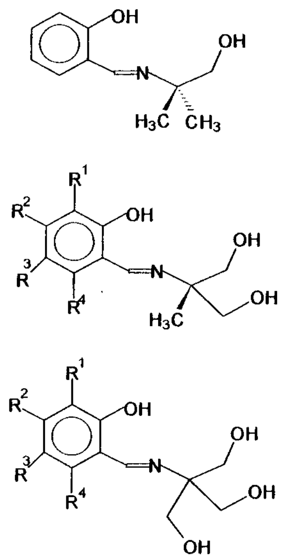

Ligand		*Complexes*
H_2L^1	H_2salamp	**1, 2**

Ligand	R^1	R^2	R^3	R^4		*Complex (es)*
H_3L^2	H	H	---C_4H_4----		H_3hnampd	**3, 4**
H_3L^7	H	H	H	H	H_3salampd	**10, 12**
H_3L^8	H	H	Me	H	H_3-5-Mesalampd	**11**

Ligand	R^1	R^2	R^3	R^4		*Complex (es)*
H_4L^3	H	H	H	H	H_4saltris	**6, 13**
H_4L^4	H	H	---C_4H_4----		H_4saltris	**5, 7**
H_4L^5	OMe	H	H	H	H_4-3-OMesaltris	**8**
H_4L^6	H	H	Br	H	H_4-5-Brsaltris	**9**

Figure 1. Schematic representation of the ligands used in this study.

dimeric vanadium complexes,[12] we have recently synthesized and structurally characterized a series of mononuclear *cis*-dioxovanadium(V) complexes with such ligands generated from 2-amino-2-methylpropan-1-ol (amp) and salicylaldehyde (or its derivatives).[13] In continuation with our interest in V(V) chemistry[13−15] and in order to understand the role of various reaction parameters, we have systematically changed the amine part to those possessing one, two, and three $-CH_2OH$ groups, viz., amp, 2-amino-2-methyl-1,3-propanediol (ampd), and (tris(hydroxymethyl)amino)methane (tris), and carried out synthetic reactions. Herein we report the synthesis, structure, and spectral and electrochemical characterization of complexes of VO_2^+ and VO^{3+} bound to such alkoxo possessing Schiff bases (L^1 to L^8), the solution stability, and their interconversion.

Methods and Materials

FTIR, electronic spectra, cyclic voltammetry, and proton NMR were recorded as detailed elsewhere.[13−15]

Amp was distilled; tris and ampd were recrystallized before use. β-Naphthol, 8-hydroxyquinoline (HQ), dimethyl sulfoxide (DMSO), and absolute EtOH were used as received. Salicylaldehyde (sal) and 3-OMe(sal) were obtained from commercial sources and used as received. The asymmetric dimer, $[VOL^1]_2(\mu\text{-O})$, was synthesized as reported earlier.[12b,13]

Experimental Details. All of the ligands (Figure 1) were prepared as reported earlier.[13,14] Prismatic single crystals of X-ray quality of saltris, H_4L^3, were obtained when the reaction mixture was kept at room temperature for 5 days. In the synthesis of the complexes, the *in situ* generated ligand preparations were used after 30 min of stirring of the reaction mixture.

[Salampr][VO$_2$L^1], 1. To $(VOL^1)_2(\mu\text{-O})$ (0.53 g, 1 mmol), in 10 mL of MeOH, is added $NaBH_4$ (0.04 g, 1.1 mmol). The solution changes color from dark red to yellow, and this solution is stirred at room temperature for 60 min. During this time the solution regains its red color. The solvent is reduced to one-tenth of its volume, and to this an excess volume of ether was added to precipitate a yellow residue. The residue is redissolved in CH_3CN and stored at 4 °C for 2 weeks, whereupon yellow crystals of **1** appeared in 49% yield. Anal. Calcd for $C_{22}H_{31}N_2O_6V$: C, 56.17; H, 6.64; N, 5.96; V, 10.83. Found: C, 56.32; H, 6.64; N, 5.81; V, 10.83. UV−vis (λ, nm (ϵ, M^{-1} cm^{-1}; in MeOH)): 310 (681), 360 (528). ^1H NMR (in DMSO-d_6; ppm): δ 14.38 (phenolic $-OH$), 4.45 (br, OH/NH), 3.48 (free $-CH_2OH$ of the cation), 3.98 (bound $-CH_2O^-$). ^{13}C NMR (in DMSO-d_6; ppm): δ 74.4 (bound CH_2O^-), 69.06 (tert C). ^{51}V NMR (in DMSO-d_6; ppm): δ −533.4 (90%), −495.1 (10%). FTIR (KBr matrix; in cm^{-1}): ν_{NH}, 2800−3000; $\nu_{C=N}$, 1635; $\nu_{V=O}$, 918 and 882.

VO(L^1)(HQ), 2. To $VO(acac)_2$ (2 mmol, 0.53 g) in 10 mL of CH_3CN or MeOH is added HQ (2 mmol, 0.29 g) in 5 mL of CH_3CN or MeOH and salamp (2 mmol, 0.39 g) in 5 mL of the same solvent. A red solution is formed, and this is refluxed for 80 min. The solvent is removed under vacuum. A dark violet residue is collected, which is recrystallized from CH_3CN to yield **2** in 51% yield as microcrystalline material. Recrystallization from CH_3CN−EtOH (95:5 (v/v)) and storing at 4 °C for 24 h yielded crystals suitable for single crystal X-ray studies. Anal. Calcd for $C_{20}H_{19}N_2O_4V$: C, 59.71; H, 4.76; N, 6.96; V, 12.66. Found: C, 59.50; H, 4.79; N, 6.86; V, 13.01. UV−vis (λ, nm (ϵ, M^{-1} cm^{-1}, in MeOH)): 280 (8375); 318 (3777); 368 (2538); 506 (628). ^1H NMR (in DMSO-d_6; ppm): δ 4.36 and 4.51 (d) (bound $-CH_2O^-$). ^{13}C NMR (in DMSO-d_6; ppm): δ 86.9 (bound CH_2O^-); 78.2 (tert C). ^{51}V NMR (in DMSO-d_6; ppm): δ −480.8. FTIR (KBr matrix; in cm^{-1}): $\nu_{C=N}$, 1630; $\nu_{V=O}$, 954.

Quantitative conversion of **1** or $[Hamp][VO_2L^1]$[13] to complex **2** was accomplished by reacting the precursor in MeOH at 60 °C in the presence of a stoichiometric amount of HQ and catalytic amount of PPh_3 for 1 h. Complex **2** could not be isolated either when the reaction temperature is lowered to 35−50 °C or when PPh_3 is not added to the reaction mixture. The asymmetric dimer, $[VOL^1]_2(\mu\text{-O})$, on simultaneous addition of $NaBH_4$ and HQ gave two products, i.e., **2** and an already reported $Na[VO_2(HQ)_2]$[16] in 8 and 60% yields, respectively.

[VOL^2]$_2$, 3. To H_3L^2 (3 mmol, 0.78 g) dissolved in 20 mL of MeOH was added $VO(acac)_2$ (3 mmol, 0.80 g) dissolved in 20 mL of MeOH, and the mixture was heated for 3 h to result in a dark brown precipitate. The precipitate was purified by stirring twice in hot MeOH for 1 h each time followed by filtration. The product was washed with ether before drying *in vacuo* to obtain **3** in 61% yield. Anal. Calcd for $(C_{15}H_{14}NO_4V)_2$: C, 55.74; H, 4.37; N, 4.33; V, 15.76. Found: C, 55.35; H, 4.30; N, 4.53; V, 15.53. UV−vis (λ, nm (ϵ, M^{-1} cm^{-1}; in DMSO or DMF)): 320 (20 779); 390 (sh, 5844); 510 (324). ^1H NMR (in DMSO-d_6; ppm): δ 4.4−4.7 (bound CH_2O^-); 4.8−5.2 (bound $-CH_2O^-$); 1.62 (CH_3). ^{13}C NMR (in DMSO-d_6; ppm): δ 88.5, 83.6 (bound CH_2O^-); 76.8 (tert C); 19.0 (CH_3). ^{51}V NMR (in DMSO-d_6; ppm): δ −531.3. FTIR (KBr matrix; in cm^{-1}); $\nu_{C=N}$, 1625; $\nu_{V=O}$, 961.

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(11) Bonadies, J. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4088.

(12) (a) Syamal, A.; Kale, K. S. *Inorg. Chem.* **1979**, *18*, 992. (b) Carrano, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944.

(13) Asgedom, G.; Sreedhara, A.; Kivikoski, J.; Valkonen, J.; Rao, C. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2459.

(14) (a) Asgedom, G.; Sreedhara, A.; Rao, C. P. *Polyhedron* **1995**, *14*, 1873. (b) Asgedom, G.; Sreedhara, A.; Kolehmainen, E.; Rao, C. P. *Polyhedron*, in press. (c) Sreedhara, A.; Susa, N.; Patwardhan, A.; Rao, C. P. *Biochem. Biophys. Res. Commun.* **1996**, *224*, 115.

(15) Asgedom, G.; Sreedhara, A.; Kivikoski, J.; Kolehmainen, E.; Rao, C. P. *J. Chem. Soc., Dalton Trans.* **1996**, 93.

(16) Giacomelli, A.; Floriani, C.; de Souza Duarte, A. O.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1982**, *21*, 3310.

Table 1. Summary of Crystallographic Data and Parameters for **1**, **2**, **5**, **8** and H_4L^3

	1	**2**	**5**	**8**	H_4L^3
mol formula	$C_{22}H_{31}N_2O_6V$	$C_{20}H_{19}N_2O_4V$	$C_{15}N_{15}NO_6VK$	$C_{24}H_{28}N_2O_{12}V_2$·2DMSO	$C_{11}H_{15}NO_4$
formula wt	470.44	402.32	395.4	794.3	225.4
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
cell constants					
a/Å	12.988(1)	12.282(3)	17.274(2)	11.991(1)	10.480(3)
b/Å	9.306(2)	11.664(2)	6.384(2)	11.696(4)	8.719(6)
c/Å	19.730(3)	12.971(4)	16.122(2)	12.564(3)	12.954(8)
β/deg	99.94(1)	97.89(2)	116.67(1)	110.47(1)	101.67(4)
V/Å^3	2348.9(7)	1840.5(8)	1588.7(7)	1650.8(8)	1126(1)
Z	4	4	4	2	4
D_c/(g cm^{-3})	1.33	1.45	1.66	1.60	1.33
F(000)	992	832	808	824	480
θ range/deg	2−26	2−26	2−26	2−26	2−26
tot reflcns	6006	4549	4277	4125	2958
unique reflcns	4596	3594	3404	3420	2197
reflcns used	3730 [$I > 2\sigma(I)$]	3024 [$I > 2\sigma(I)$]	1991 [$I > 3\sigma(I)$]	1944 [$I > 3\sigma(I)$]	1554 [$I > 2\sigma(I)$]
params	296	244	217	217	149
final R	0.031	0.035	0.039	0.045	0.060
R_w[a]	0.027	0.038	0.043	0.049	0.058

[a] $R_w = [\sum w(|F_o| - |F_c|^2/\sum w|F_o|^2]^{1/2}$. $w = 1/\sigma F^2 + 1.00$, where a Chebychev weighting scheme was employed.

Table 2. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors U(iso) for H_4L^3

atom	x	y	z	U(iso)
O(1)	0.7234(2)	0.0268(2)	0.3470(1)	0.0335
O(2)	0.4670(2)	0.2180(2)	0.4297(2)	0.0404
O(3)	0.6084(2)	0.4927(2)	0.6410(2)	0.0359
O(4)	0.7667(2)	0.1844(3)	0.7808(2)	0.0440
N(1)	0.7003(2)	0.1218(2)	0.5386(2)	0.0262
C(1)	0.8059(2)	−0.0749(3)	0.3952(2)	0.0283
C(2)	0.8450(2)	−0.0788(3)	0.5095(2)	0.0259
C(3)	0.9379(2)	−0.1873(3)	0.5600(2)	0.0317
C(4)	0.9895(3)	−0.2925(3)	0.5005(3)	0.0375
C(5)	0.9479(3)	−0.2925(4)	0.3887(3)	0.0429
C(6)	0.8595(3)	−0.1873(4)	0.3366(2)	0.0409
C(7)	0.7890(2)	0.0219(3)	0.5767(2)	0.0285
C(8)	0.6278(2)	0.2216(3)	0.6003(2)	0.0262
C(9)	0.4838(3)	0.2088(3)	0.5438(2)	0.0342
C(10)	0.6784(3)	0.3857(3)	0.5908(2)	0.0312
C(11)	0.6398(3)	0.1671(3)	0.7163(2)	0.0344

$K[VO_2HL^2]·2H_2O$, 4. To H_3L^2 (3 mmol, 0.78 g) dissolved in 35 mL of absolute EtOH was added KOH (9 mmol, 0.49 g). To this mixture was added $VO(acac)_2$ (3 mmol, 0.80 g) dissolved in 60 mL of absolute EtOH and the mixture heated for 2 h, resulting in a pale yellow precipitate. The precipitate was stirred twice in EtOH for 1 h each time followed by filtration. The product was washed with ether and dried *in vacuo* to produce **4** in 65% yield. Anal. Calcd for $C_{15}H_{15}NO_5KV·2H_2O$: C, 43.38; H, 4.61; N, 3.37; V, 12.26; K, 9.41. Found: C, 43.58; H, 4.52; N, 3.39; V, 12.57. K, 9.28. UV−vis (λ, nm (ϵ, M^{-1} cm^{-1}; in water)): 237 (55 000); 310 (14 166); 375 (6250). ^1H NMR (in DMSO-d_6; ppm): δ 5.00 (free O*H*); 4.06 (bound CH_2O^-); 3.51 (free $-CH_2OH$); 1.42 (CH_3). ^{13}C NMR (in DMSO-d_6; ppm): δ 77.3 (bound CH_2O^-), 73.2 (free CH_2OH), 68.1 (tert *C*), 21.1 (CH_3). ^{51}V NMR (in DMSO-d_6; ppm): δ −528.5. FTIR (KBr matrix; in cm^{-1}): ν_{OH}, 3310 ($\Delta\nu_{1/2} = 300$ cm^{-1}); $\nu_{C=N}$, 1624; $\nu_{V=O}$, 916 and 895.

$K[VO_2H_2L^4]·H_2O$, 5. To H_4L^4 (1 mmol, 0.28 g) in 15 mL of MeOH was added KOH (3 mmol, 0.17 g). $VO(acac)_2$ (1 mmol, 0.27 g) dissolved in 10 mL of MeOH was added to the mixture and heated for 2 h to give a pale yellow precipitate. The precipitate was purified by stirring twice in MeOH for 1 h each time, followed by filtration. The product was washed with ether and dried *in vacuo* to give pure complex **5** in 46% yield. Anal. Calcd for $C_{15}H_{15}NO_6KV·H_2O$: C, 43.59; H, 4.15; N, 3.39; V, 12.32; K, 9.46. Found: C, 43.50; H, 4.07; N, 3.31; V, 12.26. K, 9.10. UV−vis (λ, nm (ϵ, M^{-1} cm^{-1}; in water)): 237 (60 769), 313 (16 538), 378 (7692). ^1H NMR (in DMSO-d_6; ppm): δ 4.83 (free O*H*), 4.05 (bound CH_2O^-), 3.6−3.8 (free $-CH_2OH$). ^{13}C NMR (in DMSO-d_6; ppm): δ 75.9 (bound CH_2O^-), 64.1 (free CH_2OH), 73.6 (tert, *C*). ^{51}V NMR (in DMSO-d_6; ppm): δ −529.4. FTIR (KBr matrix; in cm^{-1}): ν_{OH}, 3313 ($\Delta\nu_{1/2} = 233$ cm^{-1}); $\nu_{C=N}$, 1624; $\nu_{V=O}$, 925 and 905.

$[VOHL^x]_2$ ($L^x = L^3-L^6$), 6−9. We have recently reported the preliminary studies of monooxovanadium(V) complexes with saltris, $(VOHL^3)_2$, **6**; hnaptris, $(VOHL^4)_2$, **7**; 3-OMesaltris, $(VOHL^5)_2$, **8**, 5-Brsaltris, $(VOHL^6)_2$, **9**, where the dinuclear nature of the complexes could not be established from the spectral data alone due to the presence of centrosymmetry in the molecule and also due to the lack of crystal structures.[14a] Crystals of **8** and **9** were grown from DMSO over a period of 1 week at room temperature.

$[VOL^y]_2$ ($L^y = L^7, L^8$), 10, 11. Dinuclear monooxovanadium(V) complexes of H_3L^7 [$(VOL^7)_2$], **10**, and H_3L^8 [$(VOL^8)_2$], **11**, were also synthesized following the procedure given for **3**, but the products were found to be insoluble in most of the common organic solvents, including DMF or DMSO, and hence were characterized only on the basis of analytical, diffuse reflectance, and FTIR studies in the solid state. Anal. Calcd for $C_{11}H_{12}NO_4V$, **10**: C, 48.00; H, 4.36; N, 5.09; V, 18.54. Found: C, 47.69; H, 4.23; N, 4.90; V, 18.41. FTIR (KBr matrix, in cm^{-1}): $\nu_{C=N}$, 1624; $\nu_{V=O}$, 950. Anal. Calcd for $C_{12}H_{14}NO_4V$, **11**: C, 50.17; H, 4.87; N, 4.87; V, 17.72. Found: C, 49.65; H, 4.91; N, 4.68; V, 17.91. FTIR (KBr matrix; in cm^{-1}): $\nu_{C=N}$, 1625; $\nu_{V=O}$, 955. Diffuse reflectance (λ, nm (solid)): of **10**, 370, 498; of **11**, 379, 504.

Corresponding dioxovanadium(V) complexes $K[VO_2HL^7]$, **12**, and $K[VO_2H_2L^3]$, **13**, were generated in solution following the procedures given for **4** and **5**, respectively, but could not be isolated in the solid state even after several attempts.

X-ray Crystallography. The diffraction data were collected for the ligand, H_4L^3, and complexes **1**, **2**, **5**, **8**, and **9** on an Enraf-Nonius CAD4 diffractometer at ambient temperature in the ω-2θ scan mode using Mo Kα radiation. The structures were solved using SHELXS86[17] and refined with CRYSTALS,[18] and the diagrams were generated using ORTEP.[19] The hydrogen atoms bonded to C were placed geometrically (C−H = 1.00 Å), whereas Fourier difference syntheses were used to locate the H atoms associated with the O and N atoms in the case of H_4L^3. Other details of collection and refinement are provided in Table 1. Atomic coordinates for all non-hydrogen atoms are given in Tables 2−6 respectively for H_4L^3, **1**, **2**, **5**, and **8**.

Additional material comprising F_o/F_c data, thermal parameters, and the remaining bond lengths and bond angles are given in Supporting Information.

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(17) Sheldrick, G. M. *SHELXS86*, Program for the Solution of Crystal Structures; University of Gottingen: Gottingen, Germany, 1986.

(18) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*, Chemical Crystallography Laboratory; University of Oxford: Oxford, U.K., 1990.

(19) Johnson, C. K. *ORTEP*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 3. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors *U*(iso) for **1**

atom	*x*	*y*	*z*	*U*(iso)
V(1)	0.10957(2)	0.18468(3)	0.86376(3)	0.0311
O(1)	0.00372(9)	0.2003(1)	0.78319(5)	0.0430
O(2)	0.20413(8)	0.2823(1)	0.93348(5)	0.0377
O(21)	0.1804(1)	0.4642(1)	1.02906(7)	0.0473
O(22)	0.2234(1)	0.8552(2)	0.97220(8)	0.0671
O(51)	0.17044(9)	0.0348(1)	0.85572(6)	0.0431
O(52)_	0.02219(9)	0.1583(1)	0.91419(6)	0.0427
N(1)	0.19081(9)	0.3346(1)	0.80599(6)	0.0330
N(21)	0.1738(1)	0.7335(1)	1.08893(7)	0.0390
C(1)	−0.0007(1)	0.2377(2)	0.71839(8)	0.0371
C(2)	−0.0875(1)	0.1964(2)	0.67010(9)	0.0494
C(3)	−0.0954(2)	0.2340(2)	0.6018(1)	0.0553
C(4)	−0.0183(2)	0.3144(2)	0.57926(9)	0.0544
C(5)	0.0663(1)	0.3592(2)	0.62598(8)	0.0470
C(6)	0.0771(1)	0.3216(2)	0.69591(7)	0.0361
C(7)	0.1673(1)	0.3709(2)	0.74257(8)	0.0371
C(8)	0.2847(1)	0.4011(2)	0.84862(8)	0.0390
C(9)	0.3815(1)	0.3925(3)	0.81472(9)	0.0550
C(10)	0.2575(2)	0.5551(2)	0.86471(1)	0.0577
C(11)	0.3014(1)	0.3115(2)	0.91407(8)	0.0401
C(21)	0.1257(1)	0.4147(2)	1.07737(8)	0.0395
C(22)	0.0698(2)	0.2871(2)	1.0695(1)	0.0506
C(23)	0.0179(2)	0.2415(2)	1.1210(1)	0.0575
C(24)	0.0191(2)	0.3235(2)	1.1790(1)	0.0577
C(25)	0.0732(2)	0.4519(2)	1.18625(9)	0.0490
C(26)	0.1282(1)	0.4988(2)	1.13606(8)	0.0392
C(27)	0.1954(2)	0.6290(2)	1.14739(9)	0.0467
C(28)	0.2431(1)	0.8653(2)	1.0940(1)	0.0474
C(29)	0.2226(2)	0.9562(2)	1.1544(1)	0.0624
C(30)	0.3568(2)	0.8203(3)	1.1010(1)	0.0697
C(31)	0.2077(2)	0.9452(2)	1.0266(1)	0.0531

Table 4. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors *U*(iso) for **2**

atom	*x*	*y*	*z*	*U*(iso)
V(1)	0.20572(2)	0.18927(3)	0.10789(2)	0.0349
O(1)	0.1557(1)	0.3319(1)	0.0499(1)	0.0458
O(2)	0.2703(1)	0.0943(1)	0.2101(1)	0.0447
O(3)	0.0697(1)	0.1163(1)	0.0869(1)	0.0408
O(50)	0.2540(1)	0.1385(2)	0.0091(1)	0.0569
N(1)	0.3441(1)	0.2865(1)	0.1731(1)	0.0360
N(2)	0.1119(1)	0.2626(1)	0.2433(1)	0.0412
C(1)	0.2036(1)	0.4250(2)	0.0212(1)	0.0358
C(2)	0.1439(2)	0.5006(2)	−0.0490(1)	0.0447
C(3)	0.1922(2)	0.5991(2)	−0.0798(2)	0.0525
C(4)	0.2999(2)	0.6263(2)	−0.0411(2)	0.0541
C(5)	0.3585(2)	0.5553(2)	0.0299(2)	0.0461
C(6)	0.3120(1)	0.4535(1)	0.0626(1)	0.0362
C(7)	0.3738(1)	0.3845(2)	0.1417(1)	0.0379
C(8)	0.4194(2)	0.2228(2)	0.2546(2)	0.0434
C(9)	0.5050(2)	0.1613(3)	0.1976(2)	0.0669
C(10)	0.4717(3)	0.2963(3)	0.3422(2)	0.0739
C(11)	0.3435(2)	0.1338(2)	0.2924(2)	0.0518
C(12)	−0.0068(1)	0.1287(2)	0.1496(2)	0.0379
C(13)	−0.1051(2)	0.0703(2)	0.1334(2)	0.0517
C(14)	−0.1824(2)	0.0881(3)	0.2031(3)	0.0633
C(15)	−0.1642(2)	0.1618(3)	0.2844(2)	0.0631
C(16)	−0.0649(2)	0.2246(2)	0.3021(2)	0.0499
C(17)	−0.0369(3)	0.3053(3)	0.3824(2)	0.0643
C(18)	0.0605(3)	0.3610(2)	0.3909(2)	0.0659
C(19)	0.1341(2)	0.3384(2)	0.3184(2)	0.0555
C(20)	0.0138(2)	0.2062(2)	0.2339(1)	0.0387

Table 5. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors *U*(iso) for **5**

atom	*x*	*y*	*z*	*U*(iso)
V(1)	0.34777(4)	0.2559(1)	0.39925(4)	0.0236(2)
K(1)	0.41644(5)	0.7383(2)	0.50462(5)	0.0309(4)
O(1)	0.2852(2)	−0.0031(5)	0.3565(2)	0.027(1)
O(2)	0.4272(2)	0.4365(5)	0.3835(2)	0.027(1)
O(3)	0.3373(2)	0.1456(5)	0.1220(2)	0.044(2)
O(4)	0.3429(2)	0.7237(5)	0.1216(2)	0.047(1)
O(5)	0.2917(2)	0.4006(5)	0.4349(2)	0.042(1)
O(6)	0.4253(2)	0.1487(5)	0.4926(2)	0.035(2)
N(1)	0.2863(2)	0.3170(5)	0.2516(2)	0.024(1)
C(1)	0.1607(2)	0.1063(7)	0.2198(2)	0.030(2)
C(2)	0.2040(2)	−0.0308(7)	0.2935(3)	0.029(2)
C(3)	0.1618(3)	−0.2159(7)	0.2998(3)	0.038(2)
C(4)	0.0780(3)	−0.2530(9)	0.2393(3)	0.047(2)
C(5)	0.0288(2)	−0.1104(8)	0.1682(3)	0.038(2)
C(6)	−0.0607(3)	−0.1409(9)	0.1099(3)	0.050(2)
C(7)	−0.1070(3)	0.002(1)	0.0442(3)	0.047(3)
C(8)	−0.0675(3)	0.182(1)	0.0342(3)	0.045(3)
C(9)	0.0191(3)	0.2200(9)	0.0903(3)	0.039(2)
C(10)	0.0697(2)	0.0737(8)	0.1582(3)	0.031(2)
C(11)	0.2091(2)	0.2558(7)	0.1961(2)	0.027(1)
C(12)	0.3381(2)	0.4418(6)	0.2184(2)	0.025(2)
C(13)	0.3990(3)	0.5637(7)	0.3044(2)	0.030(2)
C(14)	0.3910(2)	0.2919(7)	0.1905(3)	0.035(2)
C(15)	0.2858(3)	0.5918(7)	0.1392(3)	0.033(2)

Results and Discussion

Synthesis. Reactions between the Schiff base ligands (L^1–L^8) and $VO(acac)_2$ have resulted in the formation of mononuclear anionic complexes possessing a VO_2^+ unit, KVO_2L, or dinuclear neutral complexes possessing VO^{3+}, $(VOL)_2$, or a mixed ligand VO^{3+} complex, (VOL^1HQ), depending upon the reaction conditions.

$$H_2L^1 + VO(acac)_2 \xrightarrow{\text{MeOH}} [VOL^1]_2(\mu\text{-O}) \qquad (1)$$

$$H_2L^1 + VO(acac)_2 \xrightarrow[\text{amp}]{\text{MeOH}} [Hamp]^+[VO_2L^1]^- \qquad (2)$$

$$H_2L^1 + VO(acac)_2 + HQ \xrightarrow{\text{MeOH}} \underset{\mathbf{2}}{[VO(L^1)(HQ)]} \qquad (3)$$

$$\underset{(H_nL = H_3L^2,\ H_3L^7,\ H_4L^3,\ H_4L^4)}{H_nL + VO(acac)_2} \xrightarrow[\text{KOH}]{\text{MeOH/EtOH}} \underset{\mathbf{4},\ \mathbf{5},\ \mathbf{12},\ \mathbf{13}}{K^+[VO_2H_{n-1}L]^-} \qquad (4)$$

The ligand H_2L^1 (H_2salamp) when added to $VO(acac)_2$ under neutral conditions gave an asymmetric dimer, $[VOL^1]_2(\mu\text{-O})$ (eq 1).[12b,13] However, in the presence of an excess of the base $(Hamp)^+$, we have isolated and characterized anionic mononuclear *cis*-dioxovanadium(V) complexes of the type $[Hamp]^+[VO_2L]^-$ (eq 2).[13] Also the ligand in the presence of $VO(acac)_2$ and HQ gave a mononuclear monooxovanadium(V) complex, **2** (eq 3). While the complexes $K[VO_2H_{n-1}L]$ were isolated and characterized for H_3L^2 (H_3hnampd), **4**, and H_4L^4 (H_4hntris), **5**, these were formed only in solution in the case of H_4L^3 (H_4-saltris), **13**, and H_3L^7 (H_3salampd), **12**, and hence were detected through absorption studies.

$$\underset{(L^y = L^2,\ L^7,\ L^8)}{H_3L^y + VO(acac)_2} \xrightarrow{\text{MeOH/EtOH}} \underset{\mathbf{3},\ \mathbf{10},\ \mathbf{11}}{[VOL^y]_2} \qquad (5)$$

Though the complexes with different H_3L^y were formed (eq 5) and isolated, those with H_3L^7 (H_3salampd), **10**, and H_3L^8 (H_3-5-Me(salampd)), **11**, were found to be insoluble in common organic solvents, including DMSO or DMF. $(VOL^2)_2$, (H_3-hnampd), **3**, is isolated, characterized, and discussed below.

$$\underset{(L^x = L^3\text{–}L^6)}{H_4L^x + VO(acac)_2} \xrightarrow{\text{MeOH}} \underset{\mathbf{6}\text{–}\mathbf{9}}{[VOHL^x]_2} \qquad (6)$$

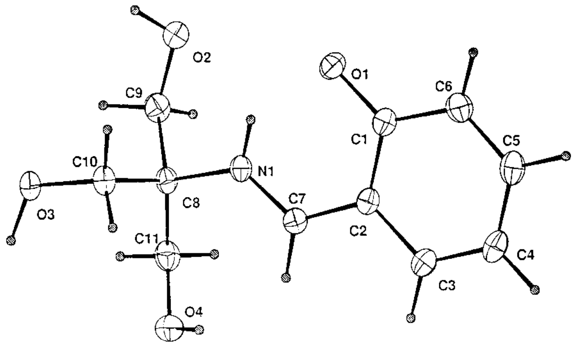

Figure 2. Molecular structure of H_4L^3 showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms.

Table 6. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Istropic Temperature Factors *U*(iso) for **8**

atom	*x*	*y*	*z*	*U*(iso)
V(1)	0.08190(6)	0.06143(7)	0.93077(6)	0.0244(3)
S(1)	−0.2917(1)	−0.0190(1)	0.6592(1)	0.0500(7)
O(1)	0.2394(2)	0.0965(3)	1.0188(3)	0.030(1)
O(2)	−0.0810(2)	0.0367(3)	0.9123(2)	0.025(1)
O(3)	−0.1093(2)	0.0737(3)	1.1207(2)	0.031(1)
O(4)	−0.2488(3)	0.3592(4)	0.9075(4)	0.054(2)
O(5)	0.4730(3)	0.0957(3)	1.0882(3)	0.038(2)
O(6)	0.0609(3)	0.1380(3)	0.8206(3)	0.038(2)
O(7)	−0.3040(4)	0.0899(4)	0.5925(4)	0.060(2)
N(1)	0.0388(3)	0.2014(3)	1.0177(3)	0.023(2)
C(1)	0.2387(4)	0.2606(4)	1.1314(4)	0.028(2)
C(2)	0.2962(4)	0.1762(4)	1.0914(4)	0.028(2)
C(3)	0.4232(4)	0.1768(4)	1.1315(4)	0.029(2)
C(4)	0.4843(4)	0.2602(5)	1.2069(4)	0.040(3)
C(5)	0.4254(4)	0.3439(5)	1.2454(5)	0.042(3)
C(6)	0.3037(4)	0.3447(5)	1.2079(4)	0.039(3)
C(7)	0.1107(4)	0.2656(4)	1.0922(4)	0.030(2)
C(8)	−0.0912(3)	0.2203(4)	0.9877(4)	0.026(2)
C(9)	−0.1494(4)	0.1380(4)	0.8915(4)	0.029(2)
C(10)	−0.1255(4)	0.1892(4)	1.0903(4)	0.030(2)
C(11)	−0.1243(4)	0.3443(5)	0.9513(5)	0.042(3)
C(12)	0.5963(4)	0.1083(5)	1.1052(5)	0.047(3)
C(13)	−0.3969(6)	−0.1123(6)	0.5719(6)	0.070(4)
C(14)	−0.1642(5)	−0.0871(6)	0.6505(5)	0.062(4)

Dinuclear complexes, $[VOHL^x]_2$, **6**−**9**, were isolated and characterized[14] (eq 6) and also their solution and redox behaviors were demonstrated for $L^x = L^3{-}L^6$. Therefore, in this paper we discuss the results of crystal structures of the ligand, and one complex of each type and solution stability and conversion of dioxo to monooxo species in the presence of acid.

Description of the Structure of Saltris, H_4L^3. The ligand assumes an extended configuration where the molecule is involved in two intramolecular (between N−H and O(1) or O(2)) and two intermolecular (between O(3)−H of symmetry related molecules and O(1) and O(2)) H-bond interactions in the lattice, with O···O/N distances in the range 2.608−2.636 Å and O···H−O/N angles in the range 106−179 Å, leaving out O(4)−H free of H-bonding. A striking feature of the ligand structure is the transfer of its phenolic proton to the imine nitrogen. The molecular structure of saltris is given in Figure 2 as an ORTEP diagram. The rather short distances noticed for C(3)−C(4) (1.364 Å) and C(5)−C(6) (1.372 Å) in comparison with the regular aromatic distances is suggestive of a contribution from a quinoid structure too. This is supported by a short distance of 1.30 Å observed for C(1)−O(1). Some important bond lengths and bond angles are given in Table 7. Similar proton transfers from phenolic oxygen to imine nitrogen have been reported in the literature for organotin complexes of picolinic and quinaldic acid.[20] Unlike the present case, the protonation of nitrogen atom effectively blocks the imine nitrogen from being involved in any coordinative interactions in Sn complexes. In the present set of complexes, it is the coordination to vanadium that is preferred over protonation. The dihedral angles C(7)−N(1)−C(8)−C(9/10/11), 105.04, 106.18, and 112.91°, respectively, are indicative of spatially favorable orientation of one of the $-CH_2OH$ groups to form a five-membered chelate ring and/or possible binding of another CH_2OH group to a neighboring metal if the complex is dinuclear, as seen in the structures of complexes **5**, **8**, and **9**.

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for H_4L^3

Bond Lengths (Å)			
O(1)−C(1)	1.300(3)	C(1)−C(6)	1.410(4)
O(2)−C(9)	1.414(3)	C(1)−C(3)	1.413(4)
O(3)−C(10)	1.413(3)	C(2)−C(7)	1.426(4)
O(4)−C(11)	1.419(4)	C(3)−C(4)	1.364(4)
N(1)−C(7)	1.293(3)	C(1)−C(5)	1.387(4)
N(1)−C(8)	1.475(3)	C(5)−C(6)	1.372(4)
C(1)−C(2)	1.414(4)		
Bond Angles (deg)			
C(8)−N(1)−C(7)	127.6(2)	C(3)−C(2)−C(1)	120.4(2)
C(2)−C(1)−O(1)	121.3(2)	C(7)−C(2)−C(1)	121.3(2)
C(6)−C(1)−O(1)	121.8(2)	C(7)−C(2)−C(3)	118.3(2)
C(6)−C(1)−C(2)	116.8(2)		

Description of the Structure of 1. Addition of $NaBH_4$ to the asymmetric dimer reduces one of the Schiff base ligands to form a C−NH moiety followed by breakage of the dimer to give an anionic *cis*-dioxovanadium(V) complex, $[salampr][VO_2L^1]$, **1**, with the reduced Schiff base (salampr) ligand as a counter cation (Figure 3). The geometry at the metal center in **1** can be best fitted to a distorted square pyramid with O(51) at the apex. The average L(axial)−M−L(basal) angle of 105° is only marginally different from the average angle of 102° for a square pyramidal complex (C_{4v}) as explained by Muetterties and Guggenberger.[21] The V atom is displaced from the mean plane passing through the four basal atoms, O(1), O(2), N(1), and O(52), by *ca.* 0.492 Å toward O(51). Important bond lengths and bond angles are given in Table 8.

In the crystal structure of **1**, the anion, $[VO_2L^1]^-$, is interconnected with the cation by three intra- and two intermolecular hydrogen bonds. Of the three intramolecular H-bonds, two are within the cation, $salampr^+$, with N(21) acting as the H-bond donor and phenolic O(21) and alkoxo O(22) acting as acceptors. The third intramolecular H-bond is between O(21)−H of the cation and O(2) of the anion. Both the V=O(51) (1.625 Å) and V=O(52) (1.652 Å) distances are as expected for singly H-bonded ones. Examination of a number of dioxovanadium structures revealed a clearcut difference in the V=O bond lengths of those not involved in H-bonding vs those involved in intermolecular H-bonding. Due to the intervention of a large cation, there are no direct interactions observed between any two VO_2^+ units in the lattice. From the structures of $[Hamp]^+[VO_2L]^-$ (where L is a Schiff base derived from the [1 + 1] condensation of sal or its derivatives and amp) synthesized through a different route, it was observed that while the coordination around the V center is similar to **1**, the cations and anions were involved only in four H-bonds, which resulted in a lattice hydrogen bonded network of spiral or zigzag type, depending upon the substitution on the aromatic ring.[13]

The $V{-}O(2)_{alkoxo}$ bond in **1** is considerably elongated (*ca.* 1.909 Å) as compared to those observed for a variety of monooxovanadium complexes, 1.719−1.819 Å (average ∼1.776

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[20] Khoo, L. E.; Charland, J.-P.; Gabe, E. J.; Smith, F. E. *Inorg. Chim. Acta* **1987**, *128*, 130.

[21] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

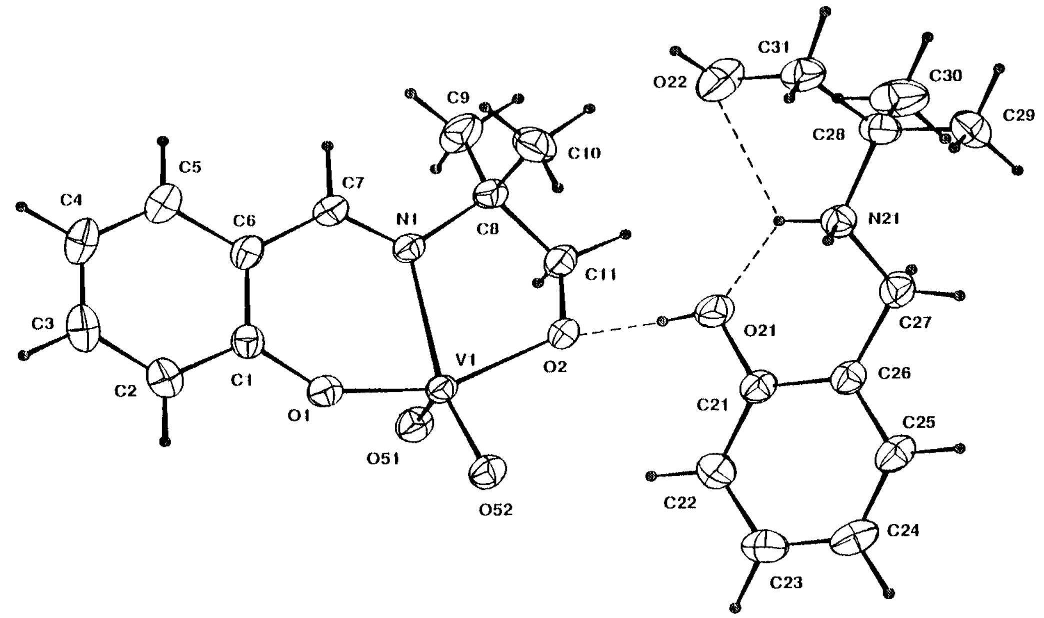

Figure 3. Molecular structure of **1** showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms.

Table 8. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

	Bond Lengths (Å)		
V(1)−O(1)	1.919(1)	V(1)−O(52)	1.652(1)
V(1)−O(2)	1.909(1)	V(1)−N(1)	2.185(1)
V(1)−O(51)	1.625(1)		
	Bond Angles (deg)		
O(2)−V(1)−O(1)	147.22(5)	O(52)−V(1)−O(51)	109.14(6)
O(51)−V(1)−O(1)	105.97(6)	N(1)−V(1)−O(1)	82.01(5)
O(51)−V(1)−O(2)	102.46(6)	N(1)−V(1)−O(2)	76.32(4)
O(52)−V(1)−O(1)	92.39(5)	N(1)−V(1)−O(51)	102.13(5)
O(52)−V(1)−O(2)	93.45(5)	N(1)−V(1)−O(52)	148.54(5)

Å)[22]. However, the same in **1** is comparable to that observed for H-bonded V—O$_{alkoxo}$ distances of dioxo complexes (1.893−1.895 Å). The V—O$_{phen}$ and V—N$_{imine}$ distances in **1**, 1.919 and 2.185 Å, are also longer than those observed for four- or five-coordinated V(V) species and lie close to the six coordinated ones.[12b,13,14,23,25]

Description of the Structure of 2. The structure of **2** shows a neutral VO^{3+} moiety with VN_2O_4 core in a distorted octahedral geometry. The atoms O(1), O(2), O(3), and N(1) define the equitorial plane from which the metal is shifted away toward O(50) by *ca.* 0.294 Å. The Schiff base ligand forms one six-membered and another five-membered chelate ring, while that of HQ^- forms one five-membered planar chelate ring around V, as seen from the ORTEP of **2** in Figure 4. Important bond lengths and bond angles are given in Table 9.

The V═O distance of 1.598 Å is within the range defined for other neutral VO^{3+} complexes of 1.55−1.60 Å.[23] The V—O$_{alkoxo}$ bond is rather long, *ca* 1.823 Å, as compared to the mean V—O$_{alkoxo}$ bond length of 1.776 Å. The V—O$_{phen}$ lengths are in the order salamp^{2-} (1.893 Å) > HQ^- (1.861 Å); corresponding C—O$_{phen}$ lengths (1.314 Å < 1.332 Å) are found in reverse order. This V—O$_{phen}$ bond length in **2** is shorter than that in *cis*-dioxovanadium(V) counterparts (1.921−1.938 Å), but longer than that found in the asymmetric dimer (1.880 Å). A similar trend was observed even with the V—O$_{alkoxo}$ distances (dioxo, 1.895 > **2**, 1.823 > asymmetric dimer, 1.805 Å). The V—O$_{HQ}$ bond length in **2** is longer than the corresponding distance found in VO^{3+}−azo-carboxylate complexes,[10] but their V—O$_{phen}$ distances are comparable. This is explainable on the basis of the weak binding of the carboxylate function to the VO^{3+} center.

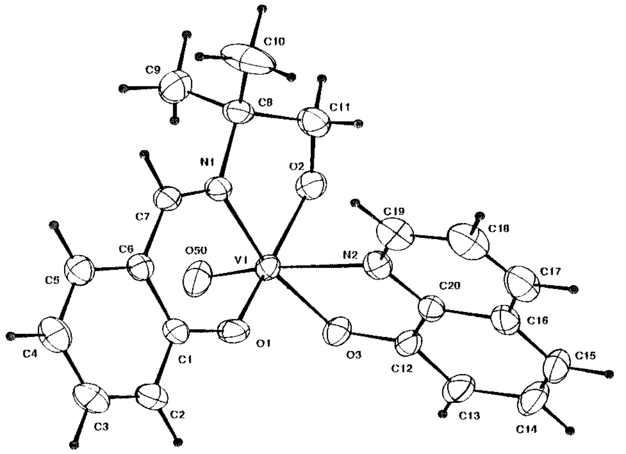

Figure 4. Molecular structure of **2** showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms.

Table 9. Selected Bond Distances (Å) and Bond Angles (deg) for **2**

	Bond Lengths (Å)		
V(1)−O(1)	1.893(1)	V(1)−N(1)	2.121(1)
V(1)−O(2)	1.823(1)	V(1)−N(2)	2.387(2)
V(1)−O(3)	1.861(1)	N(1)−C(7)	1.282(2)
V(1)−O(50)	1.598(2)	N(1)−C(8)	1.502(2)
	Bond Angles (deg)		
O(2)−V(1)−O(1)	155.17(7)	N(1)−V(1)−O(3)	163.18(6)
O(3)−V(1)−O(1)	96.19(6)	N(1)−V(1)−O(50)	98.77(7)
O(3)−V(1)−O(2)	96.96(6)	N(2)−V(1)−O(1)	79.30(6)
O(50)−V(1)−O(1)	98.24(9)	N(2)−V(1)−O(2)	83.59(6)
O(50)−V(1)−O(2)	100.69(8)	N(2)−V(1)−O(3)	75.96(6)
O(50)−V(1)−O(3)	97.91(7)	N(2)−V(1)−O(50)	173.00(7)
N(1)−V(1)−O(1)	83.50(6)	N(2)−V(1)−N(1)	87.50(6)
N(1)−V(1)−O(2)	77.87(6)		

The N(2)$_{HQ}$ atom lies trans to the V═O(50), with a trans angle

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(22) Carrano, C. J.; Mohan, M.; Holmes, S. M.; de la Rosa, R.; Butler, A.; Charnock, J. M.; Garner, C. D. *Inorg. Chem.* **1994**, *33*, 646.

(23) Cornman, C. R.; Colpas, G. J.; Hoeshele, J. D.; Kampf, J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1992**, *114*, 9925.

(24) Bergel, F.; Bray, R. C.; Harrap, K. R. *Nature (London)* **1958**, *181*, 1654.

(25) Root, C. A.; Hoeschele, J. D.; Cornman, C. R.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1993**, *32*, 3855.

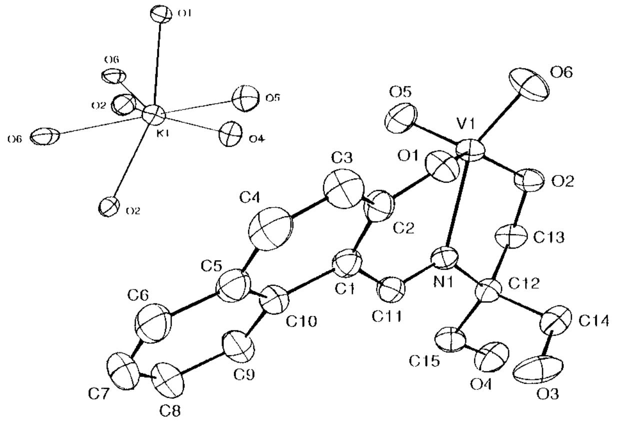

Figure 5. Molecular structure of **5** showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms.

of 173° and with a weak V—N(2) bond of 2.387 Å as generally found in the literature. Yet another possibility of geometry in this case could be the presence of O(HQ$^-$) being trans to V═O. However, in such circumstances this is expected to compete with the O(50) → V π bonding and hence not preferred.

Structurally characterized vanadium complexes containing imine N (HC═N) and C—N are of interest in understanding the mechanism of β-elimination reactions catalyzed by V.[24] Most of the V(V) complexes show the C═N and C—N in the normal range of 1.29–1.30 and 1.47–1.49 Å. To the best of our knowledge, complex **2**, has the longest reported distance of 1.502 Å for the C—N bond.

Description of the Structure of 5. In the $H_2L^4VO_2^-$ anion of complex **5** (Figure 5), the vanadium is present in a distorted square pyramidal geometry of NO_4 core with a shift from basal plane of N(1), O(1), O(6), and O(2) atoms toward O(5). The VO_2 group has a cis configuration with O(5)—V—O(6) angle of 106.5°. The ligand acts as a tridentate one with facial configuration possessing a six-membered chelate ring of phenolate binding and another five-membered ring of alkoxo binding. Thus, the ligand has two free CH_2OH groups which are involved in ion–dipole interactions with the counter cation, K^+, and thereby forming an infinite network in all of the three dimensions of the lattice.

The V—N(1) bond length, 2.163 Å, is in the acceptable range observed for many Schiff base complexes,[23] 2.08–2.17 Å, and the V—O(1) distance, 1.926 Å, deviates marginally from the usual range of 1.83–1.90 Å.[20] The V—O(2) (1.894 Å) and V—O(6) (1.648 Å) lengths are elongated significantly from those reported in the literature[22,23] due to the presence of V—O···K^+ interactions. The V—O(5) distance (1.619 Å) is found to be in the normal range for the cis VO_2 complexes. Important bond lengths and bond angles are given in Table 10.

The potassium ion fulfills its coordination through binding to seven oxygen atoms with a K···O distance range of 2.64–2.95 Å. K^+ is in a coordination sphere formed by O(1) and O(6) from one molecule, O(2) and O(6) from a second molecule, O(2) and O(5) from a third molecule, and O(4) from a fourth molecule forming a pentagonal bipyramidal geometry. All of these four molecules are related by the equivalent points of $P2_1/c$ space group.

Description of Structure of 8. Complex **8** exhibits (Figure 6) a dinuclear monooxovanadium(V) structure having an inversion center. Important bond lengths and bond angles are given in Table 11. Both vanadium atoms are in a distorted octahedral environment of NO_5 core. Out of the three CH_2OH groups, one is free and the other two are bound to the metal center upon deprotonation. Among these two, while one is bound to vanadium through a five-membered chelate and bridged between the two vanadium centers, the other binds to the vanadium that is generated by the inversion symmetry. Each vanadium center also possesses a terminal oxo (V═O), phenolate and alkoxo oxygens, and imine nitrogen in its primary coordination sphere with O(6) and O(2′) being trans and having an angle of 170.2(2)°. Thus, the dinuclear complex, **8**, can be viewed as a dimer of the distorted square pyramidal complex with a weaker ligation from the trans position by O(2′).

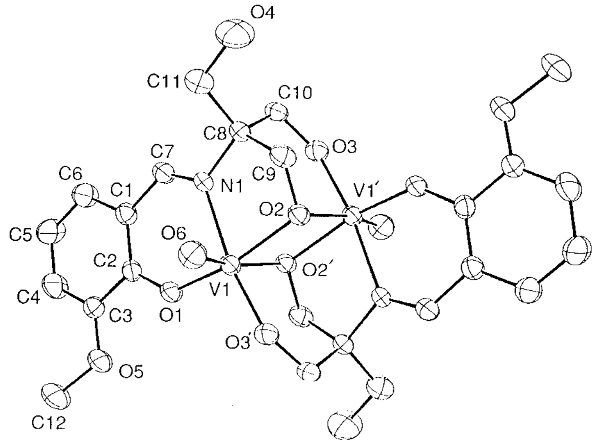

Figure 6. Molecular structure of **8** showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms.

Table 10. Selected Bond Distances (Å) and Bond Angles (deg) for **5**

	Bond Lengths (Å)		
V(1)—O(1)	1.926(3)	K(1)—O(2)	2.808(3)
V(1)—O(2)	1.894(3)	K(1)—O(4)	2.718(4)
V(1)—O(5)	1.619(4)	K(1)—O(1)	2.951(3)
V(1)—N(1)	2.163(3)	K(1)—O(2)	2.724(2)
V(1)—O(6)	1.648(3)	K(1)—O(5)	2.895(3)
		K(1)—O(6)	2.637(3)
		K(1)—O(6)	2.808(4)
	Bond Angles (deg)		
O(1)—V(1)—O(2)	143.0(1)	O(5)—V(1)—O(6)	106.5(2)
O(1)—V(1)—O(6)	93.8(1)	O(1)—V(1)—N(1)	80.9(1)
O(2)—V(1)—O(6)	92.0(1)	N(1)—V(1)—O(2)	76.7(1)
O(1)—V(1)—O(5)	106.7(2)	N(1)—V(1)—O(6)	151.2(2)
O(2)—V(1)—O(5)	106.5(2)	N(1)—V(1)—O(5)	102.2(1)

Table 11. Selected Bond Distances (Å) and Bond Angles (deg) for **8**

	Bond Lengths (Å)		
V(1)—O(1)	1.870(3)	V(1)—O(3)	1.781(3)
V(1)—O(2)	1.907(3)	V(1)—O(6)	1.593(3)
V(1)—O(2′)	2.285(3)	V(1)—N(1)	2.130(4)
	Bond Angle (deg)		
O(1)—V(1)—O(2)	152.3(1)	O(6)—V(1)—O(2′)	170.2(2)
O(1)—V(1)—O(2′)	84.7(1)	O(6)—V(1)—O(3′)	100.2(2)
O(2)—V(1)—O(2′)	73.4(1)	N(1)—V(1)—O(1)	84.5(1)
O(2)—V(1)—O(3′)	97.6(1)	N(1)—V(1)—O(2)	75.9(2)
O(1)—V(1)—O(3′)	97.7(1)	N(1)—V(1)—O(2′)	82.4(1)
O(2′)—V(1)—O(3)	85.7(1)	N(1)—V(1)—O(3′)	167.7(2)
O(6)—V(1)—O(1)	102.2(2)	N(1)—V(1)—O(6)	91.2(2)
O(6)—V(1)—O(2)	97.8(1)	V(1)—O(2)—V(1′)	106.5(2)

The V—O(1)$_{phen}$, V—N(1)$_{imine}$, and terminal oxo V═O(6) bond distances are normal. While the V—O(3′) distance of 1.781(3) Å is common for alkoxide binding,[22] the bridged one has distances of 1.907(3) and 2.285(3) Å with the two vanadium centers, respectively, showing a difference in their binding. Thus, the structure shows a V_2O_2 rhomb. The V···V nonbonded distance in **8** is 3.37 Å, marginally longer than other octahedral dimeric complexes[25] but close to a distorted trigonal bipyramidal one.[26] With comparison of V_2O_2 metric parameters of **8** with several related structures in the literature,[27−33] it is evident that the tris ligand in **8** does not impose any strain on the molecule upon complexation due to its extended configuration. This is consistent with the fact that the dihedral angles of the ligand were not affected considerably upon complexation.

Alkoxides and aryloxides usually form dimeric complexes, except $VO(OCH_3)_3$ which is polymeric.[12,27,28] The V(1)−O(2)−V(1′) angle for **8** (106.5°) is close to that observed for $[VO(cyclo\text{-}C_5H_9O)_3]_2$ [26] (108°), $VO(OCH_2CH_2Cl)_3$ [29] (109°), $[VOCl(OC(CH_3)_2CCH_3)_2O)]_2$ [30] (108.6°), $[VO(acac)OMe]_2$ [31] (105°), $(VO_2HSHED)_2$ [32] (102.4°) [H_2SHED = *N*-salicylidene-*N*′-(2-hydroxethyl)ethylenediamine] and deviate significantly from $[NH_4]_2[V(OC(CH_2CH_3)_2COO)(O)_2]_2$ [33] (71.9°).

The presence of a DMSO molecule in **8** that forms a H-bond with the uncoordinated hydroxyl group seems to be responsible for the solubility of this complex in DMSO and DMF solvents.

Though complex **9** yielded poor quality crystals, a single crystal X-ray analysis was performed,[37] and it was found that the structure is similar to that of **8**, with a dinuclear metal center forming a V_2O_2 rhomb. Substitution on a sal ring is the main differentiating factor of molecules **8** and **9**. While **8** is a 3-OMe derivative, **9** is 5-Br derivative.

Absorption Studies. Pale yellow complex **1** in MeOH showed only bands arising from lmct and intraligand transitions at 360 and 310 nm, respectively, consistent with the dioxovanadium(V) complexes.[13] Complexes **4** and **5** are highly soluble in H_2O, moderately soluble in DMSO, and less soluble in MeOH. Compounds **4** and **5** showed three bands each: ∼385, ∼305, and ∼235 nm in MeOH, H_2O, or DMSO. The first band is attributable to the lmct transition in the high-energy region due to a strong π donation of the oxo groups resulting in a net raising of the d-orbital energy[11] for *cis*-dioxo VO_2^+ complexes. The other two bands are assignable to intraligand transitions. Two absorption bands were observed at 278 and 347 nm for **12** and **13** in MeOH, indicating the formation of KVO_2L.

Monooxovanadium(V) complexes **2** and **3** on the other hand absorb strongly in the visible region, with low-energy bands at 506−520, 368−390, and 318−320 nm. Bands in the region 506−520 nm ($p_\pi \rightarrow d$) are reported for a VO^{3+} bound phenolate or a “bare” V(V) form. Presence of VO^{3+} has been confirmed by the FTIR and X-ray structure of complex **2**. Bands in the region 368−390 nm are attributable to lmct transitions from alkoxide to V(V). This assignment is supported on the basis of the fact that the spectra of VO^{3+} bound to carboxylates and azo and phenolate ligating atoms clearly lack this band.[10] Interestingly, while the haloperoxidase enzyme is proposed to have a VO_2^+−alkoxo binding, its UV absorbance is at 315 nm and not in the 368−390 nm range as seen for various alkoxo bound *cis*-dioxovanadium complexes. Intraligand transitions ($\pi \rightarrow \pi^*$) were observed at 318−320 nm. Phenolate and alkoxo bound monooxovanadium complexes **6**−**9** have shown similar electronic absorption behavior.[14]

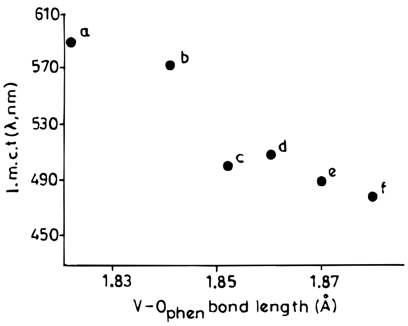

Figure 7. Plot of lmct vs V−O_{phen} bond length (Å) of various complexes: (a) $[HB(Me_2pz)_3VO(p\text{-bromophenoxide})_2]$, from ref 36; (b) [VO(*N*-salicylidene-L-phenylalaninato)(HQ), from ref 10b; (c) [VO-(4-phenylbutane-2,4-dione-α-hydroxybenzylidenehydrazone)(HQ), from ref 10c; (d) complex **2**, present work; (e) complex **8**, present work; (f) $[VO(L^1)]_2(\mu\text{-}O)$, from refs 12b and 13.

A large variation observed in the V−O_{phen} bond lengths (1.82−1.88 Å) in the case of VO^{3+} complexes is indicative of considerable O → V donation in the case of short bonds. This seems to have a bearing on the lmct band. Interestingly, for a number of complexes, a near-linear correlation is seen in the plot of lmct vs V−O_{phen} distances (Figure 7) consistent with the above observations.

Diffuse reflectance spectra of complexes **10** and **11** showed bands at 498, 370 and 504, 379 nm, respectively, indicating the presence of VO^{3+} bound to phenolate and alkoxides. The presence of VO^{3+} has also been supported by FTIR in these complexes.

Fourier Transform IR. The *cis*-dioxo nature of complexes **1**, **4**, and **5** is confirmed by the presence of two V=O bands in the regions 882−905 and 916−925 cm^{-1}. The $\nu_{C=N}$ in **1**−**11** is found around 1630 ± 5 cm^{-1}, indicating V−N binding. FTIR of complex **1** also revealed ν_{NH} of the cation. Complexes **2** and **3** showed $\nu_{V=O}$ at 954 and 961 cm^{-1}, respectively, consistent with six-coordinated vanadium complexes. Complexes **10** and **11** exhibited similar FTIR spectral features as seen for complexes **3** and **6**−**9** with $\nu_{V=O}$ at 950−955 cm^{-1}. No free ν_{OH} bands were seen in complexes **10** and **11**, indicating the involvement of both alkoxy groups in binding to the metal center through deprotonation resulting in a six-coordinated one. Variations in the frequencies of $\nu_{V=O}$, due to the changes in their interactions, are linearly related to their distances, as shown in Figure 8.

NMR Studies. The alkoxy binding is delineated both from the ^1H and ^{13}C NMR shifts in **1** and **2** as observed earlier.[13] While the ^1H and ^{13}C NMR of **3** are characteristic of both CH_2O^- groups bound to the metal, **6**−**9** showed the presence of one free CH_2OH group and two bound CH_2O^- groups.[14a] While *cis*-dioxovanadium(V) complexes **4** and **5** possess one bound CH_2O^- group, the former has only one free CH_2OH and the latter has two CH_2OH groups.

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(26) Hillerns, F.; Olbrich, F.; Behrens, U.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 447.

(27) Caughlan, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966**, *12*, 2131.

(28) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 378.

(29) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013.

(30) Crans, D. C.; Felty, R. A.; Miller, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 265.

(31) Musiani, M. M.; Milani, F.; Graziani, R.; Vidali, M.; Casellato, U.; Vigato, P. A. *Inorg. Chim. Acta* **1982**, *61*, 115.

(32) Li, X.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1988**, *27*, 4657.

(33) Hambley, T. W.; Judd, R. J.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 343.

(34) Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1994**, *33*, 4669.

(35) Asgedom, G.; Sreedhara, A.; Kivikoski, J.; Rao, C. P. *Polyhedron*, in press.

(36) Holmes, S.; Carrano, C. J. *Inorg. Chem.* **1990**, *30*, 1231.

(37) Crystal data for **9**: $C_{24}H_{28}Br_2N_2O_{11}SV_2$, triclinic, space group $P\bar{1}$; a = 10.766(2), b = 11.135(1), c = 15.185(3) Å; α = 84.88(1), β = 75.43(2), γ = 80.31(1)°; V = 1734.7(5) $Å^3$; Z = 2; D_c = 1.56 g cm^{-3}. The structure was solved by SHELXS 86 and refined by CRYSTALS using direct methods to give final R = 0.086 and R_w = 0.109. Among the 7575 measured reflections, 3502 [$I > 3.0\sigma(I)$] were used in refining 415 parameters. A residual electron density of 3.873 e $Å^{-3}$ near S was observed in the final Fourier difference map. Selected bond lengths (Å) and angles (deg) are as follows: V−O(1) = 1.87(1); V−O-(2A) = 1.911(9); V−O(2B) = 2.27(1); V−O(3) = 1.784(9); V−O-(6) = 1.60(1); V−N(1) = 2.14(1); O(1)−V−O(2) = 152.7(5); O(1)−V−O(3) = 96.3(4); O(1)−V−O(6) = 101.9(6); O(1)−V−N(1) = 85.4(4); O(2)−V−O(6) = 170.6(5); N(1)−V−O(3) = 169.0(4); O(6)−V−N(1) = 89.7(5); O(3)−V−O(6) = 100.8(5).

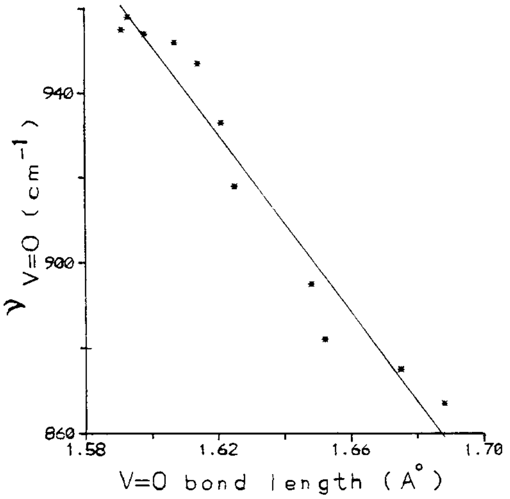


Figure 8. Plot of $\nu_{V=O}$ (cm^{-1}) vs V=O bond length (Å) for complexes reported in ref 13 and the present work.

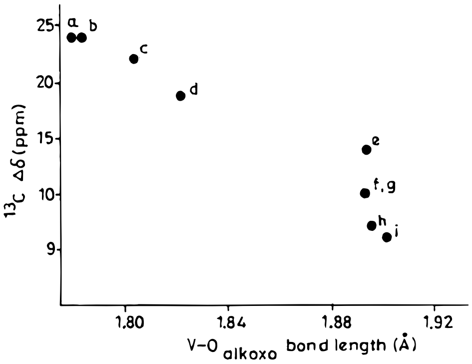


Figure 9. Plot of ^{13}C $\Delta\delta$ (ppm) vs V—O$_{alkoxo}$ bond length (Å) of the following complexes: (a) **8**; (b) **9**; (c) $[VO(L^1)]_2(\mu\text{-}O)$; (d) **2**; (e) **5**; (f−h) from ref 13; (i) **1**.

A plot of $^{13}C_{(alkoxo)}$ $\Delta\delta$ (ppm) ($\Delta\delta = \delta_{complex} - \delta_{ligand}$ (ppm)) vs the V—O$_{(alkoxo)}$ bond length of a number of V(V) complexes (Figure 9) exhibits a fairly linear trend. Interestingly, the V—O$_{alkoxo}$ bond distances indicated that the *cis*-dioxovanadium complexes exhibited longer V—O$_{alkoxo}$ bonds and hence shorter ^{13}C $\Delta\delta$, than the monooxo complexes. This is expected because V—O$_{alkoxo}$ bonds in the dioxo complexes would have to compete with two oxo → metal π bonds. Thus, the presence of an alkoxo bound *cis*-dioxovanadium (VO_2^+) moiety with a V—O$_{alkoxo}$ distance of 1.72 Å in haloperoxidase seems unlikely.

The ^{51}V NMR of **1** and **3**−**5** in DMSO showed a single peak at −533.4, −531.3, −528.5, and −529.4 ppm with respect to $VOCl_3$, respectively. The values are close to the dioxovanadium(V) complexes of similar type and also that of a vanadium−transferrin complex.[7] Complexes **6**−**9** showed only one sharp resonance in the range −536 to −545 ppm in DMSO solution, even over a period of 1 week, indicating the stability of the complexes. The literature reports include monooxovanadium(V) mononuclear complexes (∼−480 ppm)[34] and dioxovanadium(V) complexes (∼−540 ppm), but not the alkoxo bound monooxovanadium(V) dinuclear complexes.

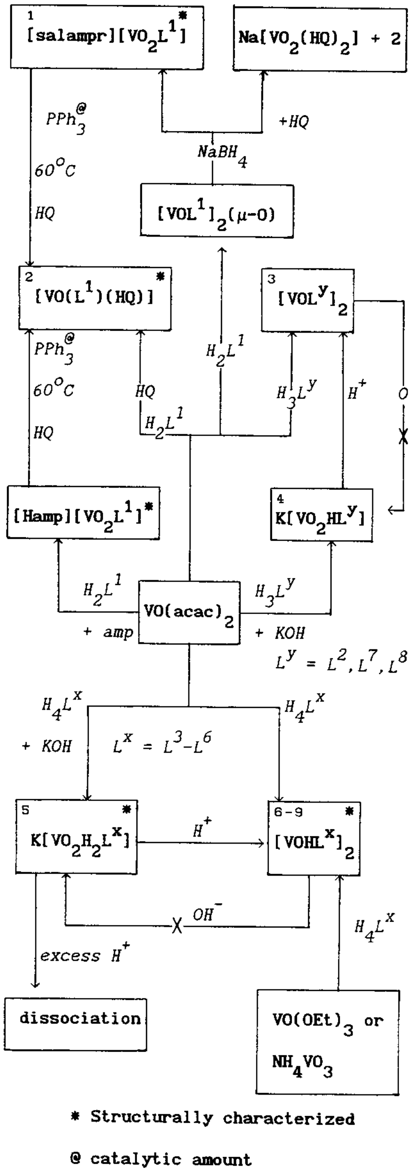
Cyclic Voltammetric Studies. Cyclic voltammetry of alkoxo bound V(V) complexes **1**−**9** were examined in the potential range of −1.5 to +1.0 V in MeOH or DMF at a scan speed of 100 mV/s at the Pt working electrode and Ag/AgCl reference electrode. All of the complexes showed reversible electrochemical behavior for the V(V)/V(IV) couple (ΔE = 70 mV; $i_p^a/i_p^c \sim 1$), and data are listed in Table 12.

Table 12. Cyclic Voltammetry Data for Complexes **1**−**9** in DMF

complex	$E_{1/2}$ (mV) wrt Ag−AgCl	complex	$E_{1/2}$ (mV) wrt Ag−AgCl
1	−68[a]	**6**	−416
2	−93[a]	**7**	−410
3	−410	**8**	−419
4	−128	**9**	−299
5	−133		

[a] In MeOH

Scheme 1



We have been able to synthesize and characterize various V(V) complexes where the V(V)/V(IV) potentials varied over a range of 1.1 V, corresponding to an energy difference of ∼106 kJ/mol. While the carboxylate bound VO species have the V(V)/V(IV) couples at more anodic potentials (∼+660 mV), the alkoxo bound ones have exhibited cathodic potentials (∼−440 mV). This indicates that the alkoxo groups favor V(V) centers more than the carboxylate counterparts. This fact has also been supported on the basis of the chemical reduction studies of **6**−**9**.[14] We have recently isolated V(IV) complexes of carboxylate containing Schiff bases.[35] Among the alkoxo bound V(V) complexes, the dioxo ones are more easily reducible than the corresponding monooxo complexes. It was observed that as the number of alkoxy groups increases, the V(V)/V(IV) potential increases toward negative potentials.

Solution Stability Studies. The solution stability of complex

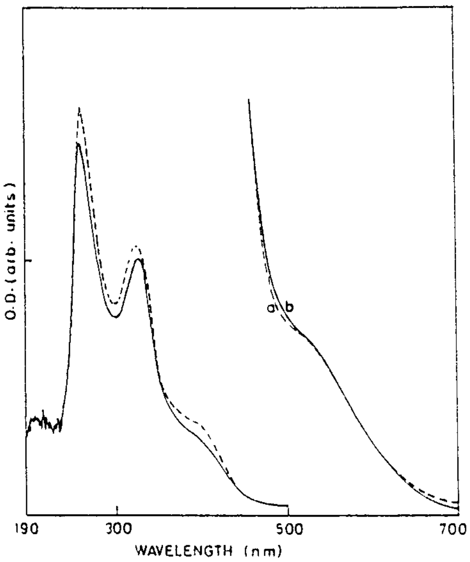


Figure 10. (a) UV−vis absorption spectra of complex **7** in DMF; (b) complex **5** after addition of 0.25 equiv of HCl in DMF.

2 in MeOH, DMSO, and DMF was checked using absorption spectra and ^{51}V NMR, in the presence and absence of added water (4:1 solvent:water), and no observable decay was found over a period of 1 week.

The stability of complex **4** or **5** in various solvent systems is in the order MeOH < H_2O < DMSO, based on absorption spectral studies. Though the Schiff base complex is expected to hydrolyze in water, the insoluble nature of the ligand in water could be responsible for pushing the equilibrium toward the complex stability as compared to MeOH where the ligand exchange is fast. Complexes **6**−**9** were found to be stable in DMSO or DMF solvents for over a period of 1 week.[13] The instability of **4** and **5** in MeOH was also shown by cyclic voltammetry.

Reactivity of Alkoxo Bound V(V) Complexes. As shown in Scheme 1, *cis*-dioxovanadium(V) complex **1** or [Hamp]-[VO_2L^1] reacts with HQ in MeOH at 60 °C in the presence of catalytic amount of PPh_3 to yield complex **2**. Simultaneous addition of $NaBH_4$ and HQ to the asymmetric dimer, $[VOL^1]_2$-(μ-O), yielded two complexes, i.e., **2** in 8% yield and another complex, Na[$VO_2(HQ)_2$], in 60% yield. Compound **2** in the presence of 1 equiv of $NaBH_4$ and HQ also gave the complex Na[$VO_2(HQ)_2$].[16]

Conversion of Dioxovanadium Complexes 4 and 5 into Corresponding Monooxovanadium Complexes. The pale yellow complex **5** changes very slowly into red-brown solution in DMSO and DMF. The rate of conversion becomes faster with addition of HCl solution. The effect of HCl solution was studied at 1:0.1, 1:0.25, 1:0.5, 1:1, and 1:2 complex to acid mole ratios. While addition of 1:0.1 mole ratio resulted in slow rate of conversion, 1:0.25 was found to be the optimal concentration for the immediate formation of the red-brown solution. The absorption spectrum of the red-brown solution in the case of **5** is similar to that of the monooxovanadium complex, **7**, in which two of the alkoxo groups are bound (Figure 10). The final spectrum observed with **4** upon the addition of 0.25 equiv of acid was comparable with that of **3**. Cyclic voltammograms of **4** and **5**, in DMSO or DMF in the presence of acid, are identical with those of **3** and **7**, respectively, in the same solvent without the acid. The conversion is shown through an equation,

$$[VO_2H_2L^5]^- \rightleftarrows [VO(OH)HL^5]^- \xrightarrow{H^+} VOHL^5 + H_2O$$

Addition of acid in the ratios of 1:1 and 1:2 resulted in dissociation, but no reduction to V(IV) was observed, as confirmed by EPR.

Conclusions

Dioxovanadium(V) complexes are gaining importance in the literature as biomimetics. Though the existence of *cis*-dioxovanadium(V) species in acidic medium is well-documented, to our knowledge the compounds reported here are the first examples where the synthesis of alkoxo bound *cis*-dioxovanadium(V) was performed from alkaline conditions and the products were isolated. Their conversion to monooxovanadium(V) was also shown in the presence of catalytic amounts of acid. Schiff base complexes of vanadium which are stable in aqueous solutions are relatively rare. Chemical modification of the Schiff base by $NaBH_4$ reduction was performed by Pecoraro and coworkers[34] to obtain vanadium(V) complexes stable in 1:4 water: DMF solvent systems. In this context the present studies are interesting.

On the basis of the present study it can be suggested that a VO_2^+−alkoxo moiety in the enzyme haloperoxidase with a bond length of 1.72 Å is rather unlikely; however, the presence of a VO_2^+ moiety along with a V−OH unit, with the distances similar to that observed in the EXAFS studies of the enzyme, cannot be ruled out. We had recently reported that hydrogen bonded V═O bonds can exhibit longer bond lengths which are close to those observed from the EXAFS of the enzyme.[13] These points are also supported by the recent X-ray determination of the azide modified haloperoxidase, which revealed a direct binding of the azide moiety to the metal center but no vanadium−alkoxo bond. Since VO^{3+} bound to phenolates exhibit lmct transitions in the visible region, such species have been ruled out as possible structural mimics for haloperoxidases.

H_3L^2 and H_4L^3−H_4L^6 are potential tetra- and pentadentate ligands, respectively. So far we have been successful in the synthesis of a large variety of alkoxo-bound oxovanadium(V) complexes using Schiff base ligands to result in dinuclear and mononuclear VO^{3+} and mononuclear VO_2^+ complexes and have demonstrated their interconversions, as shown in Scheme 1. It is noted that under neutral conditions, the VO^{3+} moiety is the favored product in which the ligands act as tetradentate where two of the CH_2OH groups are bound. In basic conditions, VO_2^+ is the favored product and these ligands act as tridentate, where only one CH_2OH is deprotonated and bound. The formation and stability of VO_2^+ or VO^{3+} are dictated by its ligating environment. While the addition of small amounts of acid converts VO_2^+ to VO^{3+}, the reverse does not happen in the presence of base.

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Supporting Information Available: Complete listings of structural data comprising atomic coordinates, thermal parameters, bond lengths, bond angles, and anisotropic displacement parameters and figures showing ORTEP diagrams of complexes **1**, **2**, **5**, **8**, and **9** and H_4L^3 (28 pages). Ordering information is given on any current masthead page.

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