© 2000 The Chemical Society of Japan

A Family of Dinuclear Vanadium(V) Complexes Containing the $\{OV(\mu\text{-}O)VO\}^{4+}$ Core: Syntheses, Structures, and Properties

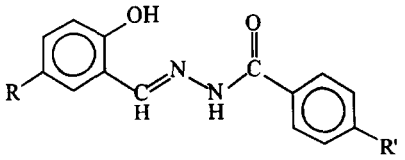
Nimma Rajaiah Sangeetha, and Samudranil Pal*

School of Chemistry, University of Hyderabad, Hyderabad 500046, India

(Received July 5, 1999)

Dark-brown complexes of $\{OV(\mu\text{-}O)VO\}^{4+}$ with the general formula $[(VOL)_2O]$ were isolated from reactions of bis(acetylacetonato)oxovanadium(IV) and aroylhydrazones of salicylaldehyde or of 5-methoxysalicylaldehyde (H_2L, two H stand for the dissociable protons at the phenol and the amide functionalities) in acetonitrile. The infrared spectra of these complexes are consistent with the dianionic form of the ligands. The electronic spectral profiles are very similar and display strong absorptions in the range 425—263 nm due to ligand-to-metal charge transfer and intraligand transitions. The proton NMR spectra suggest that in solution the two ligands in each complex are magnetically equivalent. The complexes are redox active and display a reduction response in the potential range −0.28—0.47 V (vs. Ag/AgCl). The molecular structures of the complexes were determined by X-ray crystallography. The deprotonated dianionic planar ligands coordinate the metal ions through the phenolate-O, the imine-N, and the amide-O atoms forming a six-membered and a five-membered chelate ring. The metal ions in each complex are essentially in a square-pyramidal O_4N coordination sphere. The O, N, O-donor ligand and the bridging oxygen atom constitute the square plane and the oxo group occupies the apical position. The metal center is displaced from the basal plane towards the apical oxo group by 0.44—0.57 Å. The V–O–V bridge angles in the complexes are very similar and within the range 112.86(13) to 115.89(12)°.

Studies on the coordination chemistry of oxovanadium(V) have increased considerably in recent years.[1—3] The interest in such species stems from the role played by the oxovanadium(V) moiety in several biological processes, such as haloperoxidation,[4] phosphorylation,[5] glycogen metabolism,[6] and insulin mimicking.[7] It is believed that in some haloperoxidases the oxovanadium(V) is in non-porphyrinic O, N environments.[8] Herein we report on a series of complexes containing the $\{OV^V(\mu\text{-}O)V^VO\}^{4+}$ unit with aroylhydrazones of *ortho*-hydroxy aldehydes (H_2L, **I**) (Chart 1). These hydrazones provide a phenolic-OH, an imine-N, and an amide-O as coordinating centers. It is well known that the phenolate-O and deprotonated amide functionality are very efficient in stabilising high oxidation states of first transition series metals.[9] The dianionic planar ligands can bind a metal ion via the phenolate-O, the imine-N, and the deprotonated amide-O centers. Very few structurally characterised complexes of the $\{OV^V(\mu\text{-}O)V^VO\}^{4+}$ cation are known.[3] The syntheses, molecular structures and physical properties of four complexes having the general formula $[(VOL)_2(\mu\text{-}O)]$ are described.



(I)

H_2bhsH (R = H, R' = H)
H_2ahsH (R = H, R' = OMe)
H_2bhsOMe (R = OMe, R' = H)
H_2ahsOMe (R = OMe, R' = OMe)

Chart 1.

Experimental

Materials. The hydrazones were prepared in 80—90% yield by the condensation of benzhydrazide or 4-methoxybenzhydrazide with the corresponding aldehyde in methanol by following similar methods reported earlier.[10] Bis(acetylacetonato)oxovanadium(IV) was obtained by following a reported procedure.[11] All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

Physical Measurements. Microanalytical data (C, H, N) were obtained with a Perkin–Elmer model 240C elemental analyser. Infrared spectra were recorded for KBr pellets of the complexes by using a JASCO-5300 FT-IR spectrophotometer. A JASCO-7800 UV/vis spectrophotometer was used to obtain the electronic spectra. The ^{1}H NMR spectra of the complexes in solutions were recorded on a Bruker 200 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. A JEOL FE-3X spectrometer was used to perform the EPR experiments. The magnetic susceptibilities were measured

by using a CAHN magnetic-susceptibility system consisting of a model 4600 adjustable-gap electromagnet and a model 1000 electrobalance. Electrical-conductivity measurements were performed by using a Digisun conductivity meter (model DI-909). A Cypress (model CS-1090/CS-1087) electroanalytical system was used for cyclic voltammetric experiments with methanol solutions of the complexes containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Three-electrode measurements were carried out at 298 K under a dinitrogen atmosphere with a platinum-disk working electrode, a platinum-wire auxiliary electrode and an Ag–AgCl reference electrode. The potentials reported in this work are uncorrected for junction contributions.

Preparation of Complexes. [{VO(bhsH)}$_2$O] (1). To an acetonitrile (15 cm^3) solution of [VO(acac)$_2$] (100 mg, 0.38 mmol) was added a 15 cm^3 acetonitrile solution of H_2bhsH, salicylaldehyde benzoylhydrazone (92 mg, 0.38 mmol); and the mixture was heated on a water bath for 20—30 min. The dark-brown solution was allowed to slowly evaporate in air at room temperature. The separated dark crystalline solid was collected by filtration and dried under vaccum over anhydrous $CaCl_2$. The yield was 96 mg (40%). Found: C, 53.68; H, 3.06; N, 9.12%. Calcd for $V_2C_{28}H_{20}N_4O_7$: C, 53.69; H, 3.22; N, 8.94%. The selected IR bands[12] 1595(s), 1553(s), 1523(m), 1472(m), 1443(s), 1379(m), 1341(s), 1271(s), 1223(m), 1134(w), 995(s), 899(s), 821(m), 787(m), 754(s), 700(s), 679(s), 633(s), 588(m), 486(m), 451(s) cm^{-1}.

The analytical data and the selected IR bands[12] for other complexes prepared similarly are as follows:

[{VO(ahsH)}$_2$O] (salicylaldehyde 4-methoxybenzoylhydrazone, H_2ahsH) (**2**). Found: C, 52.21; H, 3.48; N, 8.42%. Calcd for $V_2C_{30}H_{24}N_4O_9$: C, 52.49; H, 3.52; N, 8.16%. IR bands 1607(s), 1553(m), 1505(m), 1470(m), 1443(m), 1418(m), 1383(m), 1343(m), 1256(s), 1167(s), 995(s), 903(m), 837(m), 746(s), 685(s), 613(m), 561(w), 517(w), 469(s), 426(w) cm^{-1}.

[{VO(bhsOMe)}$_2$O] (5-methoxysalicylaldehyde benzoylhydrazone, H_2bhsOMe) (**3**). Found: C, 52.07; H, 3.70; N, 8.17%. Calcd for $V_2C_{30}H_{24}N_4O_9$: C, 52.49; H, 3.52; N, 8.16%. IR bands 1593(s), 1555(s), 1493(w), 1474(m), 1329(m), 1271(s), 1236(m), 1194(w), 1161(m), 1028(m), 997(s), 910(w), 845(s), 783(s), 714(s), 679(s), 584(s), 476(w), 440(m) cm^{-1}.

[{VO(ahsOMe)}$_2$O] (5-methoxysalicylaldehyde 4-methoxybenzoylhydrazone, H_2ahsOMe) (**4**). Found: C, 51.16; H, 3.89; N, 7.52%. Calcd for $V_2C_{32}H_{28}N_4O_{11}$: C, 51.49; H, 3.78; N, 7.50%. IR bands 1605(s), 1555(s), 1493(m), 1474(m), 1416(m), 1370(m), 1344(m), 1325(m), 1256(s), 1238(s), 1198(w), 1169(s), 1028(m), 991(s), 910(w), 833(s), 748(w), 700(s), 629(s), 582(m), 473(m), 426(m) cm^{-1}.

X-Ray Structure Determination. Single crystals of [{VO(ahsH)}$_2$O] (**2**) and of [{VO(bhsOMe)}$_2$O] (**3**) were obtained by the diffusion of *n*-hexane into chloroform solutions of the complexes. For [{VO(bhsH)}$_2$O] (**1**) the diffusion of *n*-hexane into a dichloromethane solution of the complex afforded X-ray quality single crystals. Slow evaporation of a methanol–xylene (1 : 1) solution of [{VO(ahsOMe)}$_2$O] (**4**) provided single crystals suitable for a structure determination. In each case, the crystal was mounted at the end of a glass fibre and the data were collected on an Enraf–Nonius Mach-3 single crystal diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) by the ω-scan method at 293 K. The unit cell parameters were determined by a least-squares fit of 25 reflections having 2θ values in the range 18—26°. The stability of the crystal was monitored by measuring the intensities of three check reflections after every 1.5 h during the data collection. None of the crystals displayed any decay during the data collection. The data were corrected for Lorentz-polarization effects. No absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 and Fourier techniques. In each case, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at the calculated positions by using the riding model for the structure factor calculation, but not refined. The calculations were performed using programs of Xtal software[13] for data reduction, and SHELX-97 programs[14] for structure solution and refinement. The ORTEX6a package[15] was used for molecular graphics. Significant crystal data for all of the complexes are summarised in Table 1.

Tables of the crystal data and a structure-determination summary, atomic positional parameters, intramolecular bond distances and angles, anisotropic thermal parameters, hydrogen atom positional parameters and the observed and calculated structure factors for **1**, **2**, **3**, and **4** are deposited as Document No. 73004 at the Office of the Editor of Bull. Chem. Soc. Jpn. and crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC136576-136579.

Results and Discussion

Synthesis and Some Properties. The hydrazones were synthesised from aroylhydrazines and *ortho*-hydroxy aldehydes. Each Schiff base has two dissociable protons at the phenolic-OH and the amide functionalities. Few vanadium(V) complexes containing the oxovanadium alkoxide motif, $\{V^VO(OR)\}$, using this class of ligands have been reported.[2,3c] Preparations of those complexes were carried out using alcohol as the solvent. In this work we used acetonitrile as the solvent instead of alcohol, and obtained the present series of dinuclear oxo bridged VO^{3+} complexes. The reaction of one equivalent of [VO(acac)$_2$] with one equivalent of the Schiff base produces the complexes in moderate yields. During the formation of the complexes, aerial oxygen acts as the oxidising agent in the oxidation of V(IV) to V(V). The elemental analyses of the complexes are satisfactory with the empirical formula, [(VOL)$_2$O], where L^{2-} = bhsH^{2-}, ahsH^{2-}, bhsOMe^{2-}, ahsOMe^{2-}. The +5 oxidation state of the metal centre in each complex is confirmed by the diamagnetic nature and EPR silence. In solutions, the complexes are electrically non-conducting.

Spectral Characteristics. The infrared spectra of the complexes do not display any stretch at ca. 3300 cm^{-1} (OH), at ca. 3100 cm^{-1} (NH) and at ca. 1675 cm^{-1} (C=O).[16] A strong peak with a shoulder observed at ca. 1600 cm^{-1} for each complex is possibly due to the conjugate C=N–N=C moiety of the coordinated ligands.[17] Thus, in the complexes the amide functionalities of the ligands exist in the enolate form and acts as a dibasic phenolate-O, imine-N, and deprotonated amide-O donor. The molecular structures of the complexes (see below) are in accordance with this type of coordination. Two medium-to-strong bands observed at ca. 1550 and ca. 1470 cm^{-1} are most likely to be due to the C=C stretches form the aromatic portions of the ligands.[18] The V=O stretch in complexes containing the VO^{3+} unit is reported to be in the range 970—1000 cm^{-1}.[1–3] Each of the

Table 1. Crystallographic Data for [{VO(bhsH)}$_2$O] (**1**), [{VO(ahsH)}$_2$O] (**2**), [{VO(bhsOMe)}$_2$O] (**3**), and [{VO(ahsOMe)}$_2$O] (**4**)

Complex	**1**	**2**	**3**	**4**
Chem. formula	$V_2C_{28}H_{20}N_4O_7$	$V_2C_{30}H_{24}N_4O_9$	$V_2C_{30}H_{24}N_4O_9$	$V_2C_{32}H_{28}N_4O_{11}$
Formula weight	626.36	686.41	686.41	746.46
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	*Pnc*2	*C*2/*c*	*Pbca*	$P\bar{1}$
a/Å	7.5951(19)	10.5625(18)	14.859(2)	10.964(2)
b/Å	14.564(3)	16.822(3)	19.742(2)	11.7346(16)
c/Å	11.859(2)	16.971(3)	19.827(2)	13.704(3)
α/deg	90	90	90	99.082(14)
β/deg	90	102.424(16)	90	102.621(15)
γ/deg	90	90	90	105.982(15)
V/Å^3	1311.8(5)	2944.9(9)	5816.2(13)	1608.8(5)
Z	2	4	8	2
D_{calcd}/g cm^{-3}	1.586	1.548	1.568	1.541
μ/mm^{-1}	0.768	0.697	0.706	0.649
Data collected	2010	2824	9232	5641
Unique data	2002	2587	8457	5641
Obsd data[a)]	1714	2005	4107	3601
Parameters	186	205	408	446
*R*1[a,b)]	0.0300	0.0333	0.0465	0.0421
*wR*2[c)]	0.0743	0.0898	0.1019	0.0996
Goodness-of-fit[d)]	1.065	1.036	1.015	1.036
Largest peak/ e Å^{-3}	0.273	0.334	0.339	0.466

a) $I > 2\sigma(I)$. b) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. c) $wR2 = \{\Sigma[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. d) Goodness-of-fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of parameters refined; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. The values of a and b are 0.0476 and 0.0954, 0.0532 and 2.3127, 0.0511 and 2.9362, and 0.0594 and 0.8245 for **1**, **2**, **3**, and **4**, respectively.

present series of complexes display a strong band at ca. 995 cm^{-1}.

The electronic spectral profiles of the complexes are almost identical. This suggests a similar gross structure for the complexes in solutions. The spectra display a shoulder in the range 425—392 nm followed by two strong absorptions in the ranges 343—313 nm and 295—263 nm (Table 2). As expected, no d–d band is observed in the visible region. The origin of the observed transitions is most probably ligand-to-metal charge transfer and intraligand transitions.

Proton NMR spectral data of the complexes are listed in Table 2. The spectra clearly indicate that in solutions the coordinated ligands in each complex are magnetically equivalent. The aromatic protons appear in the range 6.55—8.20 ppm. The spectra do not display the signals corresponding to the –NH– and OH protons. The absence of these signals conforms with deprotonation of the amide and phenol functionalities in the complexes. The protons of the methoxy substituent on the salicylaldimine moiety are observed at ca. 3.9 ppm, whereas the protons of the methoxy substituent on the aroyl fragment are observed at ca. 3.8 ppm. Signals corresponding to the =CH– proton appear in the range 8.49—8.70 ppm.

Redox Properties. The cyclic voltammetry of the complexes was studied in dichloromethane–acetonitrile or methanol solutions. The complexes display a quasi-reversible V(V)-to-V(IV) reduction in the potential range −0.28—0.47 V versus the Ag/AgCl reference electrode (Table 2). The one-electron stoichiometry of these electrode processes was validated by comparing the current heights with known one electron redox processes under identical conditions.[19] The trend in the $E_{1/2}$ values reflects the effect of substituents on the ligands. The V–O bonds in the present series of complexes are essentially σ in character, and the bond strength increases as the oxygen atom becomes a better donor. The V(V)-to-V(IV) reduction potentials decrease with an increase in these bond strengths. An electron-releasing methoxy group at the *para* position of the phenolate-O or of the aroyl moiety should make the corresponding coordinating oxygen atom a better donor than those of the ligands without the methoxy group. As expected, the potential (0.47 V) measured in CH_2Cl_2–CH_3CN (1 : 5) for complex (**1**) of the unsubstituted bhsH^{2-} is the highest. In each of the two complexes, [{VO(ahsH)}$_2$O] (**2**) and [{VO(bhsOMe)}$_2$O] (**3**), the ligand contains one methoxy group. The potentials of [{VO(bhsOMe)}$_2$O] and [{VO(ahsH)}$_2$O] measured in the same solvent mixture as in **1** are 0.42 and 0.44 V, respectively. These values are lower than that observed for **1**. The reduction potential of [{VO(ahsOMe)}$_2$O] (**4**) is expected to be the lowest because of the two methoxy groups present in ahsOMe^{2-}. Due to the solubility problem, we could not measure the potential of **4** in CH_2Cl_2–CH_3CN (1 : 5). The potential (−0.28 V) observed in methanol is very low compared to those of the other three complexes. The redox potentials are known to be influenced by the nature of the solvent used.[20] It has been observed that the metal-centerd reduction potential decreases with a decrease in the dielectric constant[20b] and the coordinating ability[20c] of the solvent.

Table 2. Electronic Spectral,[a] ^{1}H NMR,[b] and Cyclic Voltammetric[c,d,e] Data

Complex	λ_{max} (ε)/nm ($M^{-1}\,cm^{-1}$)	δ	$E_{1/2}$ (ΔE_p)/V (mV)
1	392 (15100), 313 (43600), 263 (86900)	8.49(s), 6.98—8.10(m)	0.47 (60)
2	395 (16600), 319 (43500), 295 (47700)	8.50(s), 6.55—8.05(m), 3.75(s)	0.42 (80)
3	415 (8700), 333 (32800), 284 (47900)	8.51(s), 6.98—8.20(m), 3.90(s)	0.44 (60)
4	425 (5400), 343 (26100), 293 (33300)	8.70(s), 6.90—8.07(m), 3.86(s), 3.82(s)	−0.28 (100)

a) In dichloromethane solutions. b) Symbols: s, singlet; m, multiplet; **4** in CD_3OD solution and the rest in $CDCl_3$ solutions. c) **1**, **2**, and **3** in CH_2Cl_2–CH_3CN (1 : 5) solutions and **4** in CH_3OH solution. d) Supporting electrolyte is tetrabutylammonium perchlorate (0.1 M); working electrode is platinum; reference electrode is Ag–AgCl. e) $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; peak to peak separation $\Delta E_p = E_{pa} - E_{pc}$.

Methanol is expected to be better at coordinating than acetonitrile to pentavalent vanadium. Thus, in addition to the presence of two electron-releasing methoxy groups, probably, the nature of the solvent also contributes in the lowering of the potential of **4**.

Description of Structures. The molecular structures of the complexes described in this work are depicted in Figs. 1, 2, 3, and 4. Selected intramolecular bond distances and angles are presented in Tables 3, 4, 5, and 6. In each complex the metal ions are in NO_4 coordination spheres. The geometry around the metal centre is distorted square-pyramidal. The N–N, N–C, and C–O distances observed in the =N–N=C(O$^-$)– fragments of the ligands are within 1.388(4)—1.400(3), 1.295(3)—1.300(4), and 1.315(3)—1.326(4) Å, respectively. These distances are consistent with the enolate form of the amide functionalities in the complexes.[2,3c,21] The dianionic planar ligands bind the metal ions through the phenolate-O, imine-N, and de-

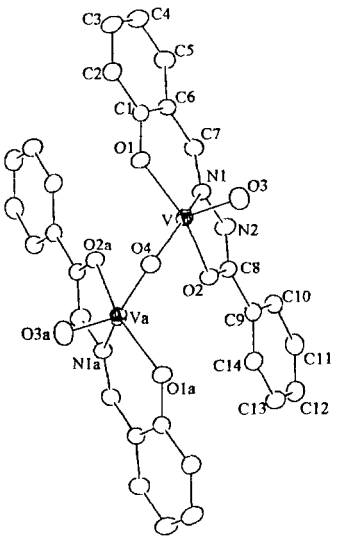


Fig. 1. Structure of [{VO(bhsH)}$_2$O] (**1**) showing the 25% probability thermal ellipsoids and the atom labelling scheme. Hydrogen atoms are omitted for clarity.

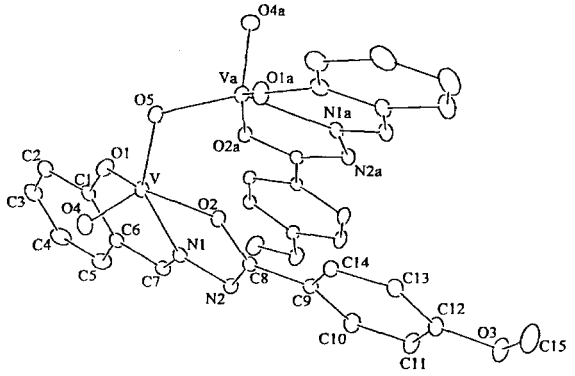


Fig. 2. Structure and the atom labelling scheme of [{VO(ahsH)}$_2$O] (**2**), showing the 10% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

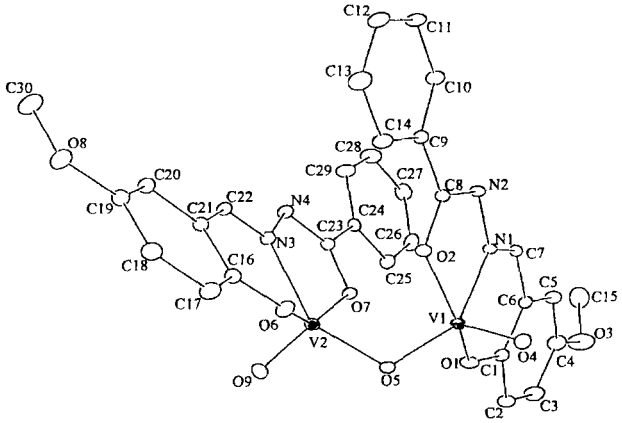


Fig. 3. Structure of [{VO(bhsOMe)}$_2$O] (**3**) showing the 10% probability thermal ellipsoids with the atom labelling scheme. For clarity, hydrogen atoms are omitted.

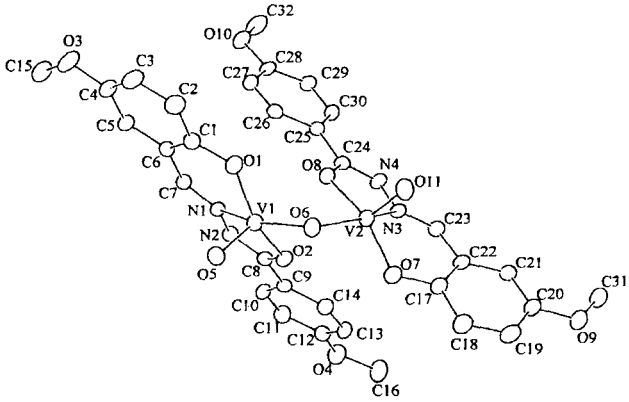


Fig. 4. Structure of [{VO(ahsOMe)}$_2$O] (**4**) with the atom labelling scheme. All atoms are represented by their 25% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (°) for [{VO(bhsH)}$_2$O][a)]

Bond lengths			
V–O(1)	1.8168(16)	V–N(1)	2.088(2)
V–O(2)	1.9484(18)	O(2)–C(8)	1.315(3)
V–O(3)	1.573(2)	N(1)–N(2)	1.394(3)
V–O(4)	1.8013(14)	N(2)–C(8)	1.292(4)
Bond angles			
O(3)–V–O(4)	107.21(11)	O(3)–V–N(1)	99.52(12)
O(3)–V–O(1)	103.50(10)	O(4)–V–N(1)	149.21(9)
O(4)–V–O(1)	104.48(7)	O(1)–V–N(1)	83.32(9)
O(3)–V–O(2)	102.93(10)	O(2)–V–N(1)	74.13(8)
O(4)–V–O(2)	85.08(7)	V(a)–O(4)–V	112.86(13)
O(1)–V–O(2)	147.62(9)		

a) Symmetry transformations used to generate equivalent atoms: $-x+1, -y, z$.

Table 4. Selected Bond Lengths (Å) and Angles (°) for [{VO(ahsH)}$_2$O][a)]

Bond lengths			
V–O(4)	1.578(2)	V–N(1)	2.076(2)
V–O(5)	1.7996(13)	O(2)–C(8)	1.315(3)
V–O(1)	1.8145(18)	N(2)–C(8)	1.299(3)
V–O(2)	1.9495(15)	N(1)–N(2)	1.395(3)
Bond angles			
O(4)–V–O(5)	109.39(9)	O(4)–V–N(1)	102.04(9)
O(4)–V–O(1)	103.79(10)	O(5)–V–N(1)	145.71(8)
O(5)–V–O(1)	101.16(7)	O(1)–V–N(1)	83.91(8)
O(4)–V–O(2)	99.83(9)	O(2)–V–N(1)	74.83(7)
O(5)–V–O(2)	86.43(6)	V(a)–O(5)–V	112.92(12)
O(1)–V–O(2)	151.00(8)		

a) Symmetry transformations used to generate equivalent atoms: $-x, y, -z+3/2$.

protonated amide-O atoms, forming a six-membered and a five-membered chelate ring. The chelate bite angle for the six-membered ring is in the range 83.32(9)—84.02(9)°, and that for the five-membered ring is in the range 73.91(10)—74.83(8)°. These three atoms and the bridging oxygen atom form a square plane in each complex. An oxo group occupies the fifth apical coordination site. The dimeric molecule of each of the two complexes, [{VO(bhsH)}$_2$O] and [{VO(ahsH)}$_2$O], lies on a crystallographically imposed two-fold axis, which coincides with the bridging oxygen atom (Figs. 1 and 2). The two-fold axis in [{VO(bhsH)}$_2$O] is at 1/2, 0, z and that in [{VO(ahsH)}$_2$O] is at 0, y, 3/4. However, for the other two complexes, the asymmetric unit contains a full dimeric molecule (Figs. 3 and 4). In each case there is a large displacement of the metal ion from the ONOO basal plane towards the apical oxo oxygen. For complex (**1**) of unsubstituted bhsH^{2-}, the magnitude of this displacement is 0.57 Å. However, for the other complexes (**2**, **3**, and **4**) this displacement is in the range 0.44—0.47 Å. The V=O distances (1.568(2)—1.580(2) Å) are typical of a double bond.[1—3] The

Table 5. Selected Bond Lengths (Å) and Angles (°) for [{VO(bhsOMe)}$_2$O]

Bond lengths			
V(1)–O(4)	1.568(2)	V(2)–O(7)	1.9502(19)
V(1)–O(1)	1.802(2)	V(2)–N(3)	2.081(2)
V(1)–O(5)	1.8068(19)	O(2)–C(8)	1.318(3)
V(1)–O(2)	1.9308(19)	N(1)–N(2)	1.398(3)
V(1)–N(1)	2.081(2)	N(2)–C(8)	1.298(3)
V(2)–O(9)	1.573(2)	O(7)–C(23)	1.317(3)
V(2)–O(5)	1.782(2)	N(3)–N(4)	1.400(3)
V(2)–O(6)	1.820(2)	N(4)–C(23)	1.295(3)
Bond angles			
O(4)–V(1)–O(1)	103.95(13)	O(9)–V(2)–O(6)	104.50(12)
O(4)–V(1)–O(5)	109.05(11)	O(5)–V(2)–O(6)	100.76(9)
O(1)–V(1)–O(5)	99.90(10)	O(9)–V(2)–O(7)	101.52(11)
O(4)–V(1)–O(2)	102.26(11)	O(5)–V(2)–O(7)	87.33(8)
O(1)–V(1)–O(2)	149.09(10)	O(6)–V(2)–O(7)	148.72(9)
O(5)–V(1)–O(2)	86.66(8)	O(9)–V(2)–N(3)	101.75(11)
O(4)–V(1)–N(1)	101.72(11)	O(5)–V(2)–N(3)	147.71(9)
O(1)–V(1)–N(1)	84.02(9)	O(6)–V(2)–N(3)	83.65(9)
O(5)–V(1)–N(1)	146.85(9)	O(7)–V(2)–N(3)	74.26(8)
O(2)–V(1)–N(1)	74.83(8)	V(2)–O(5)–V(1)	113.29(10)
O(9)–V(2)–O(5)	107.88(11)		

Table 6. Selected Bond Lengths (Å) and Angles (°) for [{VO(ahsOMe)}$_2$O]

Bond lengths			
V(1)–O(5)	1.580(2)	V(2)–O(8)	1.939(2)
V(1)–O(6)	1.788(2)	V(2)–N(3)	2.078(3)
V(1)–O(1)	1.812(3)	O(2)–C(8)	1.326(4)
V(1)–O(2)	1.929(2)	N(1)–N(2)	1.396(4)
V(1)–N(1)	2.084(3)	N(2)–C(8)	1.298(4)
V(2)–O(11)	1.571(3)	O(8)–C(24)	1.319(4)
V(2)–O(6)	1.803(2)	N(3)–N(4)	1.388(4)
V(2)–O(7)	1.812(3)	N(4)–C(24)	1.300(4)
Bond angles			
O(5)–V(1)–O(6)	107.69(12)	O(11)–V(2)–O(6)	107.56(13)
O(5)–V(1)–O(1)	103.82(13)	O(11)–V(2)–O(7)	104.76(14)
O(6)–V(1)–O(1)	101.86(12)	O(6)–V(2)–O(7)	102.54(12)
O(5)–V(1)–O(2)	103.49(12)	O(11)–V(2)–O(8)	105.90(13)
O(6)–V(1)–O(2)	87.00(11)	O(6)–V(2)–O(8)	86.52(10)
O(1)–V(1)–O(2)	147.03(11)	O(7)–V(2)–O(8)	143.55(12)
O(5)–V(1)–N(1)	97.92(12)	O(11)–V(2)–N(3)	96.49(13)
O(6)–V(1)–N(1)	151.46(11)	O(6)–V(2)–N(3)	152.47(11)
O(1)–V(1)–N(1)	83.54(11)	O(7)–V(2)–N(3)	83.51(11)
O(2)–V(1)–N(1)	74.72(10)	O(8)–V(2)–N(3)	73.91(10)
V(1)–O(6)–V(2)	115.89(12)		

V–N distances (2.076(2)—2.088(2) Å) are very similar in all of the complexes. The V–O(phenolate) bond distances (1.802(2)—1.820(2) Å) are significantly shorter than the V–O(amide) bond distances (1.9308(19)—1.9502(19) Å). This may be due to better localisation of the negative charge on the phenolate-O compared to that on the deprotonated amide-O, which results in better σ-bonding in V–O(phe-

nolate) than in V–O(amide). The two ligands in [{VO(bhsOMe)}$_2$O] as well as in [{VO(ahsOMe)}$_2$O] are not exactly equivalent in terms of the metal-to-coordinating atom distances (Tables 5 and 6). In the former the V–N(imine) distances are identical and there is a slight difference in the V–O(phenolate) distances. In the latter the metal-to-phenolate-O distances are identical and the difference in the V–N(imine) is statistically insignificant. However, in both cases the V–O(amide) distances are significantly different. The vanadium-to-bridging-oxygen distances (1.782(2)—1.8068(19) Å) are unexceptional. The V–O–V bridge angle in the complexes containing the $\{OV^{V}(\mu\text{-}O)V^{V}O\}^{4+}$ core reported in the literature covers a wide range of angles (107.18—180°).[3] In the present series of complexes this angle is very similar and varies from 112.86(13) to 115.89(12)°, and, as a consequence of this small range, the V···V distances are also very similar (2.9979(8)—3.0434(12) Å). An interesting feature of each structure is the distance (2.6806(24)—2.8535(29) Å) between each vanadium atom and the amide-O coordinated to the other vanadium centre. The O=V···O angle is in the range 167.59(13)—173.70(12)°. These distances and angles suggest a possible interaction between the metal centre and the amide-O at the site *trans* to the oxo group. Therefore, both vanadium atoms in each complex prefer hexacoordination, which is attained by weak intramolecular coordination of the amide-O.

Financial assistance received from the Council of Scientific and Industrial Research, New Delhi (Grant No. 01(1422)/96/EMR-II) is gratefully acknowledged. Ms. N. R. Sangeetha acknowledges the University Grants Commission, New Delhi, for a research fellowship. We are thankful to Prof. P. S. Zacharias for allowing the use of the electroanalytical system. X-ray crystallographic studies were performed at the National Single Crystal Diffractometer Facility, School of Chemistry, University of Hyderabad. The Department of Science and Technology, New Delhi provided funds for this facility.

References

1 a) D. L. Thorn, R. L. Harlow, and N. Herron, *Inorg. Chem.*, **35**, 547 (1996). b) G. Asgedom, A. Sreedhara, J. Kivikoski, J. Valkonen, E. Kolehmainen, and C. P. Rao, *Inorg. Chem.*, **35**, 5674 (1996). c) I. Cavaco, J. C. Pessoa, M. T. Duarte, R. T. Henriques, P. M. Matias, and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, **1996**, 1989. d) R. Fulwood, H. Schmidt, and D. Rehder, *J. Chem. Soc., Chem. Commun.*, **1995**, 1443. e) J. Chakravorty, S. Dutta, A. Dey, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, **1994**, 557, and references therein.

2 a) S. P. Rath, S. Mondal, and A. Chakravorty, *Inorg. Chim. Acta*, **263**, 247 (1997). b) W. Wang, F.-L. Zeng, X. Wang, and M.-Y. Tan, *Polyhedron*, **15**, 1699 (1996). c) W. Bansee, E. Ludwig, E. Uhlemann, F. Weller, K. Dehnicke, and W. Herrmann, *Z. Anorg. All. Chem.*, **613**, 36 (1992). d) S. Meicheng, Z. Yongjian, Z. Zeying, and T. Yougi , *Sci. Sin. Ser. B (Engl. Ed.)*, **31**, 781 (1988).

3 a) U. Casellato, P. A. Vigato, R. Graziani, M. Vidali, F. Milani, and M. M. Musiani, *Inorg. Chim. Acta*, **61**, 121 (1982). b) S. Yamada, C. Katayama, J. Tanaka, and M. Tanaka, *Inorg. Chem.*, **23**, 253 (1984). c) A. A. Diamantis, J. M. Frederickson, Md. A. Salam, M. R. Snow, and E. R. T. Tieknik, *Aust. J. Chem.*, **39**, 1081 (1986). d) K. Nakajima, M. Kojima, K. Toriumi, K. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **62**, 760 (1989). e) C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies, and V. L. Pecoraro, *Inorg. Chem.*, **29**, 944 (1990). f) S. Dutta, P. Basu, and A. Chakravorty, *Inorg. Chem.*, **32**, 5343 (1993). g) E. Ludwig, U. Schilde, E. Uhlemann, F. Weller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **619**, 669 (1993). h) J. Dai, S. Akiyama, M. Munakata, and M. Mikuriya, *Polyhedron*, **13**, 2495 (1994). i) I. Cavaco, J. C. Pessoa, M. T. Duarte, R. T. Henriques, P. M. Matias, and R. D. Gillard, *J. Chem. Soc., Dalton Trans,*, **1996**, 1989. j) H. Schmidt, M. Bashirpoor, and D. Rehder, *J. Chem. Soc., Dalton Trans.*, **1996**, 3865.

4 a) E. de Boer, M. G. Tromp, H. Plat, G. E. Krenn, and R. Wever, *Biochim. Biophys. Acta*, **872**, 104 (1986). b) M. J. Clague, N. L. Keder, and A. Butler, *Inorg. Chem.*, **32**, 4754 (1993). c) C. J. Carrano, M. Mohan, S. M. Holmes, R. de la Rosa, A. Butler, J. M. Charnock, and C. D. Garner, *Inorg. Chem.*, **33**, 646 (1994).

5 a) D. C. Crans, R. A. Felty, and M. M. Miller, *J. Am. Chem. Soc.*, **113**, 265 (1991). b) F. Hillerns, F. Olbrich, U. Behrens, and D. Rehder, *Angew. Chem., Int. Ed. Engl.*, **31**, 447 (1992).

6 a) D. C. Crans, R. L. Bunch, and L. A. Theisen, *J. Am. Chem. Soc.*, **111**, 7597 (1989). b) A. F. Nour-Elden, M. M. Craig, and M. J. Gresser, *J. Biol. Chem.*, **260**, 6836 (1985).

7 a) D. C. Crans, C. M. Simone, and J. S. Blanchard, *J. Am. Chem. Soc.*, **114**, 4926 (1992). b) K. Kustin, G. C. McLeod, T. R. Gilbert, and L. B. R. Briggs, *Struct. Bonding (Berlin)*, **53**, 139 (1983).

8 a) R. Wever and K. Kustin, *Adv. Inorg. Chem.*, **35**, 81 (1990). b) A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, **109**, 61 (1991). c) D. Rehder, *Angew. Chem., Int. Ed. Engl.*, **30**, 148 (1991).

9 a) D. W. Margerum, *Pure Appl. Chem.*, **55**, 23 (1983). b) S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, **30**, 4031 (1991). c) J. W. Gohdes and W. H. Armstrong, *Inorg. Chem.*, **31**, 368 (1992).

10 a) L. Sacconi, *Z. Anorg. Allg. Chem.*, **275**, 249 (1954). b) G. Struv, *J. Prakt. Chem.*, **50**, 295 (1894).

11 R. A. Rowe and M. M. Jones, *Inorg. Synth.*, **5**, 113 (1957).

12 Symbols: s, strong; m, medium; w, weak.

13 "Xtal3.4 User's Manual," ed by S. R. Hall, G. S. D. King, and J. M. Stewart, University of Western Australia, Perth (1995).

14 G. M. Sheldrick, "SHELX-97, Structure Determination Software," University of Göttingen, Göttingen, Germany (1997).

15 P. McArdle, *J. Appl. Crystallogr.*, **28**, 65 (1995).

16 a) W. Kemp, "Organic Spectroscopy," Macmillan, Hampshire (1987), pp. 62—65. b) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley, New York (1986), pp. 241—244.

17 L. El Sayed and M. F. Iskander, *J. Inorg. Nucl. Chem.*, **33**, 435 (1971).

18 N. S. Biradar and B. R. Havinale, *Inorg. Chim. Acta*, **17**, 157 (1976).

19 S. Pal, D. Bandyopadhyay, D. Datta, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, **1985**, 159.

20 a) K. M. Kadish, *Prog. Inorg. Chem.*, **34**, 435 (1986). b) S. L. Kelly and K. M. Kadish, *Inorg. Chem.*, **21**, 3631 (1982). c) L. A. Bottomley and K. M. Kadish, *Inorg. Chem.*, **20**, 1348 (1981).

21 a) S. Dutta, V. Manivannan, L. G. Babu, and S. Pal, *Acta Crystallogr., Sect. C*, **C51**, 813 (1995). b) N. R. Sangeetha, C. K. Pal, P. Ghosh, and S. Pal, *J. Chem. Soc., Dalton Trans.*, **1996**, 3293. c) A. Mangia, M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, **1973**, 1141. d) M. R. Maurya, D. C. Antony, S.

Gopinathan, V. G. Puranik, S. S. Tavale, and C. Gopinathan, *Bull. Chem. Soc. Jpn.*, **68**, 2847 (1995). e) N. R. Sangeetha, K. Baradi, R. Gupta, C. K. Pal, V. Manivannan, and S. Pal, *Polyhedron*, **18**, 1425 (1999).