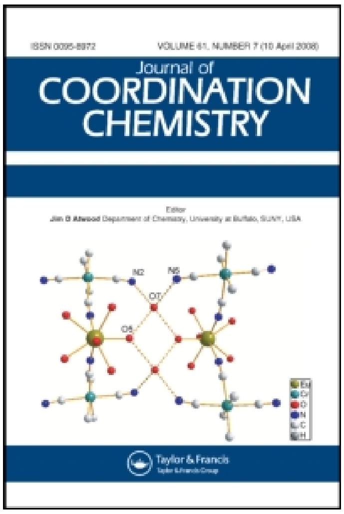

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Vanadium(V) Complexes of O,N,O-Donor Tridentate Ligands Containing the $\{V^VO(OMe)\}^2$ Unit: Syntheses, Structures and Properties

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VANADIUM(V) COMPLEXES OF O,N,O-DONOR TRIDENTATE LIGANDS CONTAINING THE $\{V^{V}O(OMe)\}^{2+}$ UNIT: SYNTHESES, STRUCTURES AND PROPERTIES

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Syntheses, characterisation and properties of two complexes containing the oxovanadium(V) methoxide unit have been described. Deprotonated benzoylhydrazones of 2-hydroxy-5-methoxybenzaldehyde (H_2bhsOMe) and 2-hydroxy-5-chlorobenzaldehyde (H_2bhsCl) were used as coligands. Crystal structures of both the complexes were determined. In solid state one of them is a dinuclear species [VO(bhsOMe)(OMe)]$_2$ (1) whereas the other one is a mononuclear complex [VO(bhsCl)(OMe)(HOMe)] (2). The dinegative ligands coordinate the metal ions *via* phenolate-O, imine-N and deprotonated amide-O atoms. In 1, the metal ions of two square pyramidal VO(bhsOMe)(OMe) units share the methoxide groups to form a dinuclear species. The oxygen of a methanol molecule completes the hexacoordination of the metal centre in 2. In each of the two distorted octahedral VO_5N moieties of 1 the bridging methoxide oxygen and in that of 2 the methanol oxygen is *trans* to the corresponding oxo group. Both the complexes are redox active. The VO^{3+} to VO^{2+} reduction potentials (*vs* Ag/AgCl) of 1 and 2 are observed at −0.25 and −0.04 V, respectively. The band positions in the electronic spectra and the redox potentials reflect the influence of the substituents present on the ligands.

Keywords: Vanadium(V) complexes; crystal structures; solid state nuclearity; substituent effect

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INTRODUCTION

Current interest in the chemistry of VO^{3+} stems from its involvement in several biological processes such as haloperoxidation[1] phosphorylation[2] and glycogen metabolism.[3] Such species are also important for their possible use as metallooxidants.[4] Recently several complexes containing oxovanadium(V) are reported.[5–7] Among these a class of complexes of O,N,O^- donor Schiff bases contain the common motif, $V^VO(OR)$.[6,7] One among the various types of Schiff bases used is tridentate amide-O, imine-N and phenolate- or enolate-O donor aroylhydrazones of salicylaldehyde or of diketones. The V(V) centre is square pyramidal[7a–c] in the case of benzoylacetone aroylhydrazone complexes, whereas a distorted octahedral geometry around the metal centre is observed for salicylaldehyde benzoylhydrazone.[7c,d] In the latter case, the oxygen of an alcohol satisfies the sixth coordination site. The reason for this difference in geometry is not readily apparent.[7c] However, an alkoxide bridged dinuclear species having hexacoordinated metal centres has been reported with acetylacetone *m*-nitrobenzoylhydrazone.[7e] In the present work we report on two new complexes of benzoylhydrazones of 5-substituted 2-hydroxybenzaldehydes (H_2bhsX, X = OMe, Cl), both containing the oxovanadium(V) methoxide motif. The complexes have been characterised by analytical, spectroscopic, electrochemical and X-ray crystallographic studies. X-ray structures of the complexes reveal that in both the complexes the metal centre is hexacoordinated. In order to achieve hexacoordination, the complex of $bhsOMe^{2-}$ dimerises by sharing the alkoxide group whereas, in the second case, a methanol oxygen occupies the vacant sixth position.

EXPERIMENTAL

Materials

The benzoylhydrazones,[8] H_2bhsX (X = OMe, Cl) were prepared in ~80–90% yield by condensing 1 equivalent of benzoylhydrazine and 1 equivalent of the corresponding aldehyde in methanol. Bis(acetylacetonato)oxovanadium(IV) was prepared by following a reported procedure.[9] All other chemicals and solvents used in this work were of analytical grade available commercially.

Physical Measurements

Microanalytical data (C, H, N) were obtained with a Perkin-Elmer model 240C instrument. Infrared spectra were recorded for KBr pellets of the complexes using a JASCO-5300 FT-IR spectrophotometer. A JASCO-7800 spectrophotometer was used to obtain the electronic spectra. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer. 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 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. The 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(bhsOMe)(OMe)]$_2$ (1)

This complex can be synthesised by following either of the two procedures ((a) and (b)) described below.

(a) To a methanol (15 cm^3) solution of H_2bhsOMe (0.292 g, 1.08 mmol) and KOH (0.122 g, 2.17 mmol), an aqueous solution (15 cm^3) of $VOSO_4 \cdot 5H_2O$ (0.274 g, 1.08 mmol) was added. The mixture was stirred at room temperature for 2 h. The solid separated was collected by filtration, washed with water and dried in vacuum over anhydrous $CaCl_2$. This dry solid was dissolved in minimum volume of methanol and filtered followed by addition of an equal amount of benzene. A dark crystalline solid was obtained by slow evaporation of this solution. The compound was collected by filtration and dried in vacuum. The yield was 0.180 g (46%). *Anal.* calcd. for $C_{32}H_{30}N_4O_{10}V_2$ (%): C, 52.47; H, 4.13; N, 7.65. Found: C, 52.12; H, 3.92; N, 7.44. Selected IR bands[†] (cm^{-1}): 1595s, 1555s, 1478m, 1354m, 1331m, 1265s, 1171m, 1017s, 970s, 841s, 787m, 700m, 590s, 480w. Electronic spectroscopic data in methanol solution [λ_{max}/nm (ε/M^{-1} cm^{-1})]: 424 (8250), 330 (36 300), 262 (61 200).

[†] Symbols: s, strong; m, medium; w, weak.

(b) To a methanol solution (15 cm^3) of 200 mg (0.75 mmol) of $[VO(acac)_2]$ was added 15 cm^3 methanol solution of H_2bhsOMe (204 mg, 0.75 mmol). The dark brown mixture was heated on water bath for 15 min and allowed to evaporate slowly in air at room temperature. The crystalline dark solid that separated was collected by filtration, washed with ice-cold methanol and finally dried under vacuum over anhydrous $CaCl_2$. The yield of $[VO(bhsOMe)(OMe)]_2$ by this method was 150 mg (54%).

[VO(bhsCl)(OMe)(HOMe)] (2)

This complex can be prepared in 40% yield from $VOSO_4 \cdot 5H_2O$, H_2bhsCl and KOH by following procedure (a) as described above or in 62% yield from $[VO(acac)_2]$ and H_2bhsCl by using procedure (b). *Anal.* calcd. for $C_{16}H_{16}N_2O_5ClV$ (%): C, 47.72; H, 4.00; N, 6.95. Found: C, 47.36; H, 3.61; N, 6.88. Selected IR bands[10] (cm^{-1}): 1603s, 1547s, 1460m, 1372m, 1335m, 1285m, 1196m, 1107m, 951m, 864s, 820w, 696m, 571w, 475w. Electronic spectroscopic data in methanol solution [λ_{max}/nm ($\varepsilon/M^{-1}\,cm^{-1}$)]: 397 (6060), 319 (18 900), 260 (26 500).

X-ray Crystallography

Single crystals of both complexes were obtained by slow evaporation of methanol–benzene (1 : 1) solutions. A Rigaku RaxisII diffractometer with image plate system and rotating anode generator was used for data collection. The radiation employed was graphite-monochromated MoKα ($\lambda = 0.71073$ Å). Data collection ranges are $2.49 < \theta < 24.78°$ and $1.94 < \theta < 24.76°$, for **1** and **2**, respectively. No absorption correction was applied in both cases. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculations at idealised positions with fixed thermal parameters, but not refined. All calculations for data reduction, structure solution and refinement were performed using SHELXTL-Plus programs.[10] Significant crystal data are listed in Table I.

RESULTS AND DISCUSSION

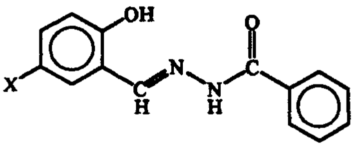
Synthesis and Some Properties

The benzoylhydrazones (H_2bhsX, X = OMe and Cl) are derived from substituted salicylaldehydes. Each of them has two dissociable protons at the

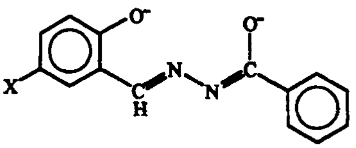
TABLE I Crystallographic data for $[VO(bhsOMe)(OMe)]_2$ (1) and [VO(bhsCl)(OMe)-(HOMe)] (2)

Complex	1	2
Empirical formula	$C_{32}H_{30}N_4O_{10}V_2$	$C_{16}H_{16}N_2O_5ClV$
Formula weight	732.48	402.70
Temperature (K)	293	293
Crystal size (mm)	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.7723(8)	18.130(4)
b (Å)	20.453(2)	12.979(3)
c (Å)	9.2270(11)	7.417(2)
β (°)	104.573(7)	98.19(3)
V (Å^3)	1602.2(3)	1727.5(6)
Z	2	4
ρ_{calc} (g cm^{-3})	1.518	1.548
μ (mm^{-1})	0.648	0.758
$F(000)$	752	824
No. of unique reflections	2731	2930
No. of observed reflections $[I > 2\sigma(I)]$	2152	1458
No. of refined parameters	217	227
$R1$	0.038	0.043
$wR2$	0.113	0.083
Goodness of fit on F^2	1.148	0.859
Largest difference peak and hole (e Å^{-3})	0.469, −0.491	0.215, −0.261

phenolic-OH and the amide functionality. Reaction of aqueous vanadyl sulphate with a methanolic solution of H_2bhsX and KOH in 1 : 1 : 2 mole ratio



H_2bhsX



$bhsX^{2-}$

or of bis(acetylacetonato)oxovanadium(IV) and H_2bhsX and (1 : 1 mole ratio) in methanol in air produces the complexes. The low reduction potentials (*vide infra*) of the complexes indicate that in the oxidation of VO^{2+} to VO^{3+} during the formation of the complexes aerial oxygen acts as the oxidising agent. Elemental analyses of the complexes are satisfactory with the empirical formula VO(bhsOMe)(OMe) and VO(bhsCl)(OMe)(HOMe). The diamagnetic nature of the complexes confirms the +5 oxidation state of the metal centre. In solution, both the complexes are electrically non-conducting.

Spectroscopic Characteristics

A broad band observed at ~3170 cm^{-1} in the infrared spectrum of **2** due to the O–H stretch of coordinated MeOH is absent in the spectrum of **1**. Peaks corresponding to the amide functionality[11] of the free ligands are not observed. The origin of the strong band near 1600 cm^{-1} with a shoulder is assigned to the conjugate C=N–N=C moiety.[12] Thus in each complex the ligand is in the enolate form and acts as a dibasic O, N, O donor. A band observed at 968 and 951 cm^{-1} for **1** and **2**, respectively, is assigned to the V=O stretch.[5–7]

Electronic spectra of both complexes in methanol are very similar. A moderately strong absorption is observed at 424 and 397 nm for **1** and **2**, respectively, followed by a shoulder at ~325 nm and an intense peak at ~260 nm. The lowest energy absorption is most likely due to the phenolate-to-metal charge transfer and the high energy bands are due to the intra-ligand transitions. Although the profiles of the spectra are very similar, the spectrum of **2** shows a high energy shift compared to that of **1**. Such a blue-shift originating from the electron withdrawing nature of the substituent has been observed previously in some manganese, iron and copper complexes.[13]

Proton NMR spectra of **1** and H_2bhsOMe have been recorded in $CDCl_3$ and those of **2** and H_2bhsCl have been recorded in CD_3CN using $SiMe_4$ as internal standard. The spectrum of H_2bhsOMe displays the $-OCH_3$, =CH–, –NH– and –OH resonances at 3.77, 8.47, 9.42, and 10.55 ppm respectively. The aromatic protons are observed in the range 6.7–7.8 ppm. Resonances observed at 8.57, 10.78 and 11.84 for H_2bhsCl are assigned to the =CH–, –NH– and –OH proton respectively. The aromatic protons appear in the range 7.1–8.1 ppm. The absence of the signals for –NH– and –OH protons in the spectra of the complexes suggest the deprotonation of the amide and phenol functionalities. The protons of the coordinated methoxide are observed at 3.58 and 3.51 ppm for **1** and **2**, respectively. The ligand methoxy protons of **1** appear at 3.94 ppm. Signal corresponding to the =CH– proton appears at 8.53 ppm for **1** and at 8.98 ppm for **2**. The aromatic protons of **1** and **2** are observed in the range 6.9–8.0 and 7.1–8.3 ppm, respectively. In general upon coordination the proton resonances display a downfield shift when compared with the resonances in the free ligand.

Redox Properties

In methanol solutions the cyclic voltammograms of the complexes display the VO^{3+} to VO^{2+} reduction at more cathodic potentials to that of Ag/AgCl couple. Figure 1 depicts the cyclic voltammogram of **2**. The one electron

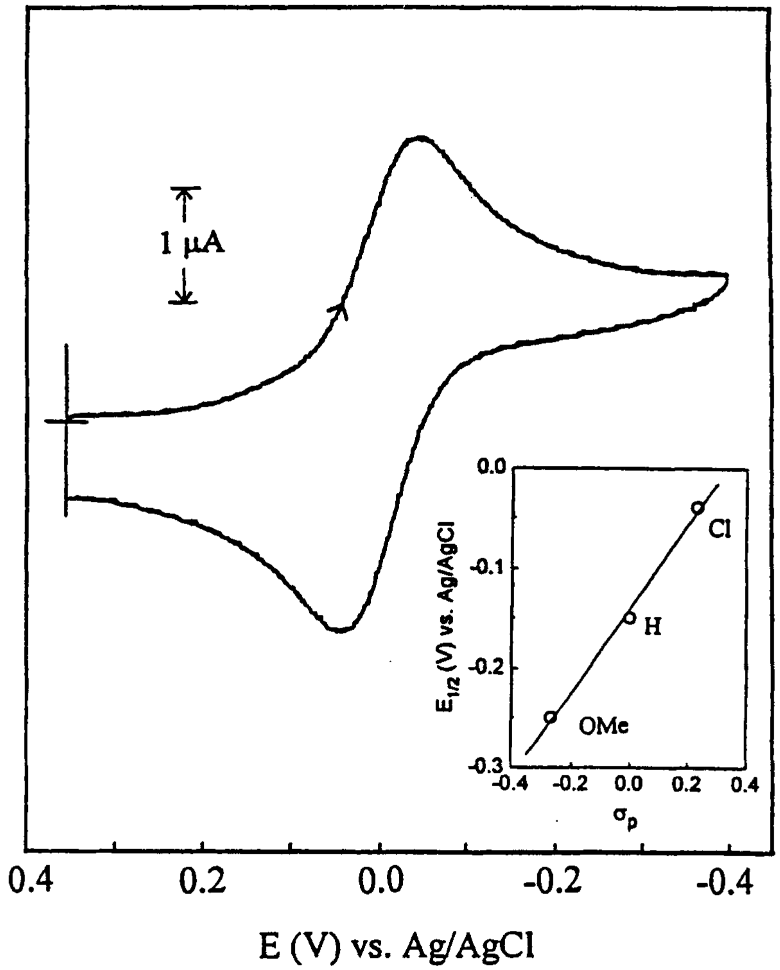


FIGURE 1 Cyclic voltammogram (scan rate 100 mV s^{-1}) of ~ 0.5 mM solution of [VO(bhsCl)-(OMe)(HOMe)] in CH_3OH (0.1 M TBAP) at a Pt-electrode (298 K). Inset: Correlation between the $E_{1/2}$ values for V(V)–V(IV) reductions and the Hammett substituent constants.

stoichiometry of these electrode processes was confirmed by comparing the current heights with known one electron redox processes under identical conditions.[14] The $E_{1/2}$ values are −0.25 and −0.04 V for **1** and **2**, respectively. The peak-to-peak separations are 90 and 80 mV for **1** and **2**, respectively. As noted earlier, the low reduction potentials are in accordance with the facile formation of the VO^{3+} complexes from VO^{2+} precursor by aerial oxidation. The lower potential of **1** compared to that of **2** is consistent with the electron donating nature of the methoxy group (in **1**) and electron withdrawing property of the chloro substituent (in 2) *para* to the coordinated phenolate functions.[13b] The potential (−0.15 V *vs* Ag/AgCl) reported[7c] for the unsubstituted complex, [VO(bhsH)(OMe)(HOMe)], is in between those of 1 and 2. A good linear fit is obtained (Figure 1) when these potentials are plotted against Hammett substituent constants.[15] In the solid state 1 exists as a methoxide bridged dinuclear species (*vide infra*). However the linear relationship of the V(V)/V(IV) potentials of 1, 2 and the unsubstituted complex with the Hammett substituent constants suggests dissociation of 1 into a solvent-coordinated mononuclear complex.

Description of Structures

The molecular structures of 1 and 2 are depicted in Figures 2 and 3, respectively. Selected bond distances and angles are listed in Tables II and III. The metal centres in both complexes are in distorted O_5N octahedral environments. In each complex the planar dianioinic tridentate ligand binds the metal ion through the phenolate-O, imine-N and deprotonated amide-O atoms forming a six- and a five-membered chelate ring. The methoxide moiety is *trans* to the imine-N in both the cases. Thus the O,N,O donor

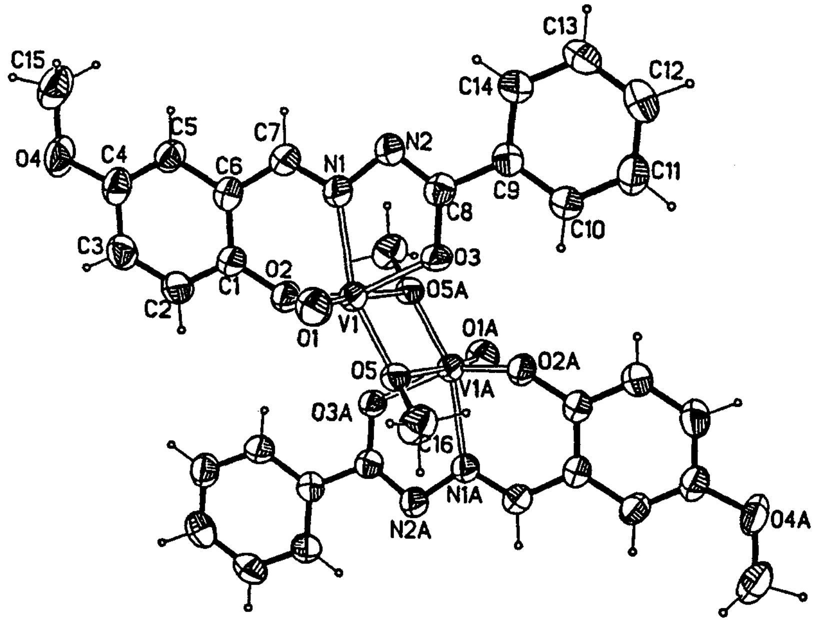


FIGURE 2 Structure of $[VO(bhsOMe)(OMe)]_2$ and the atom labelling scheme.

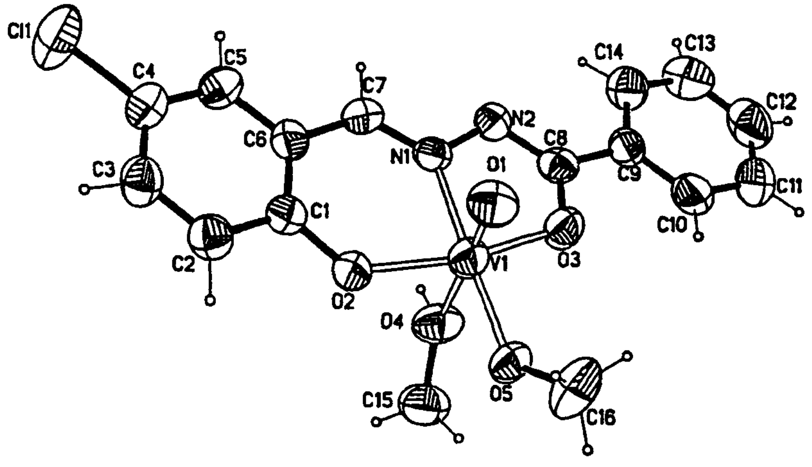


FIGURE 3 Structure of [VO(bhsCl)(OMe)(HOMe)] and the atom labelling scheme.

TABLE II Selected bond distances and angles for $[VO(bhsOMe)(OMe)]_2$ (1)[a,b]

Bond distances (Å)					
V(1)–O(1)	1.585(2)	V(1)–O(2)	1.823(2)	V(1)–O(3)	1.937(2)
V(1)–N(1)	2.112(2)	V(1)–O(5)	1.828(2)	V(1)–O(5A)	2.349(2)
N(1)–N(2)	1.397(2)	N(1)–C(7)	1.289(2)	N(2)–C(8)	1.303(4)
C(8)–O(3)	1.309(3)	C(1)–O(2)	1.340(3)		

Bond angles (°)			
O(1)–V(1)–O(2)	101.57(10)	O(1)–V(1)–O(3)	99.91(10)
O(1)–V(1)–O(5)	101.45(10)	O(1)–V(1)–O(5A)	175.38(9)
O(1)–V(1)–N(1)	95.07(10)	O(2)–V(1)–O(3)	149.81(9)
O(2)–V(1)–N(1)	83.15(8)	O(2)–V(1)–O(5)	106.61(8)
O(2)–V(1)–O(5A)	80.22(8)	O(3)–V(1)–N(1)	74.01(8)
O(3)–V(1)–O(5)	89.52(8)	O(3)–V(1)–O(5A)	80.04(7)
N(1)–V(1)–O(5)	158.49(9)	N(1)–V(1)–O(5A)	89.36(8)
O(5)–V(1)–O(5A)	73.94(8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Symmetry transformation used to generate equivalent atoms: $-x+1, -y, -z+1$.

TABLE III Selected bond distances and angles for [VO(bhsCl)(OMe)(HOMe)] (2)[a]

Bond distances (Å)					
V(1)–O(1)	1.598(3)	V(1)–O(2)	1.848(3)	V(1)–O(3)	1.957(3)
V(1)–O(4)	2.377(3)	V(1)–O(5)	1.786(3)	V(1)–N(1)	2.138(3)
N(1)–N(2)	1.415(4)	N(1)–C(7)	1.302(4)	N(2)–C(8)	1.321(4)
C(8)–O(3)	1.313(4)	C(1)–O(2)	1.349(4)		

Bond angles (°)			
O(1)–V(1)–O(2)	100.18(14)	O(1)–V(1)–O(3)	97.72(13)
O(1)–V(1)–O(4)	176.13(13)	O(1)–V(1)–O(5)	101.73(14)
O(1)–V(1)–N(1)	94.89(14)	O(2)–V(1)–O(3)	152.42(12)
O(2)–V(1)–O(4)	81.35(12)	O(2)–V(1)–O(5)	104.22(12)
O(2)–V(1)–N(1)	83.70(11)	O(3)–V(1)–O(4)	79.60(11)
O(3)–V(1)–O(5)	92.39(11)	O(3)–V(1)–N(1)	73.99(11)
O(4)–V(1)–O(5)	81.25(11)	O(4)–V(1)–N(1)	81.71(11)
O(5)–V(1)–N(1)	159.85(13)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

ligand and the methoxide-O forms a square plane. The mean deviation of these atoms from the plane is 0.040 and 0.014 Å for **1** and **2**, respectively. The fifth coordination site is occupied by the oxo oxygen giving a VO_4N square-pyramidal moiety. The displacement of the V(V) centre towards the oxo group from the O,N,O,O square plane is 0.325 and 0.298 Å in **1** and **2**, respectively. Two of such square pyramidal units form a weak dimer *via* the methoxide group (Figure 2, Table II) and the metal ions become hexacoordinated in **1**. The bridging methoxide oxygen is coordinated at the *trans* position with respect to the oxo oxygen. On the other hand, in **2**, a methanol oxygen *trans* to oxo group satisfies the sixth coordination site of the metal centre (Figure 3). The V=O distances in **1** (1.585(2) Å) and **2** (1.598(3) Å) are within the range of known VO^{3+} complexes.[5–7] Other bond distances and angles involving the metal ion in **2** are comparable to those reported for similar complexes carrying an alkoxide plus an alcohol ligand.[6,7] In **1** the metal to metal distance is 3.353 Å. The C–O, C–N and N–N distances of the five-membered chelate rings are consistent with the enolate form of the amide functionality.[5c,7] However, the C(8)–N(2) distance in **1** (1.303(4) Å) is shorter than that (1.321(4) Å) in **2**. This may be due to localisation of the negative charge on the O-atom of the amide functionality to a greater extent in **1** than that in **2**. This is also reflected in the V(1)–O(3) distances. This distance is 1.937(2) Å in **1** and 1.957(3) Å in **2**. The shorter V–O (phenolate) distance (V(1)–O(2)) in **1** (1.823(2) Å) than that in **2** (1.848(3) Å) is most probably due to the electron releasing nature of the methoxy (**1**) and electron withdrawing property of the chloro (**2**) substituent at the *para* position of the phenolate-O. The shorter V(1)–N(1) distance (2.112(2) Å) in **1** compared to that (2.138(3) Å) in **2** is most likely is a consequence of short V–O distances in the former. The structural features as discussed above suggests that the V(V) centre in {VO(OMe)(bhsX)} unit of **1** is possibly more electron rich than the metal centre in the same moiety of **2**.

The difference in the molecular structures of the two complexes in solid state may arise due to crystal packing forces or bulk solid state effects mediated by the differing substituents. Another possible rationale for the observed difference may be as follows. If only the change in entropy is considered, formation of a dinuclear species from two square-pyramidal units is always more favourable than the formation of a mononuclear complex from one VO_4N unit and a solvent molecule. However when the metal centre is electron deficient, coordination to a better donor is more preferred than dimerisation. The oxygen of a methanol molecule, at least sterically, can be a better donor than the oxygen of a methoxide coordinated to a metal ion containing other ligands. Therefore in case of 2, the sixth coordination site of the relatively more electron deficient metal centre is occupied by the oxygen of a methanol molecule giving a mononuclear complex, whereas in complex 1 the metal centre in VO_4N prefers the oxygen of a coordinated methoxide group and forms a dinuclear complex. These two complexes provide good examples for how the balancing between the demands of the metal centre and the nature of the ligands determines the nuclearity of the complexes in solid state. Such balancing acts are also relevant in natural systems such as biomineralisation.[16]

Acknowledgements

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Supplementary Material

Tables of crystal data and structure determination summary, atomic positional parameters, anisotropic thermal parameters, intramolecular bond distances and angles and hydrogen atom coordinates for both structures are available from the authors upon request.

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