

Synthesis and spectroscopic characterisation of heterobimetallic oxovanadium(V) 2,5-dimethyl-2,5-hexanediolate-alkoxides[†]

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Abstract : Reaction of $\text{VO}(\text{OPr}^i)_3$ with $\text{HOCMe}_2(\text{CH}_2)\text{CMe}_2\text{OH}$ in 1 : 2 molar ratio affords dimeric homometallic glycolate complex, $[\text{VO}(\text{OGO})(\text{OGO})]_2$ (1) (whereOGO = doubly deprotonated form of the 2,5-dimethyl-2,5-hexanediol). Reactions of (1) with different metal isopropoxides in 1 : 2 molar ratio yield a novel class of heterobimetallic isopropoxide-glycolate derivatives of formula $[\text{VO}(\text{OGO})_2\{\text{M}(\text{OPri})_{n-1}\}]_2$ (M = Al (n = 3), (2); Ti (n = 4), (3); Nb (n = 5), (4). Reactions of $[\text{VO}(\text{OGO})_2\{\text{Ti}(\text{OPr}^i)_3\}]_2$ (3) with an excess MeOH and Me_3COH afford $[\text{VO}(\text{OGO})_2\{\text{Ti}(\text{OMe})_3\}]_2$ (5) and $[\text{VO}(\text{OGO})_2\{\text{Ti}(\text{OCMe}_3)_3\}]_2$ (6), respectively. All of these new complexes have been characterised by elemental analyses, molecular weight measurements, and spectroscopic (IR, ¹H, ¹³C, ²⁷Al, ⁵¹V NMR) studies.

Keywords : Oxovanadium(V) complexes, glycolate complexes, heterobimetallic complexes.

Introduction

Although there has been significant development in the heterobimetallic alkoxide chemistry of 3d-transition metals¹⁻⁶, yet similar derivatives of vanadium(V) continue to be rare⁶. During the last two decades homo- and hetero-metallic glycolates of Ti, Zr, Nb, Ta and W have been extensively investigated^{2,3} and structures of some of these have been elucidated by X-Ray crystallographic studies²⁻⁴. Surprisingly, studies even on homometallic oxovanadium(V) glycolates are limited to a few compounds of the types : $[\text{VO}(\text{OCHCH}_3\text{CHCH}_3\text{O})(\text{OCHCH}_3\text{CHCH}_3\text{OH})]_2$ ⁷, $[\text{VO}(\text{OCH}_2\text{C}(\text{R}_1\text{R}_2)\text{CH}_2\text{O})\text{Cl}]_4$ ⁸ (where R' = R'' = H, Me; R' = Me, R'' = Et; R' = Me, R'' = Prⁿ), $[\text{VO}(\text{OCH}_2\text{CH}_2\text{O})\text{Cl}]_2$ ⁹, $[\text{VO}(\text{OCMe}_2\text{CMe}_2\text{O})\text{Cl}]_2$ ¹⁰. Furthermore, recently there has been an upsurge of interest in organic derivatives of vanadium derived from chelating ligands, primarily due to their structural features^{6,11-13} and biological importance^{14,15} including insulin mimic properties.

In our attempts to develop the chemistry of new types of heterobimetallic complexes of group 5 metals^{4,6}. We have focused our interest on the establishment of new and

convenient synthetic routes to such species. One of our recent approaches^{4,6} has been to utilize the residual hydroxy group(s) present in chelating ligand homometallic complexes to bind other metal atoms.

The present paper deals with new heterobimetallic glycolate alkoxide derivatives of oxovanadium(V), which could be used as precursors for the synthesis of heterometallic oxides of vanadium via sol-gel process^{2,3}.

Experimental

All syntheses and manipulations were carried out under strictly moisture free conditions. All oven dried (~150 °C) glassware were allowed to cool to room temperature in a moisture free atmosphere prior to use. Benzene (BDH) was dried by refluxing over Na/benzophenone, followed by distillation under anhydrous conditions. Analytical grade (BDH) isopropyl alcohol was dried by refluxing over Na, followed by refluxing over $\text{Al}(\text{OPr}^i)_3$ and distilled before use. 2,5-Dimethyl-2,5-hexanediol (Aldrich) was purified by sublimation under reduced pressure (81 °C/0.2 mm). $\text{VO}(\text{OPr}^i)_3$ was prepared from V_2O_5 ¹⁶ and distilled at 90 °C/0.5 mm as a colourless liquid.

[†]Taken from the PhD thesis of R. S. Ghadwal, University of Rajasthan, Jaipur, India (2005).

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Isopropoxides of aluminium¹⁷, titanium¹⁸, and niobium¹⁹ were prepared by the literature methods. The precursor homometallic complex [VO(OGO)(OGO)]₂ (**1**), where G = CMe₂CH₂CH₂CMe₂ was prepared by literature procedure^{6c}.

Vanadium was determined by redox titration method²⁰. Titanium and niobium were determined as their oxides²¹, whereas aluminium was determined gravimetrically by the oxinate method²¹. Isopropyl alcohol in the azeotrope was estimated oxidimetrically²².

Infrared spectra (4000–400 cm⁻¹) were recorded as Nujol mulls on a Nicolet Magna-550 spectrophotometer. ¹H (89.55 MHz; CDCl₃), ¹³C (22.49 MHz; CDCl₃), ²⁷Al (23.79 MHz; CDCl₃), and ⁵¹V NMR spectra (23.51 MHz; C₆H₆, CDCl₃ or CH₂Cl₂) were recorded on JEOL FX 90Q spectrometer. Neat VOCl₃ (δ, 0 ppm) was used as external reference for ⁵¹V NMR studies. Microanalyses (carbon and hydrogen) were performed on Perkin-Elmer 2400 CHNS/O analyser.

Molecular weights were measured ebullioscopically in benzene solution, with an accuracy of ±5%, by using a semi-micro ebullimeter (Gallenkamp, UK) fitted with a thermistor sensing device, to record the change in the boiling point of the solution in terms of the change in resistance with the help of Wheatstone bridge and a sensitive galvanometer. The molecular weight of the com-

pound can be determined by the following equation :

$$M = \frac{Kw}{\Delta R}$$

Here *M* represents molecular weight of the compound, *K* is the thermistor constant for the solvent used, *w* is the weight of the compound added, and Δ*R* is the change in resistance on addition of the compound. Naphthalene was used as the calibration solute to determine the thermistor constant (*K*). In each experiment 15 ml of solvent (anhydrous benzene) was used.

Synthesis of heterobimetallic derivatives :

[VO(OGO)₂{Al(OP^{*i*})₂}]₂ (**2**) : A benzene solution (~ 50 ml) containing (**1**) (1.26 g, 1.78 mmol) and Al(OP^{*i*})₃ (0.71 g, 3.50 mmol) was refluxed with continuous removal of isopropyl alcohol azeotropically with benzene till the distillate showed negligible presence of isopropyl alcohol. After completion of the reaction, refluxing was stopped and solution was allowed to cool to room temperature. Volatiles from the solution were removed under reduced pressure to obtain (**2**) as a white waxy solid (1.71 g, 96%). Recrystallisation from dichloromethane-*n*-hexane (2 : 1) mixture at -20 °C gave analytically pure product as a white waxy solid (1.25 g, 70%). Analytical details are summarised in Table 1.

Table 1. Analytical data for homo- and hetero-bimetallic derivatives of oxovanadium(v)

Empirical formula ^a	Yield ^b (g) (%)	Pr ^{<i>i</i>} OH (g) liberated Found (Calcd.)	Analysis (%) : Found (Calcd.)				Mol. wt. Found (Calcd.)
			V	Al/Ti/Nb	C	H	
C ₁₆ H ₃₃ O ₅ V (1)	4.56 (71)	3.2 (3.2)	14.2 (14.3)	–	53.7 (53.9)	9.2 (9.3)	733 (359)
C ₂₂ H ₄₆ AlO ₇ V (2)	1.25 (70)	0.2 (0.2)	10.1 (10.2)	5.2 (5.4)	52.5 (52.8)	9.1 (9.3)	1020 (500)
C ₂₅ H ₅₃ O ₈ TiV (3)	1.74 (72)	0.2 (0.2)	8.6 (8.8)	8.2 (8.2)	51.5 (51.7)	9.1 (9.2)	1169 (580)
C ₂₈ H ₆₀ O ₉ Nb V (4)	1.49 (60)	0.2 (0.2)	7.3 (7.4)	13.3 (13.5)	58.3 (58.7)	9.9 (10.6)	1401 (684)
C ₁₉ H ₄₁ O ₈ TiV (5)	0.96 (70)	–	10.1 (10.3)	9.6 (9.6)	45.7 (45.9)	8.1 (8.3)	1006 (496)
C ₂₈ H ₅₉ O ₈ TiV (6)	0.65 (56)	–	8.1 (8.2)	7.6 (7.7)	53.9 (54.0)	9.0 (9.6)	1267 (622)

^aAll these compounds are colourless waxy solids.

^bRefers to crystallised product.

Complexes (3) and (4) were prepared by a procedure similar to that described for (2), by using appropriate reactants in desired stoichiometry as shown below against each compound in square bracket :

$[VO(OGO)_2\{Ti(OPr^i)_3\}]_2$ (3): $[VO(OGO)(OGOHO)]_2$ (1.48 g, 2.07 mmol) and $Ti(OPr^i)_4$ (1.18 g, 4.18 mmol).

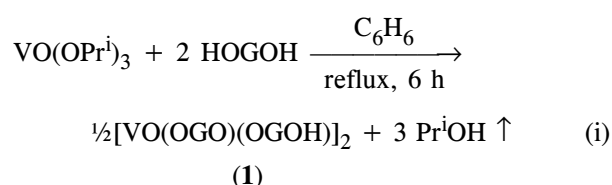
$[VO(OGO)_2\{Nb(OPr^i)_4\}]_2$ (4) : $[VO(OGO)(OGOHO)]_2$ (1.29 g, 1.80 mmol) and $Nb(OPr^i)_5$ (1.41 g, 3.60 mmol)]. Analytical details are given in Table 1.

$[VO(OGO)_2\{Ti(OMe)_3\}]_2$ (5) : Methyl alcohol (5 ml) was added to the benzene (~50 ml) solution of $[VO(OGO)_2\{Ti(OPr^i)_3\}]_2$; the solution turned from colourless to pale yellow. After the reaction mixture was stirred for 3 h at 70 °C, all volatile substances were removed under vacuum to give a cream coloured waxy solid. Yield : 1.35 g (99%). Crystallisation of the product from 1 : 2 mixture of *n*-hexane and dichloromethane at -20 °C gave (5) as a colourless waxy solid. Yield : 0.96 g (70%). Analytical details are given in Table 1.

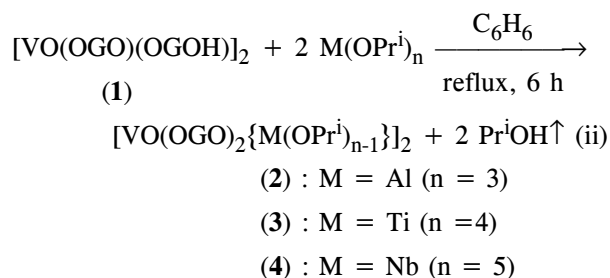
$[VO(OGO)_2\{Ti(OCMe_3)_3\}]_2$ (6) : To a solution of $[VO(OGO)_2\{Ti(OPr^i)_3\}]_2$ (1.01 g, 0.87 mmol) in benzene (70 ml) was added *tert*-butyl alcohol (~5 ml). The reaction mixture was refluxed for 6 h and the benzene-isopropyl alcohol azeotrope was removed at 72 °C (followed by benzene at 80 °C). The azeotrope collected between 72–80 °C contained isopropyl-alcohol 0.29 g (Calcd. 0.31 g). The remaining volatile components were evaporated under reduced pressure to yield white waxy solid (0.99 g, 92%). Crystallisation from *n*-hexane at -20 °C gave the title compound (6) as a white waxy solid. Yield : 0.65 g (59%). Analytical details are given in Table 1.

Results and discussion

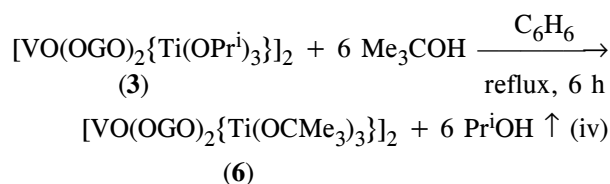
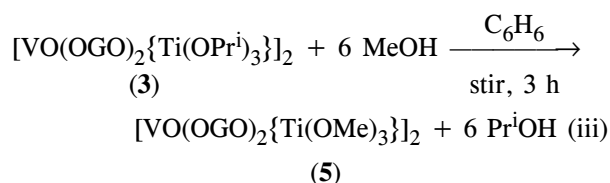
Reaction of $VO(OPr^i)_3$ with $HOCMe_2(CH_2)_2CMe_2OH$, (HOGOHO) in 1 : 2 molar ratio affords dimeric oxovanadium(V) glycolate complex^{6c} (1) :



Reactions of (1) with a number of metal isopropoxides $Al(OPr^i)_3$, $Ti(OPr^i)_4$, or $Nb(OPr^i)_5$ in benzene gave according to the eq. (ii) novel heterobimetallic derivatives :



The reaction of (3) with an excess of methyl alcohol is facile and complete replacement of isopropoxy groups could be accomplished only by heating at ~70 °C for about 3 h. By contrast, reaction of (3) with an excess of *tert*-butyl alcohol required continuous azeotropic removal of the liberated isopropyl alcohol over a period of 6 h;



All these colourless waxy solid complexes are soluble in organic solvents and depict dimeric nature ebullioscopically in benzene solution.

IR spectra :

Infrared spectrum of the homometallic glycolate (1) shows (Table 2) characteristic absorptions at 1071 and 1036 cm^{-1} for $\nu(C-O)$ stretching vibrations, 1465 cm^{-1} for $\nu(CH_2)$ deformation, 957 cm^{-1} for $\nu(V=O)$, and 3314 cm^{-1} for $\nu(O-H)$ stretching vibrations. The observed strong band at 957 cm^{-1} for $\nu(V=O)$, which is 40 cm^{-1} lower than that found (1000 cm^{-1}) in $VO(OPr^i)_3$ is characteristic of vanadium in six-coordinate^{23,24} environment. The shifting of $\nu(O-H)$ band towards higher (~29 cm^{-1}) wave number with respect to free glycol (3285 cm^{-1}) is due to the formation of intramolecular $V \leftarrow OH$ dative bond. The new band observed at 443 cm^{-1} may be assigned to $\nu(V \leftarrow O)$.

The heterobimetallic glycolate-isopropoxides (2)-(4) showed infrared absorptions characteristic of glycolate moiety at 1070 ± 10, 1032 ± 4 $\nu(C-O)$, 1465 ± 5

Table 2. IR data (cm⁻¹) of new oxovanadium(v) complexes (1)-(6)

Complex	v(C-O)	v(OPr ⁱ)	v(V=O)	v(V-O)	v(M-O)	v(V←O)	v(M←O)
1	1071, 1036	-	957	529	-	443	-
2	1072, 1035	1185, 1140	963	542	600	442	500
3	1066, 1031	1178, 1142	957	531	565	452	471
4	1079, 1029	1180, 1149	966	540	516	450	439
5	1080, 1030	-	967	535	566	450	466
6	1078, 1029	-	966	533	560	450	460

v(CH₂) deformation; metal attached isopropoxy groups at 1080 ± 5, 1144 ± 5 v(OPrⁱ) along with v(V=O) at 962 ± 5 cm⁻¹.

NMR spectra :

¹H NMR spectrum of (1) shows signals (Table 3) at δ 1.24, 1.60 and 2.21 for CMe₂, CH₂, and OH protons, respectively. The spectra of the new heterobimetallic com-

Unfortunately these complexes did not yield single-crystals of sufficient quality for X-ray crystallographic characterization. It is, however, worth noting that evidence in favour of proposed structures for homo- (Fig. 1a, Refs.^{6c,7}) and hetero- (Fig. 1b, Refs.^{6c,d}) bimetallic complexes are available in the literature^{6,7}. It may be noted, that compounds containing many alkoxo and/or

Table 3. NMR data (δ, ppm) for oxovanadium(v) complexes (1)-(6)

Complex	¹ H ^a	⁵¹ V
1	1.24 (24H, s, CMe ₂); 1.60 (8H, s, CH ₂); 2.21 (1H, br, OH)	-679
2	1.20 (36H, br, CMe ₂ + OCHMe ₂); 1.60 (8H, s, CH ₂); 4.02 (2H, m, OCHMe ₂)	-682
3	1.20 (24H, s, CMe ₂); 1.27 (18H, d, J 6 Hz, HCMe ₂); 1.58 (8H, s, CH ₂); 4.80 (3H, m, OCHMe ₂)	-664
4	1.23 (48H, d, CMe ₂ + OCHMe ₂); 1.61 (8H, s, CH ₂); 4.12 (4H, m, OCHMe ₂)	-665
5	1.23 (24H, s, CMe ₂); 1.57 (8H, s, CH ₂); 3.19 (9H, s, OCH ₃)	-683
6	1.22 (24H, s, CMe ₂); 1.37 (27H, s, CMe ₃); 1.62 (8H, s, CH ₂)	-680

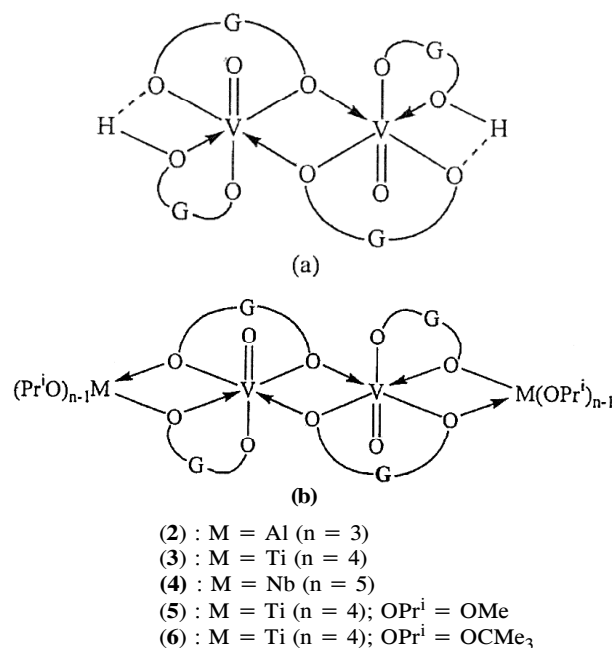
^as = singlet, d = doublet, m = multiplet, br = broad.

plexes (2)-(4) exhibit singlets at δ 1.20-1.23 for CMe₂ and at 1.60 ± 0.2 for CH₂ protons. The isopropoxy group protons CHMe₂ and CHMe₂ appear as a doublet and a multiplet, respectively at δ 1.20 ± 0.5 and 4.07 ± 0.05.

The ¹³C NMR spectrum of 2,5-dimethyl-2,5-hexanediol shows signals at δ 29.4 (CH₃), 37.7 (CH₂), and 70.5 (C-O), whereas these signals in the complex (1) appear at δ 29.8, 30.0 (CH₃); 38.2, 38.6 (CH₂); 70.9, 72.3 (C-O). The complex (2) also exhibits signals due to OPrⁱ groups at δ 25.9 (CH₃) and 64.8 (OCHMe₂) along with the signals due to glycolate moiety at 29.8, 30.0 (CH₃); 38.3, 38.6 (CH₂); 71.0, 72.6 (C-O).

Derivative (2) shows a broad (ω_{1/2} = 188 Hz) ²⁷Al NMR signal at δ 48 ppm, which is characteristic of four-coordinate²⁵ aluminium compounds.

The observed ⁵¹V NMR signals in the complexes (1)-(6) in the δ -664 to -683 range, are characteristic of dimeric oxovanadium(v) compounds involving six-coordinate⁸ vanadium atom (Fig. 1).

**Fig. 1.** Plausible structures (a) for (1) and (b) for (2), (3), (4), (5) and (6).

similar groups are often not amenable to characterization by X-ray crystallography, due to some inherent difficulties^{5,26} (e.g. twinning, plasticity, and loss of crystallinity) associated with them. Under these circumstances, based on molecular weight determinations and spectroscopic studies, the envisaged structures in Fig. 1 appear to be more convincing.

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