

Synthesis and spectroscopic properties of homo- and heterobimetallic complexes of oxovanadium(V)[†]

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Abstract. Equimolar interaction of $\text{VO}(\text{OPr}^i)_3$ with N-phenyldiethanolamine (H_2L) affords the dimeric complex $[\text{VO}(\text{L})(\text{m-OPr}^i)]_2$ (**1**), which on reaction with different glycols yields a new class of oxovanadium(V) complexes of the type: $\text{VO}(\text{L})(\text{OGO})$ (where $\text{L} = \text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH}_2\text{O}^-)_2$ and $\text{G} = \text{G}^1$ ($\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$) **2**, G^2 ($\text{CHMeCH}_2\text{CMe}_2$) **3**, G^3 ($\text{CH}_2\text{CMe}_2\text{CH}_2$) **4**, G^4 ($\text{CH}_2\text{CEt}_2\text{CH}_2$) **5**, G^5 (CHMeCHMe) **6**, G^6 (CMe_2CMe_2) **7**), featuring N-phenyldiethanolamine and glycolate moieties. Complexes (**2**)–(**7**) react with $\text{Al}(\text{OPr}^i)_3$ to afford novel heterobimetallic coordination complexes of the type: $\text{VO}(\text{L})\{\text{OGO}\}\text{Al}(\text{OPr}^i)_2$ ($\text{G} = \text{G}^1\text{--}\text{G}^6$). All these complexes have been characterised by elemental analyses and molecular weight measurements. Spectroscopic (IR, UV–Vis and (^1H , ^{27}Al , ^{51}V) NMR) properties of the new complexes have been investigated and their plausible structures suggested.

Keywords. Mixed-ligand complexes; oxovanadium(V) complexes; metalloligands; heterobimetallic complexes; spectroscopic studies.

1. Introduction

Recent work in our laboratory has involved the synthesis of heterometallic alkoxide coordination compounds featuring deprotonated forms of polyhydroxy ligands, such as glycols, di- and tri-ethanolamines as well as those of simple alcohols.^{1–5}

There are many motivations for the preparations of such heterobimetallic complexes, not the least of which is the beauty of structure that such complexes display.^{1,6–8} However, a more theoretical and major objective has been the search for new examples of complexes whose structures can be easily predicted with the help of spectroscopic data. Another attractive feature of such mixed-ligand complexes is their potential as precursors^{1,2,6} for the syntheses of novel mixed-metal oxides.

In view of the above, we report in this paper the syntheses and spectroscopic properties of a new series of homo- and heterobimetallic complexes of oxovanadium(V), featuring N-phenyldiethanolamine, glycolate, and isopropoxo groups.

2. Experimental

All syntheses and manipulations were performed under moisture-free environment using oven-dried (150–200°C) glassware fitted with interchangeable quickfit joints. Analytical (Merck, India) grade solvents were dried and purified by the literature methods.^{3,5,9} N-Phenyldiethanolamine and glycols (Aldrich) were completely dried by refluxing over $\text{Al}(\text{OPr}^i)_3$ followed by distillation (°C/mm Hg): N-Phenyldiethanolamine, H_2L (160/1.0); 2,5-dimethyl-2,5-hexanediol, HOG^1OH (80/0.1); 2-methyl-2,4-pentanediol, HOG^2OH (178/756); 2,2-dimethyl-1,3-propanediol, HOG^3OH (92/0.4); 2,2-diethyl-1,3-propanediol, HOG^4OH (92/0.4); 2,3-butanediol, HOG^5OH (180/756); 2,3-dimethyl-2,3-butanediol, HOG^6OH (176/756). $[\text{VO}(\text{L})(\text{OPr}^i)]_2$ (**1**) was prepared by the literature method.³

$\text{VO}(\text{OPr}^i)_3$ ¹⁰ and $\text{Al}(\text{OPr}^i)_3$ ¹¹ were prepared by the methods reported in the literature. Vanadium was determined by redox titration method.¹² Aluminium was determined gravimetrically as oxinate.¹³ Nitrogen was estimated by Kjeldahl's method.¹³ Isopropyl alcohol in the azeotrope was determined by oxidimetric method.¹⁴

Infrared spectra were recorded on a Nicolet Magna 550 spectrophotometer as nujol mulls or KBr

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[†]Dedicated to the memory of our mentor, the late Prof. R C Mehrotra

pellets. ^1H (300-40 MHz, CDCl_3 , TMS), ^{27}Al (78-18 MHz, CDCl_3 , $\text{Al}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), and ^{51}V (78-90 MHz, CDCl_3 , VOCl_3) NMR spectra were recorded on JEOL AL300 FT-NMR spectrometer. Microelemental (C, H, and N) analyses were performed on a Perkin-Elmer Series II CHNS/O analyser.

2.1 Synthesis of homometallic oxovanadium(V) precursor complexes (2)–(7)

Oxovanadium(V) N-phenyldiethanolamine-isopropoxide $[\text{VO}(\text{L})(\text{OPr}^i)]_2$ has been prepared³ by the equimolar reaction of $\text{VO}(\text{OPr}^i)_3$ with N-phenyldiethanolamine (H_2L), under refluxing conditions in benzene. Homometallic oxovanadium(V) N-phenyldiethanolamine-glycolate complexes $\text{VO}(\text{L})(\text{OGO}H)$ **2**–**7** were prepared by the reactions of **1** with different glycols. Due to the similarity in synthetic procedures for **(2)**–**(7)**, details of only one typical complex **(2)** is described herein.

2.1a $\text{VO}(\text{L})(\text{OG}^1\text{OH})$ (**2**): To a red benzene (40 ml) solution of **1** (3.55 g, 5.82 mmol) was added 2,5-dimethyl-2,5-hexanediol, HOG^1OH (1.70 g, 11.62 mmol) and the resulting wine-red solution was refluxed under a fractionating column (10 cm), followed by continuous azeotropic removal of the liberated isopropyl alcohol. When the required amount of isopropyl alcohol (0.70 g) was removed as an azeotrope and further distillate showed negligible presence of oxidisable species, refluxing was stopped and the reaction mixture was allowed to cool to room (30°C) temperature for 8 h, during which an orange solid compound **(2)** crystallised out. Supernatant liquid was decanted off and residue was dried under reduced (10 mm Hg) pressure to obtain an orange solid compound **(2)** in 3.59 g (80%) yield, m.p., 105°C. Analysis – Calcd. for $\text{C}_{18}\text{H}_{30}\text{NO}_5\text{V}$ (391) **2**: C, 55.23; H, 7.72; N, 3.58; V, 13.01%. Found: C, 55.06; H, 7.73; N, 3.40; V, 12.97%. Mol. wt., 402. IR (KBr, cm^{-1}): 3271 $\nu(\text{O-H})$; 2812 $\nu(\text{C-H})$; 1374, 1234 $\nu(\text{C-N})$; 1093, 1078, 1062 $\nu(\text{C-O})$; 961 $\nu(\text{V=O})$; 733, 702 $\delta(\text{C}_6\text{H}_5)$; 554 $\nu(\text{V-O})$; 523 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.24 (s, 12H, OCMe_2); 1.80 (s, 4H, CH_2); 2.05 (s, 1H, CMe_2OH); 3.59 (m, 4H, NCH_2); 3.87 (m, 4H, CH_2O); 6.71–7.32 (m, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –550.8.

Complexes **3**–**7** were also prepared by methods similar to that adopted for the synthesis of **2**. Preparative, analytical, and spectroscopic details are given below.

2.1b $\text{VO}(\text{L})(\text{OG}^2\text{OH})$ (**3**) [prepared from **1** (3.80 g, 6.22 mmol); HOG^2OH (1.47 g, 12.44 mmol)]: Black solid, m.p., 97–100°C. Yield: 3.17 g (70%). Analysis – Calcd. for $\text{C}_{16}\text{H}_{26}\text{NO}_5\text{V}$ (363): C, 52.88; H, 7.21; N, 3.85; V, 14.02%. Found: C, 52.69; H, 7.14; N, 3.78; V, 13.94%. PrⁱOH found: 0.73 g (Calcd., 0.73 g). Mol. wt., 377. IR (nujol, cm^{-1}): 3280 $\nu(\text{O-H})$; 2843 $\nu(\text{C-H})$; 1374, 1230 $\nu(\text{C-N})$; 1140, 1109, 1078 $\nu(\text{C-O})$; 957 $\nu(\text{V=O})$; 725, 704 $\delta(\text{C}_6\text{H}_5)$; 570 $\nu(\text{V-O})$; 539 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.23 (m, 9H, $\text{OCMe}_2 + \text{CHMe}$); 1.65 (s, 2H, CH_2); 2.15 (s, 1H, CMe_2OH); 3.55 (m, 4H, NCH_2); 3.78 (br, 4H, CH_2O); 4.20 (m, 1H, OCHMe); 6.70–7.30 (m, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –550.7.

2.1c $\text{VO}(\text{L})(\text{OG}^3\text{OH})$ (**4**) [prepared from **1** (3.31 g, 5.42 mmol); HOG^3OH (1.13 g, 10.85 mmol)]: Black solid, m.p., 98–100°C. Yield: 2.92 g (77%). Analysis – Calcd. for $\text{C}_{15}\text{H}_{24}\text{NO}_5\text{V}$ (349): C, 51.57; H, 6.92; N, 4.01; V, 14.58%. Found: C, 51.34; H, 6.66; N, 3.89; V, 14.51%. PrⁱOH found: 0.65 g (Calcd., 0.65 g). Mol. wt., 340. IR (nujol, cm^{-1}): 3291 $\nu(\text{O-H})$; 2851 $\nu(\text{C-H})$; 1382, 1220 $\nu(\text{C-N})$; 1073, 1055 $\nu(\text{C-O})$; 963 $\nu(\text{V=O})$; 727, 711 $\delta(\text{C}_6\text{H}_5)$; 563 $\nu(\text{V-O})$; 516 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 0.95 (s, 6H, CMe_2); 3.35 (br, 1H, CH_2OH); 3.57 (m, 4H, NCH_2); 3.80 (m, 4H, CH_2O); 4.35 (s, 4H, CH_2O); 6.73–7.26 (m, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –540.2.

2.1d $\text{VO}(\text{L})(\text{OG}^4\text{H})$ (**5**) [prepared from **1** (4.04 g, 6.62 mmol); HOG^4OH (1.74 g, 13.24 mmol)]: Black solid, m.p., 95–96°C. Yield: 3.59 g (72%). Analysis – Calcd. for $\text{C}_{17}\text{H}_{28}\text{NO}_5\text{V}$ (377): C, 54.10; H, 7.48; N, 3.71; V, 13.50%. Found: C, 53.85; H, 7.29; N, 3.58; V, 13.32%. PrⁱOH found: 0.77 g (Calcd., 0.79 g). Mol. wt., 381. IR (nujol, cm^{-1}): 3287 $\nu(\text{O-H})$; 2843 $\nu(\text{C-H})$; 1381, 1215 $\nu(\text{C-N})$; 1078, 1046 $\nu(\text{C-O})$; 953 $\nu(\text{V=O})$; 730, 707 $\delta(\text{C}_6\text{H}_5)$; 562 $\nu(\text{V-O})$; 509 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 0.85 (s, 6H, CH_2Me); 1.27 (br, 4H, CH_2Me); 2.18 (s, 1H, CH_2OH); 3.60 (m, 4H, CH_2O); 3.87 (br, 8H, CH_2O); 6.74–7.37 (m, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –530.7.

2.1e $\text{VO}(\text{L})(\text{OG}^5\text{H})$ (**6**) [prepared from **1** (2.27 g, 3.72 mmol); HOG^5OH (0.67 g, 7.43 mmol)]: Black solid, m.p., 95–97°C. Yield: 1.89 g (76%). Analysis – Calcd. for $\text{C}_{14}\text{H}_{22}\text{NO}_5\text{V}$ (333): C, 50.15; H, 6.61; N, 4.18; V, 15.19%. Found: C, 50.19; H, 6.33; N, 4.07; V, 15.02%. PrⁱOH found: 0.44 g (Calcd., 0.44 g).

Mol. wt., 353. IR (nujol, cm^{-1}): 3296 $\nu(\text{O-H})$; 2828 $\nu(\text{C-H})$; 1380, 1219 $\nu(\text{C-N})$; 1084, 1016 $\nu(\text{C-O})$; 955 $\nu(\text{V=O})$; 718, 696 $\delta(\text{C}_6\text{H}_5)$; 566 $\nu(\text{V-O})$; 515 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.20 (*m*, 6H, CHMe); 2.06 (*m*, 1H, CHMeOH); 3.60 (*m*, 4H, NCH_2); 3.87 (*m*, 4H, CH_2O); 4.25 (*m*, 2H, OCHMe); 6.74–7.41 (*m*, 5H, aromatic- $\underline{\text{H}}$). ^{51}V NMR (CDCl_3 ; **d**, ppm): –534.6.

2.1f $\text{VO}(\text{L})(\text{OG}^6\text{H})$ (**7**) [prepared from **1** (2.79 g, 4.57 mmol); HOG^6OH (1.08 g, 9.14 mmol)]: Black solid, m.p., 100–102°C. Yield: 2.16 g (65%). Analysis – Calcd. for $\text{C}_{16}\text{H}_{26}\text{NO}_5\text{V}$ (363): C, 52.88; H, 7.21; N, 3.85; V, 14.02%. Found: C, 52.45; H, 6.91; N, 3.76; V, 13.98%. Pr^iOH found: 0.55 g (Calcd., 0.55 g). Mol. wt., 376. IR (nujol, cm^{-1}): 3299 $\nu(\text{O-H})$; 2831 $\nu(\text{C-H})$; 1374, 1221 $\nu(\text{C-N})$; 1098, 1060 $\nu(\text{C-O})$; 957 $\nu(\text{V=O})$; 720, 700 $\delta(\text{C}_6\text{H}_5)$; 560 $\nu(\text{V-O})$; 511 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.23 (*s*, 12H, OCMe_2); 1.82 (*s*, 1H, CMe_2OH); 3.58 (*m*, 4H, NCH_2); 3.89 (*m*, 4H, CH_2O); 6.77–7.31 (*m*, 5H, aromatic- $\underline{\text{H}}$). ^{51}V NMR (CDCl_3 ; **d**, ppm): –528.0.

2.2 Synthesis of heterobimetallic oxovanadium(V) complexes (**8**)–(**13**)

Heterobimetallic complexes **8**–**13** have been prepared by the reactions of homometallic precursor complexes **2**–**7** with $\text{Al}(\text{OPr}^i)_3$. Due to similarity in the preparative procedures for the complexes **8**–**13**, details of only a typical complex (**8**) are described below.

2.2a *Synthesis of $\text{VO}(\text{L})\{\text{OG}^1\text{O}\}\text{Al}(\text{OPr}^i)_2$ (**8**)*: An orange-red benzene (20 ml) solution of **2** (1.92 g, 4.90 mmol) and $\text{Al}(\text{OPr}^i)_3$ (1.00 g, 4.89 mmol) was stirred at room temperature (30°C) for 4 h. Volatile components from the solution were removed under reduced pressure to yield a brown solid (2.59 g, 99%). Recrystallisation from a 1 : 2 mixture of dichloromethane and *n*-hexane at –20°C afforded analytically pure compound (**8**) as a brown solid in 1.89 g (72%) yield, m.p., 109–111°C. Analysis – Calcd. for $\text{C}_{24}\text{H}_{43}\text{AlNO}_7\text{V}$ (535) **8**: C, 53.82; H, 8.09; N, 2.61; Al, 5.04; V, 9.51%. Found: C, 53.70; H, 8.15; N, 2.48; Al, 5.01; V, 9.46%. Mol. wt., 540. IR (nujol, cm^{-1}): 2796 $\nu(\text{C-H})$; 1382, 1225 $\nu(\text{C-N})$; 1195, 1148 $\nu(\text{OPr}^i)$; 1117, 1054 $\nu(\text{C-O})$; 961 $\nu(\text{V=O})$; 726, 700 $\delta(\text{C}_6\text{H}_5)$; 617 $\nu(\text{Al-O})$; 562 $\nu(\text{V-O})$; 531 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.22 (*d*, $J = 6.04$ Hz, 12H, OCHMe_2); 1.25 (*s*, 12H, OCMe_2); 1.65 (*m*, 4H, CH_2); 3.62 (*br*, 4H, NCH_2); 4.05 (*m*,

4H, CH_2O); 4.23 (*m*, 2H, OCHMe_2); 6.70–7.40 (*m*, 5H, aromatic- $\underline{\text{H}}$). ^{51}V NMR (CDCl_3 ; **d**, ppm): –560.0. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 53.70.

Preparative, analytical, and spectroscopic details of compounds **9**–**13** prepared by the procedure described for **8** are given below.

2.2b $\text{VO}(\text{L})\{\text{OG}^2\text{O}\}\text{Al}(\text{OPr}^i)_2$ (**9**) [prepared from **3** (0.98 g, 2.70 mmol); $\text{Al}(\text{OPr}^i)_3$ (0.55 g, 2.69 mmol)]: Black solid, m.p., 110–113°C. Yield: 0.96 g (70%). Analysis – Calcd. for $\text{C}_{22}\text{H}_{39}\text{AlNO}_7\text{V}$ (507): C, 52.06; H, 7.74; N, 2.76; Al, 5.32; V, 10.04%. Found: C, 51.79; H, 7.67; N, 2.61; Al, 5.18; V, 9.83%. Mol. wt., 518. IR (nujol, cm^{-1}): 2815 $\nu(\text{C-H})$; 1377, 1217 $\nu(\text{C-N})$; 1178, 1130 $\nu(\text{OPr}^i)$; 1078, 1043 $\nu(\text{C-O})$; 963 $\nu(\text{V=O})$; 730, 711 $\delta(\text{C}_6\text{H}_5)$; 633 $\nu(\text{Al-O})$; 551 $\nu(\text{V-O})$; 510 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.25 (*m*, 21H, $\text{OCMe}_2 + \text{OCHMe} + \text{OCHMe}_2$); 1.66 (*s*, 2H, CH_2); 3.60 (*m*, 4H, NCH_2); 4.03 (*m*, 4H, CH_2O); 4.27 (*m*, 3H, $\text{OCHMe} + \text{OCHMe}_2$); 6.70–7.44 (*m*, 5H, aromatic- $\underline{\text{H}}$). ^{51}V NMR (CDCl_3 ; **d**, ppm): –557.8. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 54.31.

2.2c $\text{VO}(\text{L})\{\text{OG}^3\text{O}\}\text{Al}(\text{OPr}^i)_2$ (**10**) [prepared from **4** (0.85 g, 2.70 mmol); $\text{Al}(\text{OPr}^i)_3$ (0.50 g, 2.44 mmol)]: Black solid, m.p., 106–107°C. Yield: 0.79 g (66%). Analysis – Calcd. for $\text{C}_{21}\text{H}_{37}\text{AlNO}_7\text{V}$ (493): C, 51.10; H, 7.56; N, 2.84; Al, 5.47; V, 10.32%. Found: C, 51.00; H, 7.41; N, 2.82; Al, 5.29; V, 10.20%. Mol. wt., 499. IR (nujol, cm^{-1}): 2823 $\nu(\text{C-H})$; 1370, 1211 $\nu(\text{C-N})$; 1181, 1146 $\nu(\text{OPr}^i)$; 1082, 1037 $\nu(\text{C-O})$; 971 $\nu(\text{V=O})$; 730, 714 $\delta(\text{C}_6\text{H}_5)$; 620 $\nu(\text{Al-O})$; 560 $\nu(\text{V-O})$; 523 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 0.93 (*s*, 6H, CMe_2); 1.21 (*d*, 12H, OCHMe_2); 3.59 (*m*, 4H, NCH_2); 3.93 (*m*, 4H, CH_2O); 4.15 (*m*, 2H, OCHMe_2); 4.51 (*br*, 4H, CH_2O); 6.74–7.40 (*m*, 5H, aromatic- $\underline{\text{H}}$). ^{51}V NMR (CDCl_3 ; **d**, ppm): –534.6. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 52.06.

2.2d $\text{VO}(\text{L})\{\text{OG}^4\text{O}\}\text{Al}(\text{OPr}^i)_2$ (**11**) [prepared from **5** (1.07 g, 2.83 mmol); $\text{Al}(\text{OPr}^i)_3$ (0.58 g, 2.84 mmol)]: Black solid, m.p., 114–116°C. Yield: 0.96 g (65%). Analysis – Calcd. for $\text{C}_{23}\text{H}_{41}\text{AlNO}_7\text{V}$ (521): C, 52.96; H, 7.92; N, 2.62; Al, 5.17; V, 9.77%. Found: C, 52.70; H, 7.63; N, 2.54; Al, 5.06; V, 9.67%. Mol. wt., 549. IR (nujol, cm^{-1}): 2835 $\nu(\text{C-H})$; 1374, 1220 $\nu(\text{C-N})$; 1169, 1132 $\nu(\text{OPr}^i)$; 1076, 1031 $\nu(\text{C-O})$; 957 $\nu(\text{V=O})$; 727, 706 $\delta(\text{C}_6\text{H}_5)$; 641 $\nu(\text{Al-O})$; 557 $\nu(\text{V-O})$; 516 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 0.85 (*s*, 6H, CH_2Me); 1.21 (*d*, $J = 6.05$ Hz, 12H, OCHMe_2); 1.27 (*m*, 4H, CH_2Me);

3.61 (*m*, 4H, NCH_2); 3.92 (*m*, 4H, CH_2O); 4.10 (*m*, $J = 6.05$ Hz, 2H, OCHMe_2); 4.24 (*br*, 4H, CH_2O); 6.77–7.36 (*m*, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –534.8. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 49.82.

2.2e $\text{VO}(\text{L})\{(\text{OG}^5\text{O})\text{Al}(\text{OPr}^i)_2\}$ (**12**) [prepared from **6** (0.72 g, 2.15 mmol); $\text{Al}(\text{OPr}^i)_3$ (0.44 g, 2.15 mmol)]: Black solid, m.p., 117–120°C. Yield: 0.71 g (69%). Analysis – Calcd. for $\text{C}_{20}\text{H}_{35}\text{AlNO}_7\text{V}$ (479): C, 50.09; H, 7.36; N, 2.92; Al, 5.62; V, 10.62%. Found: C, 49.79; H, 7.41; N, 2.75; Al, 5.39; V, 10.42%. Mol. wt., 493. IR (nujol, cm^{-1}): 2820 $\nu(\text{C-H})$; 1380, 1231 $\nu(\text{C-N})$; 1173, 1129 $\nu(\text{OPr}^i)$; 1086, 1061 $\nu(\text{C-O})$; 953 $\nu(\text{V=O})$; 722, 701 $\delta(\text{C}_6\text{H}_5)$; 636 $\nu(\text{Al-O})$; 567 $\nu(\text{V-O})$; 518 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.24 (*m*, 18H, $\text{OCHMe} + \text{OCHMe}_2$); 3.60 (*t*, 4H, NCH_2); 4.00 (*m*, 4H, CH_2O); 4.68 (*br*, 4H, $\text{OCHMe} + \text{OCHMe}_2$); 6.88–7.29 (*m*, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –535.6. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 47.21.

2.2f $\text{VO}(\text{L})\{(\text{OG}^6\text{O})\text{Al}(\text{OPr}^i)_2\}$ (**13**) [prepared from **7** (1.55 g, 4.27 mmol); $\text{Al}(\text{OPr}^i)_3$ (0.87 g, 4.26 mmol)]: Black solid, m.p., 110–113°C. Yield: 1.23 g (61%). Analysis – Calcd. for $\text{C}_{22}\text{H}_{39}\text{AlNO}_7\text{V}$ (507): C, 52.06; H, 7.74; N, 2.76; Al, 5.32; V, 10.04%. Found: C, 52.12; H, 7.61; N, 2.49; Al, 5.29; V, 9.93%. Mol. wt., 521. IR (nujol, cm^{-1}): 2821 $\nu(\text{C-H})$; 1370, 1213 $\nu(\text{C-N})$; 1179, 1133 $\nu(\text{OPr}^i)$; 1087, 1043 $\nu(\text{C-O})$; 961 $\nu(\text{V=O})$; 731, 708 $\delta(\text{C}_6\text{H}_5)$; 629 $\nu(\text{Al-O})$; 560 $\nu(\text{V-O})$; 524 $\nu(\text{V} \leftarrow \text{N})$. ^1H NMR (CDCl_3 ; **d**, ppm): 1.22 (*br*, 24H, $\text{OCMe}_2 + \text{OCHMe}_2$); 3.62 (*t*, 4H, NCH_2); 3.96 (*m*, 4H, CH_2O); 4.21 (*m*, 2H, OCHMe_2); 6.75–7.36 (*m*, 5H, aromatic-H). ^{51}V NMR (CDCl_3 ; **d**, ppm): –540.2. ^{27}Al NMR (CDCl_3 ; **d**, ppm): 52.06.

3. Results and discussion

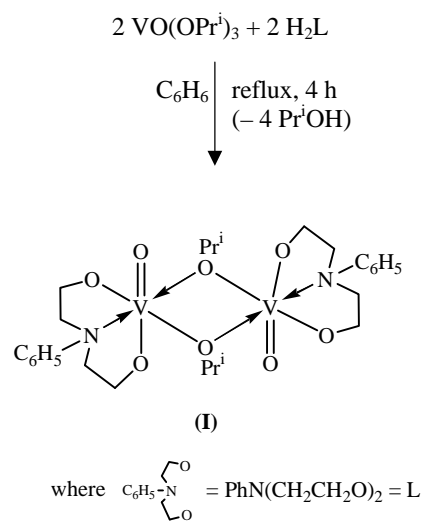
Equimolar reaction of $\text{VO}(\text{OPr}^i)_3$ with N-phenyl-diethanolamine yields $[\text{VO}(\text{L})(\text{OPr}^i)]_2$ (**1**) (scheme 1).

Reactions of **1** with different glycols in 1 : 2 molar ratio afford oxovanadium(V) N-phenyldiethanolamine-glycolate complexes **2–7** (scheme 2).

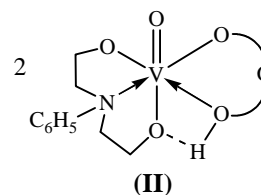
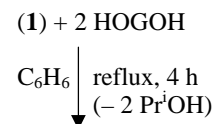
The precursor complexes **2–7** on reactions in 1 : 1 molar ratio with $\text{Al}(\text{OPr}^i)_3$ at room (30°C) temperature yield a new class of heterobimetallic mixed-ligands alkoxide complexes **8–13** (scheme 3).

The new complexes (when freshly prepared) are either brown or black solids (see §2) and soluble in common organic (e.g., benzene, toluene, tetrahydrofuran, dichloromethane, chloroform) solvents. Com-

plex **1** is dimeric, whereas **2–13** exhibit monomeric nature in benzene solutions.

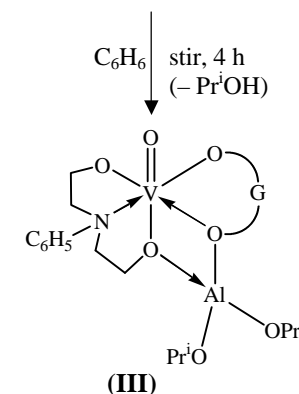


Scheme 1.



where $\text{G} = \text{G}^1$ ($\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$) (**2**); G^2 ($\text{CHMeCH}_2\text{CMe}_2$) (**3**); G^3 ($\text{CH}_2\text{CMe}_2\text{CH}_2$) (**4**); G^4 ($\text{CH}_2\text{CEt}_2\text{CH}_2$) (**5**); G^5 (CHMeCHMe) (**6**); G^6 (CMe_2CMe_2) (**7**)

Scheme 2.



$\text{G} = \text{G}^1$, (**8**); G^2 , (**9**); G^3 , (**10**); G^4 , (**11**); G^5 , (**12**); G^6 , (**13**)

Scheme 3.

3.1 IR spectra

Homometallic complexes **2–7** show infrared absorption bands characteristic of metal attached organic groups (see §2). For example, homometallic complexes **2–7** show broad absorption bands due to hydrogen-bonded $\nu(\text{O–H})$ groups at $3285 \pm 14 \text{ cm}^{-1}$, along with absorptions for aromatic¹⁵ and aliphatic¹⁶ $\nu(\text{C–N})$ amino groups at 1376 ± 6 and $1222 \pm 12 \text{ cm}^{-1}$ respectively. These bands show a lowering of $\sim 20 \text{ cm}^{-1}$ in comparison to that observed in the parent H_2L ligand. Such lowering in wave numbers may be due to the formation of $\text{N} \rightarrow \text{V}$ dative bond (structure II). Strong bands at 1085 ± 13 and $1039 \pm 13 \text{ cm}^{-1}$ are assignable to $\nu(\text{C–O})$ vibrations. Complexes **2, 3**, and **7** also exhibit strong bands at $1116 \pm 23 \text{ cm}^{-1}$ for $\nu(\text{C–O})$ of tertiary alcoholic group¹⁷. Strong bands at $958 \pm 5 \text{ cm}^{-1}$ in the complexes **2–7** are characteristic of $\nu(\text{V=O})$ vibrations, in six-coordinated^{18–21} oxovanadium(V) complexes. Variable intensity bands at 562 ± 8 and $524 \pm 15 \text{ cm}^{-1}$ may be assigned to $\nu(\text{V–O})$ ²² and $\nu(\text{V} \leftarrow \text{N})$ vibrations, respectively.

Heterobimetallic complexes **8–13** show bands for deprotonated N-phenyldiethanolamine and glycols in the expected region as found in homometallic complexes **2–7** (see §2). As expected the band due to $\nu(\text{O–H})$ vibration is absent in heterobimetallic derivatives. Strong to medium intensity bands at 1182 ± 13 and $1139 \pm 9 \text{ cm}^{-1}$ are characteristic of metal-attached isopropoxy groups. Appearance of strong bands in the $953\text{--}971 \text{ cm}^{-1}$ region for $\nu(\text{V=O})$ in these complexes is consistent with six-coordinate oxovanadium(V) complexes (structure III). The variable intensity bands for $\nu(\text{Al–O})$, $\nu(\text{V–O})$, and $\nu(\text{V} \leftarrow \text{N})$ vibrations appear at 629 ± 12 , 559 ± 8 , and $520 \pm 11 \text{ cm}^{-1}$, respectively.

3.2 NMR spectra

¹H NMR spectra of complexes **2–7** (see §2) exhibit signals due to N-phenyldiethanolamine and mono-deprotonated glycolate moieties in the expected regions. Some salient features of ¹H NMR studies are (i) the appearance of broad signals in the δ 1.82–3.35 ppm region for hydrogen-bonded O–H protons, (ii) multiplets due to phenyl group protons are slightly downfield shifted by $\sim \delta$ 0.10 ppm with respect to N-phenyldiethanolamine. This observation may be taken as an indication of the involvement of amino nitrogen in the formation of intramolecular

$\text{N} \rightarrow \text{V}$ dative bond, and (iii) the signals due to NCH_2 and CH_2O protons in all of these complexes are slightly downfield shifted.

Heterobimetallic complexes **8–13** show signals (see §2) characteristic of N-phenyldiethanolamine, glycolate and isopropoxy groups. The broad signals due to O–H protons are absent in these complexes. A doublet (OCHMe_2) and a multiplet (OCHMe_2) characteristic of metal attached isopropoxy groups appear at δ 1.23 ± 0.02 and 4.39 ± 0.29 ppm, respectively. However, multiplets are observed instead of expected doublets for methyl protons of the isopropoxy groups in complexes **9, 12**, and **13** due to the overlap of signals arising from methyl groups of glycolate moieties. Positions of signals due to other groups remain almost unaltered.

⁵¹V NMR spectra of the complexes **2–13** exhibit sharp signals at δ -544 ± 16 ppm, consistent with vanadium in six-coordinate^{23–26} environment (Structure III).²⁷ Al NMR spectra of **8–13** show broad ($w_{1/2} = 160 \pm 20$ Hz) signals at δ 50.76 ± 3.55 ppm, consistent with four-coordinate^{7,27} aluminium complexes (structure III).

3.3 Electronic spectra

The electronic spectra of the freshly prepared complexes show an intense band in the 360–390 nm region along with a much weaker band/shoulder at 460–470 nm, which may be assigned to the ligand to metal charge transfer transitions.^{23,28–30}

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