

Synthesis, Reactivity, and X-ray Crystal Structure of Some Mixed-Ligand Oxovanadium(V) Complexes: First Report of Binuclear Oxovanadium(V) Complexes Containing 4,4'-Bipyridine Type Bridge

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Reaction of the tridentate ONO Schiff-base ligand 2-hydroxybenzoylhydrazone of 2-hydroxybenzoylhydrazine (H_2L) with $VO(acac)_2$ in ethanol medium produces the oxoethoxovanadium(V) complex $[VO(OEt)L]$ (**A**), which reacts with pyridine to form $[VO(OEt)L \cdot (py)]$ (**1**). Complex **1** is structurally characterized. It has a distorted octahedral O_4N_2 coordination environment around the V(V) acceptor center. Both complexes **A** and **1** in ethanol medium react with neutral monodentate Lewis bases 2-picoline, 3-picoline, 4-picoline, 4-amino pyridine, imidazole, and 4-methyl imidazole, all of which are stronger bases than pyridine, to produce dioxovanadium(V) complexes of general formula $BH[VO_2L]$. Most of these dioxo complexes are structurally characterized, and the complex anion $[VO_2L]^-$ is found to possess a distorted square pyramidal structure. When a solution/suspension of a $BH[VO_2L]$ complex in an alcohol (ROH) is treated with HCl in the same alcohol, it is converted into the corresponding monooxoalkoxo complex $[VO(OR)L]$, where R comes from the alcohol used as the reaction medium. Both complexes **A** and **1** produce the 4,4'-bipyridine-bridged binuclear complex $[VO(OEt)L]_2(\mu-4,4'-bipy)$ (**2**), which, to the best of our knowledge, represents the first report of a structurally characterized 4,4'-bipyridine-bridged oxovanadium(V) binuclear complex. Two similar binuclear oxovanadium(V) complexes **3** and **4** are also synthesized and characterized. All these binuclear complexes (**2–4**), on treatment with base B, produce the corresponding mononuclear dioxovanadium(V) complexes (**5–10**).

Introduction

Coordination chemistry of vanadium received a shot in the arm in recent times because of (a) the discovery of the presence of vanadium in some sea squirts,^{1,2} mushrooms,^{3,4} and the vanadium-dependent enzymes nitrogenases⁵ and haloperoxidases;⁶ (b) the involvement of vanadium in the

inhibition of phosphate-metabolizing enzymes⁷ and stimulation of phosphomutases;⁸ (c) anticancer activity;⁹ (d) insulin-mimetic activity¹⁰ of some vanadium(IV) and (V) complexes; and (e) the catalytic activity of vanadium(V) complexes in some N–O donor ligands in α -olifine polymerization.¹¹ Works on V(V) complexes of ONO Schiff bases in general are well-reported in the recent litera-

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- (1) Frank, P.; Carlson, R. M. K.; Carlson, E. J.; Hodgson, K. O. *J. Inorg. Biochem.* **2003**, *94*, 59–71.
- (2) Frank, P.; Carlson, R. M. K.; Carlson, E. J.; Hodgson, K. O. *Coord. Chem. Rev.* **2003**, *237*, 31–39.
- (3) Berry, R. E.; Armstrong, E. M.; Beddoes, R. L.; Collison, D.; Ertok, S. N.; Helliwell, M.; Garner, C. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 795–797.
- (4) (a) Kanamori, K. *Cord. Chem. Rev.* **2003**, *237*, 147–161. (b) Rehder, D. *Inorg. Chem. Commun.* **2003**, *6*, 604–617.
- (5) Eady, R. R. *Coord. Chem. Rev.* **2003**, *237*, 23–30 and references therein.

- (6) (a) Weyand, M.; Hecht, H.-J.; Kiess, M.; Liaud, M.-F.; Vilter, H.; Schomburg, D. *J. Mol. Biol.* **1999**, *293*, 595–611. (b) Carter-Franklin, J. N.; Parrish, J. D.; Tchirret-Guth, R. A.; Little, R. D.; Butler, A. *J. Am. Chem. Soc.* **2003**, *125*, 3688–3689. (c) Rehder, D.; Santoni, G.; Licini, G. M.; Schulzke, C.; Meier, B. *Coord. Chem. Rev.* **2003**, *237*, 53–63.
- (7) Stankiewicz, P. J.; Tracy, A. S.; Crans, D. S. In *Vanadium and its Role in Life, Metal Ions in Biological Systems*; Sigel, H., Sigel, A., Eds.; Marcel Dekker: New York, 1995; Vol. 31, Chapter 9.
- (8) Mendz, G. L. *Arch. Biochem. Biophys.* **1991**, *291*, 201–211.
- (9) (a) Liasko, R.; Cabanos, T. A.; Karkabounus, S.; Malamas, M.; Tasiopoulos, J. A.; Stefanou, D.; Collery, P.; Evangelou, A. *Anticancer Res.* **1998**, *18*, 3609. (b) Evangelou, A. *Crit. Rev. Oncol. Hematol.* **2002**, *42*, 249.

ture.^{12–24,26–28} Stable mononuclear V(V) complexes of such ONO donor ligands containing a coordinated alkoxide moiety are not so numerous.^{17,20,21,23,25,54}

- (10) (a) Sakurai, H.; Tsuchiya, K.; Nukatsuka, M.; Kawada, J.; Ishikawa, S.; Yoshida, H.; Komatsu, M. *J. Clin. Biochem. Nutr.* **1990**, *8*, 193–200. (b) Tapscott, R. E.; Belford, R. L. *Inorg. Chem.* **1967**, *6*, 735–743. (c) McNeill, J. H.; Yuen, V. G.; Hoveyda, H. R.; Orvig, C. *J. Med. Chem.* **1992**, *35*, 1489–1491. (d) Crans, D. C.; Mahroof-Tahir, M.; Shin, P. K.; Karamidas, A. D. *Mol. Cell. Biochem.* **1995**, *153*, 17. (e) Thompson, K. H.; Orvig, C. *Coord. Chem. Rev.* **2001**, *219*–221, 1033–1053. (f) Sakurai, H.; Kojima, Y.; Yoshikawa, Y.; Kawabe, K.; Yasui, H. *Coord. Chem. Rev.* **2002**, *226*, 187–198. (g) Dikanov, S. A.; Liboiron, B. D.; Orvig, C. *J. Am. Chem. Soc.* **2002**, *124*, 2969–2978. (h) Song, B.; Aebischer, N.; Orvig, C. *Inorg. Chem.* **2002**, *41*, 1357–1364. (i) Rehder, D.; Pessoa, J. C.; Geraldes, C. F. *J. Biol. Inorg. Chem.* **2002**, *7*, 675. (j) Crans, D. C.; Yang, L.; Alfano, J. A.; Chi, L. H.; Jin, W.; Mahroof-Tahir, M.; Robbins, K.; Toloue, M. M.; Chan, L. K.; Plante, A. J.; Grayson, R. Z.; Willsky, G. R. *Coord. Chem. Rev.* **2003**, *237*, 13–22.
- (11) (a) Wolff, F.; Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2003**, *42*, 7839–7845. (b) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257. (c) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357–364. (d) Gambartotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229–243. (e) Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2003**, *42*, 673–675.
- (12) (a) Crans, D. C.; Smei, J. J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A.; Meyer, T. J., Eds.; Elsevier: New York, 2004; Vol. 4, pp 175–239. (b) Carranon, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944–951.
- (13) Dai, J.; Akiyama, S.; Munakata, M.; Mikuriya, M. *Polyhedron* **1994**, *13*, 2495–2499.
- (14) Cornman, C. R.; Zovinka, E. P.; Boyajian, Y. D.; Geiser-Bush, K. M.; Boyle, P. D.; Singh, P. *Inorg. Chem.* **1995**, *34*, 4213–4219.
- (15) Schulz, D.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chim. Acta* **1995**, *240*, 217–219.
- (16) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
- (17) Wei, W.; Fu-Li, Z.; Xin, W.; Min-Yu, T. *Polyhedron* **1996**, *15*, 169–1703.
- (18) Schmidt, H.; Bashirpoor, M.; Rehder, D. *J. Chem. Soc., Dalton Trans.* **1996**, 3865–3870.
- (19) Asgedom, G.; Sreedhara, A.; Rao, C. P.; Kolehmainen, E. *Polyhedron* **1996**, *15*, 3731–3739.
- (20) Palacios, M. S.; Rocío, M. J.; Domínguez, S.; Gili, P.; Ruiz-Pérez, C.; Rodríguez-Romero, F. V.; Dance, J. M. *Polyhedron* **1997**, *16*, 1143–1147.
- (21) Rath, S. P.; Mondal, S.; Chakravorty, A. *Inorg. Chim. Acta* **1997**, *263*, 247–253.
- (22) Asgedom, G.; Sreedhara, A.; Kivikoski, J.; Valkonen, J.; Kolehmainen, E.; Rao, C. P. *Inorg. Chem.* **1996**, *35*, 5674–5683.
- (23) Tsiamis, C.; Voulgaropoulos, B.; Charistos, D.; Voutsas, G. P.; Kavounis, C. A. *Polyhedron* **2000**, *19*, 2003–2010.
- (24) Moon, M.; Pyo, M.; Myoung, Y. C.; Ahn, C.; Lah, M. S. *Inorg. Chem.* **2001**, *40*, 554–557.
- (25) Dinda, R.; Sengupta, P.; Ghosh, S.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 1684–1688 and references therein.
- (26) Grüning, C.; Schmidt, H.; Rehder, D. *Inorg. Chem. Commun.* **1999**, *2*, 57–59.
- (27) Maurya, M. R.; Khurana, S.; Schulzke, C.; Rehder, D. *Eur. J. Inorg. Chem.* **2001**, 779–788.
- (28) Kimblin, C.; Bu, X.; Butler, A. *Inorg. Chem.* **2002**, *41*, 161–163.
- (29) Chatterjee, M.; Wu, B. M.; Mak, T. C. W.; Ghosh, S. *Polyhedron* **1998**, *17*, 1369.
- (30) Chatterjee, M.; Nandi, A. K.; Ghosh, S. *Trans. Met. Chem.* **1999**, *24*, 183–185.
- (31) Maity, A.; Ghosh, S. *J. Inorg. Biochem.* **1989**, *36*, 131–139.
- (32) Maity, A.; Ghosh, S. *Proc.—Indian Acad. Sci., Chem. Sci.* **1992**, *104*, 369.
- (33) Crans, D. C. *J. Inorg. Biochem.* **2000**, *80*, 123–131.
- (34) Crans, D. C.; Yang, L.; Jakusch, T.; Kiss, T. *Inorg. Chem.* **2000**, *39*, 4409–4416.
- (35) Rowe, R. A.; Jones, M. M. *Inorg. Synth.* **1957**, *5*, 113.
- (36) Dinda, R. Ph.D. thesis, Jadavpur University, India, 2002.
- (37) Dutta, R. L.; Ghosh, S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 247.
- (38) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.
- (39) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.
- (40) Sheldrick, G. M. *SHELX86; Acta Crystallogr., Sect. A* **1990**, *46*, 467.
- (41) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 15.

In a continuation of our work on vanadium(IV) and (V) complexes of multidentate N–O donor ligands,^{25,29–32} we report the following findings in this work: (i) preparation, structural characterization, and exploration of the reactivity of the monooxoalkoxovanadium(V) complexes **A** and **I**, in which L^{2–} is the dianion of the tridentate ONO donor ligand; (ii) preparation and structural characterization of several BH-[VO₂L] type water soluble complexes, where B = 4-methylimidazole, imidazole, 2-picoline, 3-picoline, 4-picoline, and 4-amino pyridine; (iii) preparation and study of three binuclear vanadium(V) complexes in which N,N'-bidentate linear spacers such as 4,4'-bipyridine act as bridging ligands. Two of these binuclear complexes are structurally characterized by X-ray analysis. To the best of our knowledge, this is the first report of a structurally characterized 4,4'-bipyridine-bridged binuclear oxovanadium(V) complex. (iv) Reversible transformations involving monooxoalkoxo and dioxovanadium(V) complexes and the generation of different oxoalkoxovanadium(V) species from a single dioxo precursor under ambient conditions are also reported. Recent reports on insulin-mimetic activity^{33,34} by vanadium(V) complexes in some dianionic tridentate ONO ligands makes us optimistic about the possible insulin-mimetic behavior of our water-soluble complexes.

Experimental Section

Materials. [VO(acac)₂] was prepared as described in the literature³⁵ and is used as the source of vanadium, which is oxidized to vanadium(V) spontaneously under aerobic conditions.⁵⁴ Reagent-grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, obtained from commercial sources, and used without further purification. Spectroscopic-grade solvents were used for spectral measurements.

Synthesis of the Ligand H₂L. The Schiff-base ligand 2-hydroxybenzoylhydrazine of 2-hydroxybenzoylhydrazine (H₂L) was prepared by a previously reported procedure.²⁵ Yield: 70%. Mp: 170° C. Anal. Calcd for C₁₄H₁₂N₂O₃: C, 65.62; H, 4.72; N, 10.94. Found: C, 65.58; H, 4.64; N, 10.92. ¹H NMR (DMSO-d₆, δ):

- (42) Sheldrick, G. M. *SHELXL: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.
- (43) Farrugia, L. J. *ORTEP-3 for WINDOWS*; University of Glasgow: Glasgow, Scotland, 1999.
- (44) Perrin, D. D. *IUPAC Stability Constant of Metal-Ion Complexes: Part B, Organic Ligands*, 1st ed.; Pergamon Press: Oxford, U. K., 1979.
- (45) (a) Samanta, S.; Ghosh, D.; Mukhopadhyay, S.; Endo, A.; Weakley, T. J. R.; Chaudhury, M. *Inorg. Chem.* **2003**, *42*, 1508–1517. (b) Sammes, P. G.; *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, U.K., 1979; Vol. 4: Heterocyclic Chemistry, p 364.
- (46) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry Principles of Structures and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993; p 389.
- (47) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
- (48) Schulz, D.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chim. Acta* **1995**, *240*, 217–229 and related references therein.
- (49) Moon, M.; Pyo, M.; Myoung, Y. C.; Ahn, C.; Lah, M. S. *Inorg. Chem.* **2001**, *40*, 554–557.
- (50) Glas, H.; Herdtweck, E.; Artus, G. R. J.; Thil, W. R. *Inorg. Chem.* **1998**, *37*, 3644–3646.
- (51) Soon, Y.; Melchior, M.; Summers, D. A.; Thompson, R. C.; Retting, S. J.; Orvig, C. *Inorg. Chem.* **1998**, *37*, 3119–3121.
- (52) Li, X.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1988**, *27*, 4657–4664.
- (53) Mondal, S.; Rath, S. P.; Rajak, K. K.; Chakravorty, A. *Inorg. Chem.* **1998**, *37*, 1713–1719.
- (54) Maurya, M. R. *Coord. Chem. Rev.* **2003**, *237*, 163–181.

7.91–6.91 (m, 8H, C₆H₄), 8.68 (s, 1H, –CH=N), 11.18 (s, 1H, NH), 11.76 (s, 1H, OH), 12.02 (s, 1H, OH). IR (KBr, cm⁻¹): 3195 (ν_{OH}), 3075 (ν_{NH}), 1660 (ν_{C=O}), 1618 (ν_{C=N}).

Synthesis of Mononuclear Oxovanadium(V) Complexes. [VO(OEt)L] (A). This complex was prepared by a reported method.³⁶ Ligand H₂L (0.26 g, 1.0 mmol) was dissolved in 30 mL of ethanol, and 0.27 g (1.0 mmol) of VO(acac)₂ was added to this solution. On being stirred, the solution changed from a greenish color to dark brown. After 6 h of being stirred in open air, the solution was filtered; the filtrate was kept in air for 3 days, at which point dark brown crystals were deposited. Yield: 70%. Anal. Calcd for C₁₆H₁₅N₂O₅V: C, 52.42; H, 4.12; N, 7.64; V, 13.93. Found: C, 52.50; H, 4.21; N, 7.63; V, 13.87. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (13 452), 335 (15 913), 321 (15 468), 306 (14 364). IR (KBr, cm⁻¹): 3195 (ν_{OH}), 1245 (ν_{C–O/enolic}), 1602 (ν_{C=N}), 1038 (ν_{N–N}), 992 (ν_{V=O}). ¹H NMR (CDCl₃, δ): 10.18 (s, 1H, OH), 8.59 (s, 1H, –CH=N), 7.98–6.78 (m, 8H, C₆H₄), 5.5 (q, 2H, CH₂, OEt), 1.74 (t, 3H, CH₃, OEt).

[VO(OEt)L(py)] (1). To 25 mL of an ethanol solution of [VO(OEt)L] (A) (0.37 g, 1.0 mmol) was added excess pyridine (6–8 mL), and the mixture was refluxed for 4 h on a steam bath. The color of the solution slowly changed from dark brown to reddish brown. The solution was filtered and allowed to evaporate slowly in a refrigerator. After 8–10 days, yellowish brown single crystals separated out that were suitable for X-ray diffraction analysis. Yield: 70%. Anal. Calcd for C₂₁H₂₀N₃O₅V: C, 56.63; H, 4.49; N, 9.44; V, 11.46. Found: C, 56.60; H, 4.38; N, 9.50; V, 11.34. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 398 (9730), 335 (12 370), 321 (12 171), 306 (11 510), 254 (19 135). IR (KBr, cm⁻¹): 3448 (ν_{OH}), 1264 (ν_{C–O/enolic}), 1604 (ν_{C=N}), 1036 (ν_{N–N}), 969 (ν_{V=O}). ¹H NMR (CDCl₃, δ): 10.19 (s, 1H, OH), 8.57 (s, 1H, –CH=N), 8.51 (br, 2H, CH), 7.91–6.85 (m, 11H, C₆H₄ and C₆H₅N), 5.42 (q, 2H, CH₂, OEt), 1.71 (t, 3H, CH₃, OEt).

Synthesis of Dinuclear Oxovanadium(V) Complexes. [VO(OEt)L]₂(μ-4,4'-bipy) (2). This complex was obtained as yellowish brown crystals using the procedure adopted for complex 1 using a 30 mL ethanol solution of complex A (0.37 g, 1.0 mmol) and 0.80 g (0.50 mmol) of 4,4'-bipyridine. After 8–10 days, yellowish brown single crystals separated out that were suitable for X-ray diffraction analysis. Yield: 70%. Anal. Calcd for C₄₂H₃₈N₆O₁₀V₂: C, 56.75; H, 4.28; N, 9.46; V, 11.48. Found: C, 56.72; H, 4.26; N, 9.44; V, 11.42. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 398 (22 375), 335 (29 013), 321 (28 693), 306 (27 455). IR (KBr, cm⁻¹): 3435 (ν_{OH}), 1254 (ν_{C–O/enolic}), 1605 (ν_{C=N}), 1031 (ν_{N–N}), 954 (ν_{V=O}). ¹H NMR (CDCl₃, δ): 10.26 (s, 2H, OH), 8.94 (s, 2H, –CH=N), 8.58 (m, 4H, CH, C₁₀H₈N₂), 7.98–6.92 (m, 20H, C₆H₄ and C₁₀H₈N₂), 5.36 (q, 4H, CH₂, OEt), 1.68 (t, 6H, CH₃, OEt).

[VO(OEt)L]₂(μ-1,2-bis(4-pyridyl)ethylene) (3). This complex was isolated as a dark brown crystalline solid by following the method adopted in the preparation of 2 using 1,2-bis(4-pyridyl)-ethylene in place of 4,4'-bipyridine. Yield: 80%. Anal. Calcd for C₄₄H₄₀N₆O₁₀V₂: C, 57.77; H, 4.38; N, 9.19; V, 11.16. Found: C, 56.74; H, 4.36; N, 9.15; V, 11.12. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (18 383), 334 (22 186), 294 (48 655), 285 (49 599). IR (KBr, cm⁻¹): 3433 (ν_{OH}), 1254 (ν_{C–O/enolic}), 1605 (ν_{C=N}), 1050 (ν_{N–N}), 963 (ν_{V=O}). ¹H NMR (CDCl₃, δ): 10.23 (s, 2H, OH), 8.87 (s, 2H, –CH=N), 8.57 (m, 4H, CH, C₁₂H₁₀N₂), 7.91–6.85 (m, 22H, C₆H₄, C₂H₂ and C₁₂H₁₀N₂), 5.39 (q, 4H, CH₂, OEt), 1.76 (t, 6H, CH₃, OEt).

[VO(OEt)L]₂(μ-1,2-bis(4-pyridyl)ethane) (4). It was isolated as a dark brown crystalline solid following a procedure similar to that adopted in the preparation of 2 using 1,2-bis(4-pyridyl)ethane in place of 4,4'-bipyridine. Yield: 75%. Anal. Calcd for C₄₄H₄₂N₆

O₁₀V₂: C, 57.64; H, 4.58; N, 9.17; V, 11.13. Found: C, 56.61; H, 4.56; N, 9.11; V, 11.10. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (16 959), 335 (21 035), 321 (20 728), 306 (19 389), 254 (33 318). IR (KBr, cm⁻¹): 3437 (ν_{OH}), 1253 (ν_{C–O/enolic}), 1604 (ν_{C=N}), 1048 (ν_{N–N}), 960 (ν_{V=O}). ¹H NMR (CDCl₃, δ): 10.21 (s, 2H, OH), 8.48 (s, 2H, –CH=N), 8.41 (m, 4H, CH, C₁₂H₁₂N₂), 7.93–6.82 (m, 22H, C₆H₄ and C₁₂H₁₂N₂), 5.39 (q, 4H, CH₂, OEt), 2.85 (s, 4H, C₂H₄), 1.76 (t, 6H, CH₃, OEt).

Complexes A and 1–4 are soluble in alcohol, acetonitrile, and dichloromethane but insoluble in water.

Synthesis of Dioxovanadium(V) Complexes. [4-Me imzH][VO₂L] (5). To 30 mL of an ethanol solution of A (0.37 g, 1.0 mmol) was added 4(5)-methyl imidazole (0.10 g, 1.2 mmol), and the mixture was refluxed for 5 h on a steam bath. The color of the solution slowly changed from dark brown to reddish yellow. The solution was filtered and allowed to evaporate slowly in open air at room temperature. After 4–5 days, a yellow crystalline product separated out. On recrystallization from methanol, yellow crystals suitable for X-ray diffraction studies were collected. This complex is water-soluble. Yield: 80%. Anal. Calcd for C₁₈H₁₇N₄O₅V: C, 51.43; H, 4.05; N, 13.33; V, 12.14. Found: C, 51.38; H, 4.06; N, 13.30; V, 12.12. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399.5 (13 621), 335 (15 704), 321 (15 372), 305 (14 380). IR (KBr, cm⁻¹): 3140 (ν_{OH}), 1259 (ν_{C–O/enolic}), 1612 (ν_{C=N}), 1071 (ν_{N–N}), 943, 912 (ν_{V=O}). ¹H NMR (D₂O, δ): 8.68 (s, 1H, –CH=N), 8.31 (s, 1H, CH, C₄H₆N₂), 7.71–6.77 (m, 9H, C₆H₄ and C₄H₆N₂), 2.17 (s, 3H, CH₃).

[4-Me imzH][VO₂L]·2H₂O (5A). Orange-yellow single crystals were obtained by recrystallizing the compound [Me imdzH][VO₂L] (5) from water. Yield: 70%. Anal. Calcd for C₁₈H₂₁N₄O₇V: C, 47.37; H, 4.60; N, 12.28; V, 11.18. Found: C, 47.31; H, 4.63; N, 11.12; V, 11.16. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (12 821), 335 (15 314), 321 (15 042), 306 (14 780). IR (KBr, cm⁻¹): 3151 (ν_{OH}), 1259 (ν_{C–O/enolic}), 1610 (ν_{C=N}), 1070 (ν_{N–N}), 938, 908 (ν_{V=O}).

[imzH][VO₂L] (6). This compound was prepared using a procedure similar to that adopted for 5 using imidazole in place of 4-methyl imidazole. Yield: 74%. Anal. Calcd for C₁₇H₁₅N₄O₅V: C, 50.25; H, 3.69; N, 13.79; V, 12.56. Found: C, 50.21; H, 3.72; N, 13.82; V, 12.55. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (18 732), 335 (21 540), 321 (20 880), 305 (19 149). IR (KBr, cm⁻¹): 3120 (ν_{OH}), 1260 (ν_{C–O/enolic}), 1614 (ν_{C=N}), 1076 (ν_{N–N}), 947, 911 (ν_{V=O}). ¹H NMR (D₂O, δ): 8.64 (s, 1H, –CH=N), 8.28 (s, 1H, CH, C₃H₄N₂), 7.68–6.64 (m, 10H, C₆H₄ and C₃H₄N₂).

[2-picH][VO₂L] (7). To 30 mL of an ethanol solution of A (0.37 g, 1.0 mmol) was added excess 2-picoline (6–8 mL), and the mixture was refluxed for 5 h on a steam bath. The color of the solution slowly changed from dark brown to yellow. The solution was filtered and allowed to evaporate slowly at room temperature. After 5–6 days, a yellow crystalline product separated out. Yield: 80%. Anal. Calcd for C₂₀H₁₈N₃O₅V: C, 55.68; H, 4.18; N, 9.74; V, 11.83. Found: C, 55.62; H, 4.2; N, 9.72; V, 11.8. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (13 156), 335 (15 097), 321 (14 786), 306 (13 877), 256 (21 165). IR (KBr, cm⁻¹): 3438 (ν_{OH}), 1220 (ν_{C–O/enolic}), 1605 (ν_{C=N}), 1060 (ν_{N–N}), 938, 907 (ν_{V=O}).

¹H NMR (CDCl₃, δ): 10.39 (s, 1H, OH), 8.73 (m, 1H, CH, C₅H₄N), 8.69 (s, 1H, –CH=N), 7.71–6.77 (m, 11H, C₆H₄ and C₅H₄N), 2.90 (s, 3H, CH₃).

[3-picH][VO₂L] (8). This compound was prepared using the same procedure described above for 7 but using 3-picoline in place of 2-picoline. Yield: 75%. Anal. Calcd for C₂₀H₁₈N₃O₅V: C, 55.68; H, 4.18; N, 9.74; V, 11.83. Found: C, 55.62; H, 4.2; N, 9.72; V, 11.8. λ_{max} (CH₃CN, nm (ε, L M⁻¹ cm⁻¹)): 399 (10 746), 335

(12 348), 321 (11 902), 307 (10 767), 256.5 (16 306). IR (KBr, cm^{-1}): 3452 (ν_{OH}), 1230 ($\nu_{\text{C-O/enolic}}$), 1606 ($\nu_{\text{C=N}}$), 1061 ($\nu_{\text{N-N}}$), 958, 905 ($\nu_{\text{V=O}}$). ^1H NMR (CDCl_3 , δ): 10.50 (s, 1H, OH), 8.72 (br, 1H, CH, $\text{C}_5\text{H}_4\text{N}$), 8.61 (s, 1H, $-\text{CH=N}$), 7.71–6.77 (m, 11H, C_6H_4 and $\text{C}_5\text{H}_4\text{N}$), 2.43 (s, 3H, CH_3).

[4-picH][VO₂L] (9). This compound was prepared using the same procedure mentioned above for **7** but using 4-picoline in place of 2-picoline. Yield: 80%. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_5\text{V}$: C, 55.68; H, 4.18; N, 9.74; V, 11.83. Found: C, 55.62; H, 4.2; N, 9.72; V, 11.8. λ_{max} (CH_3CN , nm (ϵ , $\text{L M}^{-1} \text{cm}^{-1}$)): 399 (12 027), 334 (14 211), 321 (13 786), 225 (18 387). IR (KBr, cm^{-1}): 3089 (ν_{OH}), 1251 ($\nu_{\text{C-O/enolic}}$), 1602 ($\nu_{\text{C=N}}$), 1062 ($\nu_{\text{N-N}}$), 955, 937 ($\nu_{\text{V=O}}$). ^1H NMR (CDCl_3 , δ): 10.66 (s, 1H, OH), 8.72 (s, 1H, $-\text{CH=N}$), 8.59 (m, 2H, CH, $\text{C}_5\text{H}_4\text{N}$), 7.60–6.93 (m, 10H, C_6H_4 and $\text{C}_5\text{H}_4\text{N}$), 2.44 (s, 3H, CH_3).

[4-ampyH][VO₂L] (10). This compound was prepared using a procedure similar to that adopted for **5** using 4-amino pyridine in place of 4-methyl imidazole. Yield: 75%. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_5\text{V}$: C, 52.77; H, 3.94; N, 12.96; V, 11.80. Found: C, 52.72; H, 3.98; N, 12.98; V, 11.78. λ_{max} (CH_3CN , nm (ϵ , $\text{L M}^{-1} \text{cm}^{-1}$)): 399 (6611), 335 (7651), 321 (7461), 306 (6922), 260 (16 311). IR (KBr, cm^{-1}): 3160 (ν_{OH}), 1265 ($\nu_{\text{C-O/enolic}}$), 1610 ($\nu_{\text{C=N}}$), 1065 ($\nu_{\text{N-N}}$), 954, 912 ($\nu_{\text{V=O}}$). ^1H NMR (CDCl_3 , δ): 10.15 (s, 1H, OH), 8.59 (s, 1H, $-\text{CH=N}$), 7.87–6.22 (m, 12H, C_6H_4 and $\text{C}_5\text{H}_4\text{N}$), 3.62 (s, 2H, NH_2).

All complexes **2–10** were also obtained by the same procedure, using complex **1** instead of complex **A** as the starting material. All these dioxovanadium(V) complexes are fairly soluble in water but not in alcohol or acetonitrile.

Synthesis of Monoalkoxovanadium(V) Complexes from Dioxovanadium(V) Complexes. Preparations of two representative oxoalkoxo (methoxo and butoxo) complexes are describe here.

[VO(OMe)L] (11). To 20 mL of a methanolic suspension of [4-ampyH][VO₂L] (**10**) (0.43 g, 1.0 mmol) was added methanolic solution of HCl to lower the pH to ~4, and the mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and allowed to evaporate slowly at room temperature. After 2–3 days, reddish brown crystalline product separated out. Yield: 68%. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_5\text{V}$: C, 51.14; H, 3.69; N, 7.95; V, 14.49. Found: C, 51.10; H, 3.72; N, 7.92; V, 14.46. λ_{max} (CH_3CN , nm (ϵ , $\text{L M}^{-1} \text{cm}^{-1}$)): 399 (9598), 334 (11 616), 321 (11 345), 306 (10 534). IR (KBr, cm^{-1}): 3180 (ν_{OH}), 1238 ($\nu_{\text{C-O/enolic}}$), 1604 ($\nu_{\text{C=N}}$), 1034 ($\nu_{\text{N-N}}$), 988 ($\nu_{\text{V=O}}$). ^1H NMR (CDCl_3 , δ): 10.17 (s, 1H, OH), 8.59 (s, 1H, $-\text{CH=N}$), 7.99–6.80 (m, 8H, C_6H_4), 5.34 (s, 3H, CH_3 , OMe).

[VO(OⁿBu)L] (12). This compound was prepared using the same procedure mentioned above for **11** but using *n*-butanol in place of methanol. Yield: 65%. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_5\text{V}$: C, 54.82; H, 4.82; N, 7.11; V, 12.94. Found: C, 54.80; H, 4.78; N, 7.13; V, 12.91. λ_{max} (CH_3CN , nm (ϵ , $\text{L M}^{-1} \text{cm}^{-1}$)): 399 (9917), 334 (11 844), 321 (11 598), 306 (10 799). IR (KBr, cm^{-1}): 3187 (ν_{OH}), 1251 ($\nu_{\text{C-O/enolic}}$), 1605 ($\nu_{\text{C=N}}$), 1048 ($\nu_{\text{N-N}}$), 995 ($\nu_{\text{V=O}}$). ^1H NMR (CDCl_3 , δ): 10.18 (s, 1H, OH), 8.58 (s, 1H, $-\text{CH=N}$), 7.96–6.93 (m, 8H, C_6H_4), 5.59 (t, 2H, CH_2 , OBU), 2.05 (m, 2H, OBU), 1.5 (m, 2H, CH_2 , OBU), 1.06 (t, 3H, CH_3 , OBU).

Complexes **11** and **12** are soluble in alcohol and acetonitrile but insoluble in water.

Physical Measurements. Elemental analyses (C, H, and N) were done with a Perkin–Elmer 2400 CHNS/O analyzer, and vanadium contents (%) of the complexes were determined gravimetrically as V_2O_5 .³⁷ Electronic spectra of the complexes in acetonitrile were recorded on a Hitachi U-3501 spectrophotometer, and IR spectra (as KBr pellets) were recorded using a Perkin–Elmer RXI FT-IR

Table 1. Crystal Data and Structure Determination Summary of Complexes **1–3**

	1	2	3^a
empirical formula	$\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_5\text{V}$	$\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{10}\text{V}_2$	$\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_5\text{V}$
fw	445.34	888.66	457.35
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$
<i>a</i> (Å)	10.540(12)	12.740(14)	10.681(14)
<i>b</i> (Å)	13.682(15)	10.200(13)	12.596(14)
<i>c</i> (Å)	15.952(17)	17.159(19)	15.086(14)
α (deg)	101.73(1)	(90)	105.45(10)
β (deg)	105.23(1)	109.86(1)	90.92(1)
γ (deg)	101.82(1)	(90)	104.35(1)
<i>V</i> (Å ³)	2090(4)	2097(4)	1888
<i>Z</i>	4	2	3
<i>D</i> _{calcd} (g cm ^{−3})	1.415	1.407	1.207
data/restraints/params	7350/0/546	3304/0/273	
no. of obsd rflns	5920	2447	
<i>[I</i> > 2 σ (<i>I</i>)			
<i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i>) (obsd data) ^b	0.0540, 0.1254	0.1106, 0.2998	
<i>R</i> (<i>F</i> ²), <i>wR</i> (<i>F</i> ²) (all data) ^b	0.0707, 0.1342	0.1344, 0.3148	
<i>R</i> _{int}	0.029	0.062	
peaks in final difference map (e Å ^{−3})	0.55, −0.34	1.61, −0.73	
GOF on <i>F</i> ²	1.02	1.089	

^a Complex **3** was found to be disordered. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $^a wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}$.

spectrophotometer. ^1H NMR spectra were recorded on a Bruker model DPX300 advance spectrometer. Electrochemical measurements were performed with a PAR model 362 scanning potentiostat, and cyclic voltammograms were recorded at 25 °C in the designated solvent under dry dinitrogen with the electroactive component at ca. 1×10^{-3} M. Tetraethylammonium perchlorate (NET_4ClO_4 , 0.1 M) was used as the supporting electrolyte. A three-electrode configuration was employed with a platinum working electrode, calomel reference electrode, and platinum auxiliary electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as the internal standard.³⁸ Molar conductance values of the complexes in aqueous solution were measured with a Systronics 304 digital conductivity meter. Room-temperature magnetic susceptibilities of complexes were measured in the polycrystalline state on a PAR 155 sample vibrating magnetometer using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant.

Crystal Structure Determinations. Diffraction data for suitable single crystals of complexes **1**, **2**, **5**, **5A**, **8**, and **10** were measured with Mo K α radiation using the MARresearch image plate system. The crystals were positioned 70 mm from the image plate. A total of 95 frames was measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program.³⁹ The structures were solved using direct methods with the SHELX-86 program.⁴⁰ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the DIFABS program.⁴¹ The structures were refined on *F*² using SHELXL.⁴² The structures were generated using ORTEP-3.⁴³ Crystallographic data are summarized in Tables 1 and 3.

Results and Discussion

Our attempt to prepare adducts of the type $[\text{VO}(\text{OEt})\text{L} \cdot \text{B}]$ (where B is a monodentate Lewis base) led to an interesting observation and guided us to a general method of generating dioxovanadium complexes from the monoalkoxoV(V) complexes. It was found that adduct formation took place with pyridine ($\text{p}K_a = 5.48$), and the complex

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complexes **1** and **2**

	1a	1b	2
V(1)–O(21)	1.586(3)	1.580(4)	1.581(7)
V(1)–O(2)	1.855(3)	1.850(4)	1.850(7)
V(1)–O(13)	1.976(3)	1.968(4)	1.982(7)
V(1)–O(22)	1.785(3)	1.791(4)	1.799(7)
V(1)–N(10)	2.131(3)	2.152(4)	2.139(7)
V(1)–N(25)	2.476(4)	2.426(4)	2.385(8)
O2–V1–O13	151.85(10)	150.87(13)	151.7(3)
O2–V1–O21	100.32(14)	100.75(15)	101.6(3)
O2–V1–O22	104.38(11)	104.22(14)	105.0(3)
O2–V1–N10	83.09(11)	82.55(12)	83.9(3)
O2–V1–N25	82.31(11)	81.26(12)	79.8(3)
O13–V1–O21	98.68(13)	98.54(14)	97.7(3)
O13–V1–O22	91.58(10)	93.25(13)	90.8(3)
O13–V1–N10	74.89(10)	74.95(12)	74.7(3)
O13–V1–N25	77.38(11)	77.65(11)	79.8(3)
O21–V–O22	102.24(13)	100.89(15)	102.2(3)
O21–V–N10	94.44(12)	92.57(14)	92.6(3)
O21–V–N25	175.02(11)	174.27(12)	176.4(3)
O22–V1–N10	160.01(11)	163.36(13)	160.6(3)
O22–V1–N25	81.06(13)	83.70(13)	80.5(3)
N10–V1–N25	81.64(11)	82.37(12)	84.3(3)

[VO(OEt)L(py)] was structurally characterized by the single-crystal X-ray diffraction technique. However, when any one of the other bases, such as 2-picoline ($pK_a = 6.13$), 3-picoline ($pK_a = 6.02$), 4-picoline ($pK_a = 6.17$), imidazole ($pK_a = 7.33$), 4-methyl imidazole ($pK_a = 7.61$), and 4-amino pyridine ($pK_a = 9.53$), all of which are stronger bases than pyridine ($pK_a = 5.48$),⁴⁴ is used, the product isolated is the dioxovanadium complex BH[VO₂L]. Similar observations were reported previously.⁴⁵ All complexes **1–12** are found to be diamagnetic, as expected for a d⁰ system. Molar conductance values of these dioxovanadium(V) complexes in water (Table 6) support their 1:1 electrolytic nature.^{46,47} Structure determinations of these dioxovanadium(V) complexes have firmly established these findings.

These dioxovanadium(V) complexes were found to undergo an interesting transformation. When a suspension of any one of them in an alcohol (ROH) was treated with a solution of HCl in the same alcohol, it was found to be converted into the corresponding monooxoalkoxo species [VO(OR)L], in which the R-group comes from the alcohol used as the reaction medium under ambient conditions. So this process could be utilized as a general method for preparing [VO(OR)L] type oxoalkoxo complexes from any BH[VO₂L] species using different alcohols as the reaction medium under ambient conditions. Reaction of complexes **A** and **1** with the 4,4'-bipy type bridging ligands in a 2:1 molar ratio in refluxing ethanol led to isolation of the binuclear 4,4'-bridged complexes **2–4**, of which **2** and **3** were structurally characterized. All of the above reactions are presented in Scheme 1.

One of our objectives for preparing dinuclear vanadium(V) complexes, in which two V(V) acceptor centers are bridged by 4,4'-bipyridine and related ligands, is to get access to the domain of mixed-valence divanadium(IV,V) complexes⁴⁸ through selective electrochemical reduction of one of the two V(V) centers to the V(IV) state. Unfortunately, all three such dinuclear complexes **2–4** are found to undergo simultaneous one-electron reduction at both V(V) centers in

both CH₃CN and CH₂Cl₂ solutions. This is probably due to the symmetrical character of the bridging ligands used and the fact that the structures of the dinuclear complexes are centrosymmetric. Then we tried unsymmetrical ligand 4-aminopyridine, which has the potential to act as a neutral (exobidentate) bridging ligand like 4,4'-bipyridine. But the resulting complex, instead of being the expected dinuclear one, was found to be a mononuclear dioxo species BH-[VO₂L] (BH⁺ = monoprotonated 4-amino pyridine protonated at the pyridine nitrogen). When we looked into the structure of **2**, we found that the 4,4'-bipyridine moiety is firmly attached to the respective V(V) centers, which is reflected in the much shorter V(V)–N(bipy) bond distance compared to the V(V)–N(pyridine) bond distance present in **1**. This dinuclear species **2** is very stable and is formed even if 4,4'-bipyridine is kept in large excess (1:10) in alcohol and either of the complexes **A** or **1** is added very slowly to it as a very dilute alcohol solution under ice cold conditions. Our attempts to prepare a mono bipy adduct did not succeed.

When **2** is refluxed in alcohol with a base B in a 1:2 molar ratio, the product obtained is the monomeric dioxo [BH]⁺[VO₂L][–] species and not the expected {[VO₂L]₂(μ-4,4'bipy)}^{2–} type dinuclear complexes. Our attempt to prepare the 4,4'-bipyridine-bridged dioxovanadium(V) dinuclear species did not succeed. When we took complex **2** in ethanol and first refluxed with imidazole (in a 1:2 molar ratio), yellow [imzH][VO₂L] (**6**) was precipitated. Thereafter, careful addition of ethanolic HCl to this mixture until the pH of the reaction mixture became ~4 resulted in the reddish-brown solution depositing golden yellow crystals when kept at room temperature for 2–3 days. These crystals were identified as the starting dinuclear species **2**. Similar observations were also recorded in the cases of complexes **3** and **4**. The above results point to the reluctance of the dioxo species to form the dinuclear-bridged complexes and also indicate the urge of the oxoalkoxo complexes to form dinuclear-bridged species. Thus complexes **5** and **6–10** can also be prepared from any one of dinuclear complexes **2–4**.

Description of Crystal Structures. (a) [VO(OEt)L(py)] (**1**). Figure 1 displays a perspective view of the vanadium(V) mixed-ligand complex **1**, and bond parameters are included in Table 2. There are two molecules in the asymmetric unit, named **1a** and **1b**, with very similar geometries. The vanadium atom in the molecule is hexacoordinated, existing in a distorted octahedral environment in which the basal plane is made of phenolic oxygen O(2), enolic oxygen O(13), imine nitrogen N(10) from the tridentate ligand, and O(22) from the ethoxide oxygen. Unequal lengths of the O(2)–V(1), O(21)–V(1), O(22)–V(1), O(13)–V(1), N(10)–V(1), and N(25)–V(1) bonds as well as unequal angles generated by these bonds at the V(1) acceptor center point to a significant distortion of the coordination octahedron.

The Schiff-base ligand salicylaldehydehydrazone of 2-hydroxybenzoylhydrazine (H₂L) forms one six-membered and another five-membered chelate ring at the V(V) acceptor center, with the corresponding bite angles being 83.1(1) and

Table 3. Crystal Data and Structure Determination Summary of Complexes **5**, **5A**, **8**, and **10**

	5	5A	8	10
empirical formula	C ₁₈ H ₁₇ N ₄ O ₅ V	C ₁₈ H ₂₁ N ₄ O ₇ V	C ₂₀ H ₁₈ N ₃ O ₅ V	C ₁₉ H ₁₇ N ₄ O ₅ V
fw	420.30	456.30	431.31	432.31
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No.2)	<i>P</i> 2 ₁ / <i>a</i> (No.14)	<i>P</i> 2 ₁ / <i>n</i> (No.14)	<i>P</i> $\bar{1}$ (No.2)
<i>a</i> (Å)	8.622(9)	15.151(17)	11.161(14)	9.662(12)
<i>b</i> (Å)	10.431(12)	7.078(10)	14.194(17)	10.443(12)
<i>c</i> (Å)	12.233(14)	18.68(2)	24.40(3)	10.640(12)
α (deg)	111.98(1)	(90)	(90)	89.40(1)
β (deg)	93.82(1)	99.16(1)	100.47(1)	63.54(1)
γ (deg)	109.00(1)	(90)	(90)	88.40(1)
<i>V</i> (Å ³)	942.1(18)	2090(4)	3801(8)	961(2)
<i>Z</i>	2	4	8	2
D _{calc} d(g cm ⁻³)	1.482	1.529	1.507	1.494
data/restraints/params	2845/0/255	3252/0/273	5309/0/528	3364/0/264
no. of obsd reflns [<i>I</i> > 2 σ (<i>I</i>)]	1434	2723	4554	2850
R(<i>F</i>), wR(<i>F</i> ²) (obsd data) ^a	0.1177, 0.2245	0.1310, 0.2581	0.1102, 0.2436	0.0476, 0.1089
R(<i>F</i> ²), wR(<i>F</i> ²) (all data) ^a	0.2044, 0.2722	0.1497, 0.2666	0.1287, 0.2533	0.0615, 0.1152
<i>R</i> _{int}	0.099	0.085	0.078	0.030
peaks in final difference map (e Å ⁻³)	0.38, -0.33	1.44, -0.45	0.45-0.39	0.40-0.32
GOF on <i>F</i> ²	1.06	1.251	1.217	1.023

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^a wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}.$$

Table 4. Selected Bond Distances (Å) and Angles (deg) in **5**, **5A**, **8**, and **10**

	5	5A	8a	8b	10
V(1)–O(21)	1.633(9)	1.627(9)	1.612(7)	1.602(7)	1.630(3)
V(1)–O(22)	1.637(9)	1.603(9)	1.638(6)	1.649(8)	1.630(4)
V(1)–O(2)	1.911(8)	1.901(7)	1.898(7)	1.902(6)	1.892(3)
V(1)–O(13)	1.981(8)	1.989(7)	1.980(6)	1.994(6)	1.982(3)
V(1)–N(10)	2.157(9)	2.106(8)	2.129(6)	2.156(6)	2.151(4)
O2–V1–O13	150.6(4)	156.0(3)	156.0(2)	147.9(2)	154.60(9)
O2–V1–O21	103.1(4)	100.3(4)	100.5(3)	104.8(3)	101.49(10)
O2–V1–O22	94.1(4)	96.1(4)	97.7(3)	97.9(3)	96.77(12)
O2–V1–N10	80.9(3)	82.2(3)	82.5(2)	82.2(2)	82.58(9)
O13–V–O21	101.0(4)	96.4(4)	94.4(3)	101.3(3)	97.30(10)
O13–V–O22	93.6(4)	94.9(4)	95.1(3)	91.2(3)	92.75(11)
O13–V–N10	75.9(3)	74.4(3)	73.8(2)	73.5(2)	73.67(8)
O21–V–O22	109.4(5)	108.1(4)	108.7(3)	108.6(4)	109.78(14)
O21–V–N10	108.0(4)	121.2(3)	119.4(3)	104.1(3)	117.02(12)
O22–V–N10	142.5(4)	130.3(4)	131.1(3)	146.1(3)	132.38(12)

74.9(1)° in **1a** and 81.3(1) and 74.9(1)° in **1b**. The two axial positions are occupied by the O(21) oxo atom and N(25) atom of the secondary ligand pyridine. The short V(1)–O(21) distances of 1.586(3) and 1.580(4) Å in **1a** and **1b**, respectively, indicate the presence of a vanadium–oxygen double bond (V=O), which is commonly found in five- and six-coordinate octahedral complexes of vanadium(IV) and (V). In both molecules **a** and **b** of complex **1**, the four V–O bond lengths are unequal with the V=O bond being the shortest and the V–O (enolate oxygen O(13)) bond the longest. The vanadium–oxygen bond lengths follow the order V–O(oxo) < V–O(alkoxide) < V–O(phenoxide) < O(enolate). These data indicate stronger binding of the alkoxo group compared to those of phenoxo and enolate oxygen atoms, which is not uncommon for V(V) complexes of related ligands.^{49–51} The V(1)–N(25) bond distances at 2.476(4) and 2.426(4) Å are significantly longer than the other V(1)–N(10) bonds at 2.131(3) and 2.152(4) Å, indicating that the secondary ligand (pyridine) is weakly bonded to the central vanadium atom.

(b) [VO(OEt)L]₂(μ-4,4'-bipy) (**2**). The golden yellow complex [VO(OEt)L]₂(μ-4,4'-bipy) (**2**) crystallizes such that the dinuclear molecule contains a crystallographic center of

Table 5. Hydrogen Bond Distances (Å) and Bond Angles (deg) of Complexes **1**, **2**, **5**, **5A**, **8**, and **10**

D–H···A	<i>d</i> (H···A)	∠DHA	<i>d</i> (D···A)	symmetry
Complex 1a				
O20–H20···N11	1.87	145	2.59	
Complex 1b				
O20–H20···N11	1.89	146	2.607	
Complex 2				
O20–H20···N11	1.92	144	2.628	
Complex 5				
O20–H20···N11	1.85	145	2.567	
N25–H25···O20	2.62	121	3.154	
N23–H23···O2	2.19	165	3.034	<i>x</i> – 1, <i>y</i> – 1, <i>z</i> – 1
N25–H25···O13	2.34	151	3.122	2 – <i>x</i> , 2 – <i>y</i> , 2 – <i>z</i>
Complex 5A				
O20–H20···N11	1.84	144	2.557	
O29–H29a···O30	1.88	162	2.698	
O29–H29b···O22	2.11	147	2.862	
O30–H30a···O2	2.18	144	2.910	– <i>x</i> + 1/2, <i>y</i> – 1/2, – <i>z</i>
O30–H30a···O22	2.47	148	3.224	– <i>x</i> + 1/2, <i>y</i> – 1/2, – <i>z</i>
O30–H30b···O13	2.36	140	3.058	– <i>x</i> + 1/2, 1/2 + <i>y</i> , – <i>z</i>
O30–H30b···O21	2.48	149	3.235	– <i>x</i> + 1/2, 1/2 + <i>y</i> , – <i>z</i>
N23–H23···O21	1.86	174	2.718	1 – <i>x</i> , – <i>y</i> , – <i>z</i>
N25–H25···O29	1.91	168	2.761	– <i>x</i> + 1/2, 1/2 + <i>y</i> , – <i>z</i>
Complex 8a				
O20–H20···N11	1.86	147	2.585	
N23–H23···O22	1.78	166	2.625	
Complex 8b				
O20–H20···N11	1.87	146	2.593	
N23–H23···O22	1.83	167	2.676	
Complex 10				
O20–H20···N11	1.883	147	2.607	
N23–H23···O22	2.120	139	2.829	<i>x</i> , 1 + <i>y</i> , <i>z</i>
N23–H23···O20	2.642	116	3.119	– <i>x</i> + 1, – <i>y</i> + 1, – <i>z</i>
N29–H29a···O21	2.078	159	2.896	
N29–H29b···O21	2.209	147	2.969	– <i>x</i> , – <i>y</i> + 1, – <i>z</i> + 1

symmetry. This symmetry is reflected in the electrochemical behavior of **2**, with the two V(V) centers undergoing reduction at the same potential. The molecular structure and atom-labeling scheme of **2** are illustrated in Figure 2, and dimensions are provided in Table 2.

Each half of the binuclear complex closely resembles the structure of **1**, which essentially consists of the same donor

Table 6. Molar Conductance and Cyclic Voltammetric Data of Vanadium(V) Complexes

compound	molar conductance Λ_M^a ($\Omega^{-1} \text{ cm}^2 \text{ M}^{-1}$)	$E_{1/2}$ (V) (ΔE_p^b (mV))
[VO(OEt)L] (A)	non-electrolyte ^c	0.42 (150) ^d
[VO(OEt)L(Py)] (1)	non-electrolyte ^c	0.415 (70) ^d
[VO(OEt)L] ₂ (μ -4,4'-bipy) (2)	non-electrolyte ^c	0.42 (60) ^{d,e}
[VO(OEt)L] ₂ (μ -1,2-bis(4-pyridyl)ethylene) (3)	non-electrolyte ^c	0.435 (110) ^{d,e}
[VO(OEt)L] ₂ (μ -1,2-bis(4-pyridyl)ethane) (4)	non-electrolyte ^c	0.405 (152) ^{d,e}
[4-Me imzH][VO ₂ L] (5)	66.6 ^f	0.39 (138) ^d
[4-Me imzH][VO ₂ L]·2H ₂ O (5A)	70.6 ^f	0.409 (126) ^d
[imzH][VO ₂ L] (6)	71.1 ^f	0.439 (108) ^d
[2-picH][VO ₂ L] (7)	67.0 ^f	0.442 (142) ^d
[3-picH][VO ₂ L] (8)	67.8 ^f	0.453 (109) ^d
[4-picH][VO ₂ L] (9)	69.1 ^f	0.445 (130) ^d
[4-ampyH][VO ₂ L] (10)	69.3 ^f	0.433 (74) ^d
[VO(OMe)L] (11)	non-electrolyte ^c	0.416 (142)
[VO(O ⁿ Bu)L] (12)	non-electrolyte ^c	0.408 (136) ^d

^a Λ_M observed in 0.001 molar solution. ^b $\Delta E_p = E_{pa} - E_{pc}$. ^c In dry methanol at 25 °C. Complexes **A**, **1–4**, **11**, and **12** are insoluble in water but soluble in methanol. ^d In acetonitrile. ^e In dichloromethane; scan rate of 50 mVs⁻¹; $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. ^f In water at 25 °C.

atoms attached to its V(V) center in the same geometric pattern with closely matching dimensions. This is expected because complex **2** is obtained from complex **1** by simply replacing the pyridine nitrogen atom by one nitrogen atom of the 4,4'-bipyridine bridging nitrogen ligand. The only significant difference observed in the case of **2** is that the V(1)–N(25) bond involving the vanadium acceptor center and the N(25) aromatic nitrogen atom of 4,4'-bipy is shorter (2.385(8) Å) than the corresponding V(1)–N(25) bonds in **1**, which are 2.476(4) and 2.426(4) Å. This shortening indicates comparatively stronger binding of 4,4'-bipy nitrogen N(25) to the V(V) center and may be responsible for the facile transformation of [VO(OEt)L(py)] to [VO(OEt)L]₂(μ -4,4'-bipy). The two pyridine rings of 4,4'-bipy lie in the same plane and are perpendicular to the equatorial planes of the two halves of the two [VO(OEt)L] units. The vanadium acceptor center in **2** is displaced by 0.30 Å toward the oxo oxygen atom. Similar distances are found in the two molecules of **1**, e.g., 0.29 and 0.31 Å in **a** and **b**, respectively.

(c) [VO(OEt)L]₂(μ -1,2-bis(4-pyridine)ethylene) (**3**). The structure of complex **3** was disordered. There were two discrete molecules in the structure. One, shown in Figure 3, contains a crystallographic center of symmetry. The second is disordered over a center of symmetry with 50% occupancy. It was not possible to refine the structure below an R1 value of 0.18 and so the dimensions are not reported here. However, as illustrated by the ORTEP diagram of **3** shown in Figure 3, the structure of the ordered molecule exhibits close structural similarity to **2** and indeed also contains a crystallographic center of symmetry. This structure is consistent with the spectral and electrochemical properties of this complex.

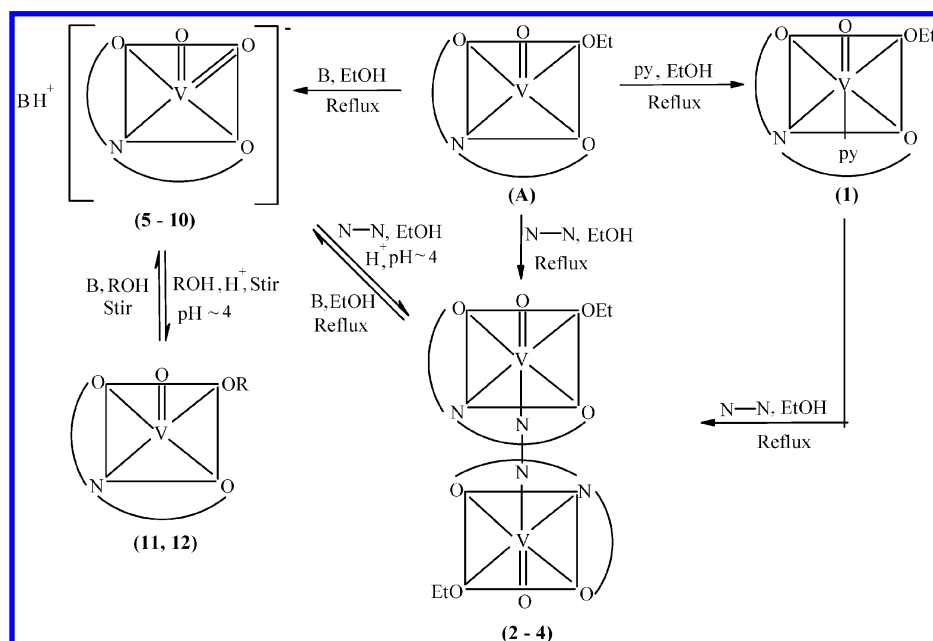
(d) **Structure of the Anionic [VO₂L]⁻ Complexes of Type [BH]⁺[VO₂L]⁻.** ORTEP diagrams of the complexes of type [BH]⁺[VO₂L]⁻ are presented in Figures 4–7, and the relevant dimensions are listed in Table 4. The formulas for the four complexes are [4-Me imzH]⁺[VO₂L]⁻ for **5**, [4-Me

imzH]⁺[VO₂L]⁻·2H₂O for **5A**, [3-picH]⁺[VO₂L]⁻ for **8**, and [4-ampyH]⁺[VO₂L]⁻ for **10**. There are two molecules in the asymmetric unit of **8**, marked **8a** and **8b**. In all four structures, the complex anion [VO₂L]⁻ contains the V(V) acceptor center surrounded by a O₄N⁻ donor set. As shown in Table 4, structures **5** and **8b** are close to being square pyramidal in geometry, whereas **5A**, **8a**, and **10** are distorted more toward trigonal bipyramidal geometry. A good indicator of the distortion is provided by the O(22)–V(1)–N(10) angle, which is 142.5(4)° in **5** and 146.1(3)° in **8b**, whereas it is 130.3(4)° in **5A**, 131.1(3)° in **8a**, and 132.4(1)° in **10**.

However, all structures can be described adequately in terms of distorted square pyramidal geometry. The dianionic tridentate ligand (L²⁻) occupies three positions of the basal plane, forming one five- and one six-membered chelate ring around the V(V) center; the bite angles range from 73.5(2) to 75.9(3)° and 80.9(3) to 82.6(1)° in the five structures. There are two terminal oxygen atoms, O(21) and O(22), with V=O distances in the range of 1.602(9)–1.649(8) Å. These values are slightly longer than the values found in **1** and **2**, which contain only one terminal oxygen atom. The angle between the two terminal oxygen atoms ranges from 108.1(4)–109.8(1)°. In the square pyramid, O(21) occupies an axial position and O(22) an equatorial position, but there is no significant difference between these V=O bond lengths. Along with O(22), the basal plane is formed by two equatorially placed oxygen atoms, phenolate oxygen O(2) and enolate oxygen O(13), the fourth corner of the square plane being occupied by azomethine nitrogen N(10). The apical vanadyl oxygen subtends angles at the metal with the atoms in the basal plane in the range of 94.4(3)–121.2(3)°, with the smallest angles to O(13). In the ligand, the V–O distances are significantly shorter than the V–N distance. Such observations are reported previously^{49–51} and suggest some π donation leading to partial multiple-bond character, which is often observed for oxygen coordination in V(V) complexes. An additional reason may well be that the nitrogen atom is approximately trans to terminal multiple-bonded oxygen O(22). It is also noted that the V–O bond involving phenolate oxygen O(2) is shorter than the similar bond involving enolate oxygen O(13).

The V(V) acceptor centers are all displaced from the average basal plane defined previously toward apical oxo-oxygen O(21) by a distance in the range 0.48–0.52 Å. Such a displacement of the V(V) center makes it somewhat inaccessible to a donor, which may approach from the direction trans to this apical oxo-oxygen.

In all the structures, there is an intramolecular hydrogen bond between O(20) and N(11). N···H···O bond distances and other related details are given in Table 5. This hydrogen bond enables the ligand to remain closely planar in the crystal structures. The presence of cations in these crystal structures gives rise to intermolecular hydrogen bonds between the cations and anions; details are given in Table 5. Complex **5** contains the anion [VO₂L]⁻ and the 4-methyl imidazolium cation [4-Me imzH]⁺. The two N–H groups on the cation are both hydrogen bonded to the chelating oxygen atoms O(2) and O(13) of two different anions. **5A** also contains

Scheme 1^a

^a B = 4-methyl imidazole (5), imidazole (6), 2- picoline (7), 3-picoline (8), 4-picoline (9), 4-amino pyridine(10). N-N = 4,4'-bipyridine (2), 1,2-bis(4-pyridyl)ethylene (3), 1,2-bis(4-pyridyl)ethane (4). R = CH₃ (11) and ⁿC₄H₉ (12).

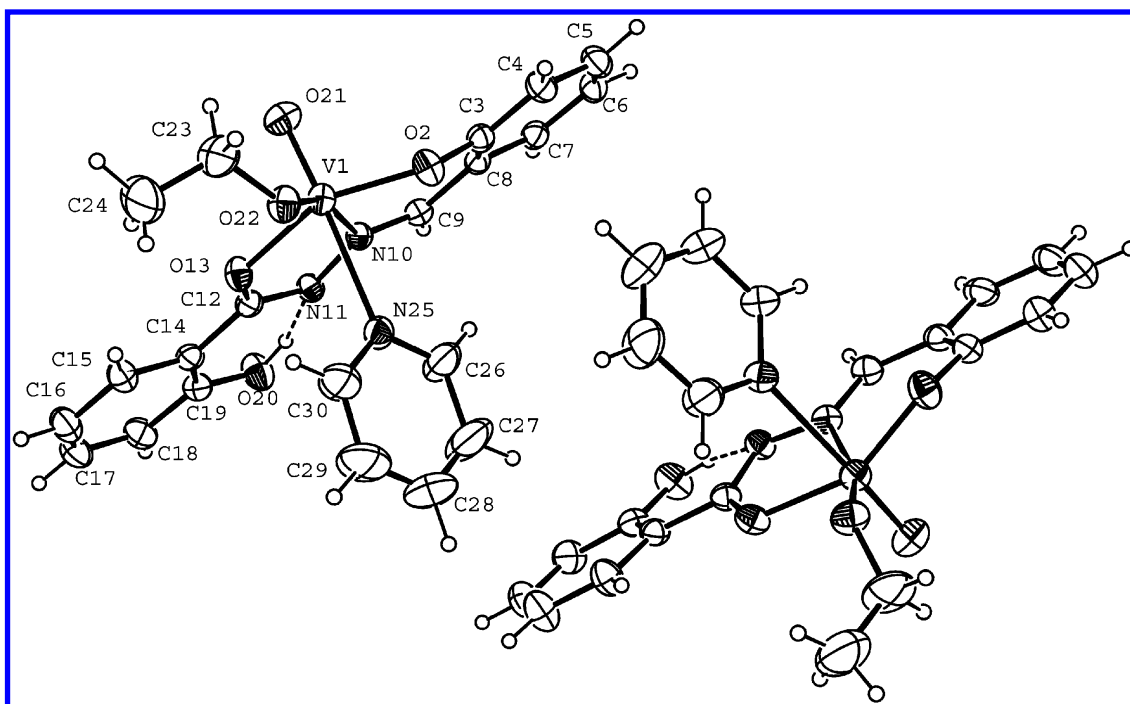


Figure 1. Molecular structure and atom-numbering scheme for complex **1**, with thermal ellipsoids drawn at the 30% probability level. Two equivalent molecules in the asymmetric unit, **1a** and **1b**, are shown. The intramolecular hydrogen bond is shown as a dotted line.

the complex anion [VO₂L][−] and the 4-methyl imidazolium cation [4-Me imzH]⁺, as well as two water molecules. The two N–H groups both form hydrogen bonds; in this case, one nitrogen is hydrogen bonded to terminal oxygen atom O(22) of the anion, whereas the other is hydrogen bonded to a water molecule. There are also several hydrogen bonds between the water molecules and both terminal oxygen atoms as well as one between each other. By contrast, **8** contains two 3-methyl-pyridinium cations together with two anions. Both N–H groups are hydrogen bonded to a terminal oxygen

atom of an anion. In **10**, the cation is 4-amino-pyridinium. The pyridinium nitrogen atom is hydrogen bonded to O(20), whereas the two amine hydrogen atoms are hydrogen bonded to the terminal oxygen atoms of two different anions.

IR and ¹H NMR spectroscopy. IR spectra of all the monooxoalkoxo complexes contain all the characteristic bands of the coordinated tridentate anionic ligand given in the Experimental Section. In addition, the $\nu(\text{V}=\text{O})$ bands are observed in the 918–995 cm^{−1} range.^{21,25,38,55} In the case of the dioxovanadium(V) complexes, the only difference

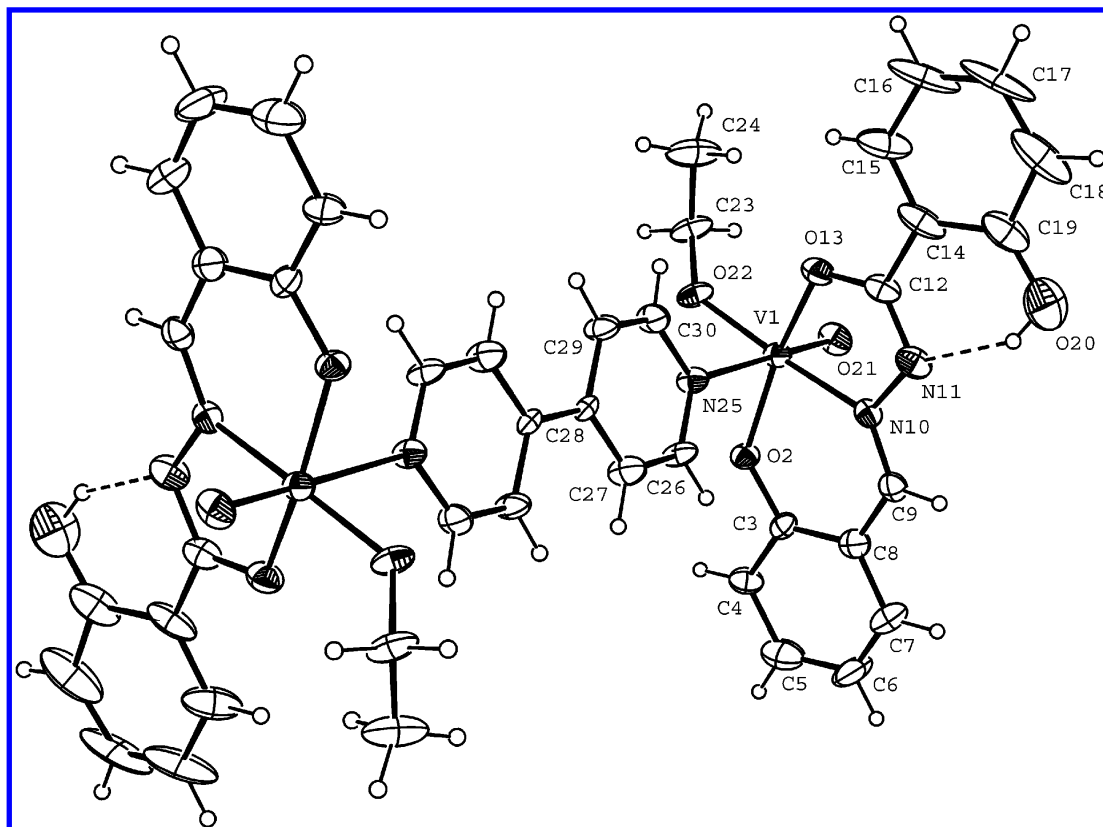


Figure 2. Molecular structure and atom-numbering scheme for complex **2**, with thermal ellipsoids drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dotted lines.

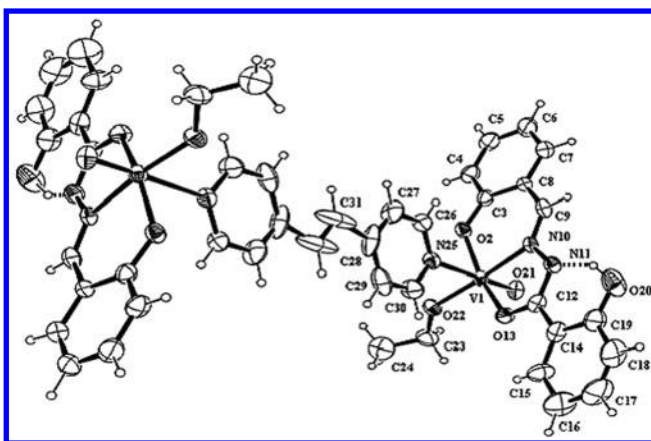


Figure 3. ORTEP view of the ordered molecule in complex **3**. Intramolecular hydrogen bonds are shown as dotted lines.

observed is the appearance of two $\nu(\text{V}=\text{O})$ modes that correspond to the symmetric and antisymmetric pair of cis $\text{V}=\text{O}$ groups.^{50,52} The positions of these two $\nu(\text{V}=\text{O})$ bands differ very little from complex to complex, because complex anion $[\text{VO}_2\text{L}]^-$ is the same in all the complexes; it differs only in the cation outside the coordination zone of the $\text{V}(\text{V})$ acceptor center.

^1H NMR data of all the complexes are given in the Experimental Section. Complexes $[\text{VO}(\text{OMe})\text{L}]$ (**11**) and $[\text{VO}(\text{O}^i\text{Bu})\text{L}]$ (**12**) were identified by their respective NMR spectra in CDCl_3 . Apart from all the proton signals of the

coordinated ligand, the spectrum of **11** exhibited one singlet at 5.34 ppm that corresponds to three protons of the OCH_3 group. Similarly, the spectrum of **12** displayed the characteristic proton signals of the *n*-butoxy group at 1.06, 1.5, 2.05, and 5.59 ppm that correspond to a triplet of three protons, multiplet of two protons, multiplet of two protons, and triplet of two protons, respectively.

Electronic Spectra. The electronic spectral data of the free ligand (H_2L) and the vanadium(V) complexes are given in the Experimental Section. The electronic spectra of all the vanadium(V) complexes (**1**–**12**) in CH_3CN solution exhibit one intense absorption band in the 399–398 nm region, which is assignable to $\text{L} \rightarrow \text{V}$ ($d\pi$) LMCT transition,²⁵ and three other absorption bands in the 335–285 nm region, which correspond to intraligand transitions.

Electrochemistry. Cyclic voltammetric data for all the complexes are presented in Table 6. Cyclic voltammograms of monooxoalkoxo complexes **A**, **11**, and **12** in CH_3CN exhibit irreversible one-step, one-electron responses around +0.41 V, and complex **1** shows a reversible one-step one-electron response at +0.415 V, corresponding to $\text{V}(\text{V})/\text{V}(\text{IV})$ reduction. The binuclear $\text{V}(\text{V})$ complexes are usually expected to undergo a two-step, one-electron reduction, with the first step leading to the formation of the mixed-valence $\text{V}(\text{V})\text{--V}(\text{IV})$ species. But contrary to such an expectation, binuclear complexes **2**–**4** were found to undergo only one-step reduction in both CH_3CN and CH_2Cl_2 in the +0.40–0.435 V potential range, which is reversible in the case of **2** but irreversible for **3** and **4**. The centrosymmetric structure

(55) Nakamoto, K. *Infrared and Raman Spectra of Inorganic Coordination Compounds*, Wiley: New York, 1984; p 341.

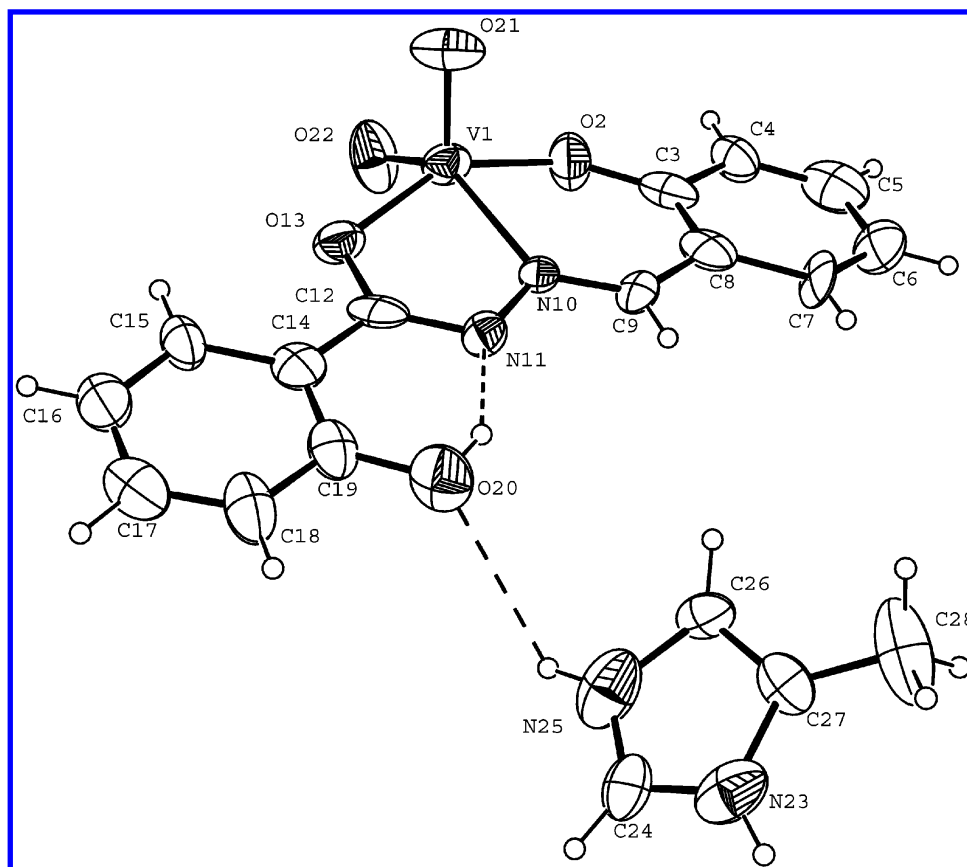


Figure 4. Molecular structure and atom-numbering scheme for complex **5**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen bonds are shown as dotted lines.

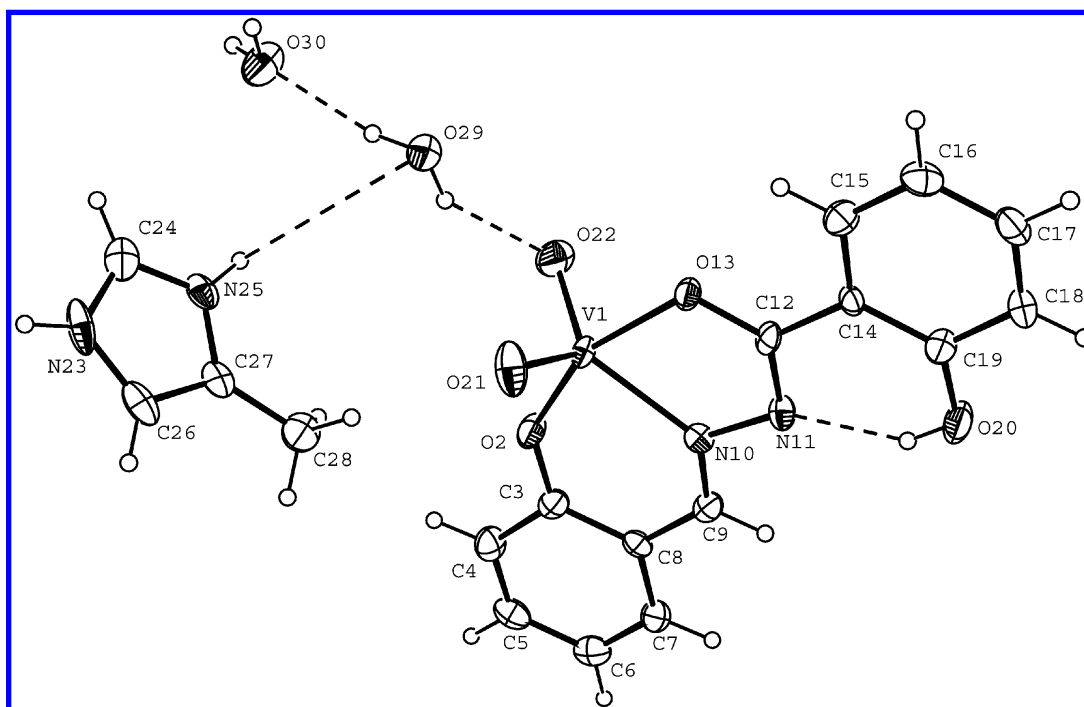


Figure 5. Molecular structure and atom-numbering scheme for complex **5A**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen bonds are shown as dotted lines.

of **2** confirms that the coordination environments of the two V(V) centers are identical and explains their simultaneous reduction at the same potential. The similar values of $E_{1/2}$

for the monooxoalkoxo complexes can be related to similarity in the donor environments of the V(V) centers in each complex.

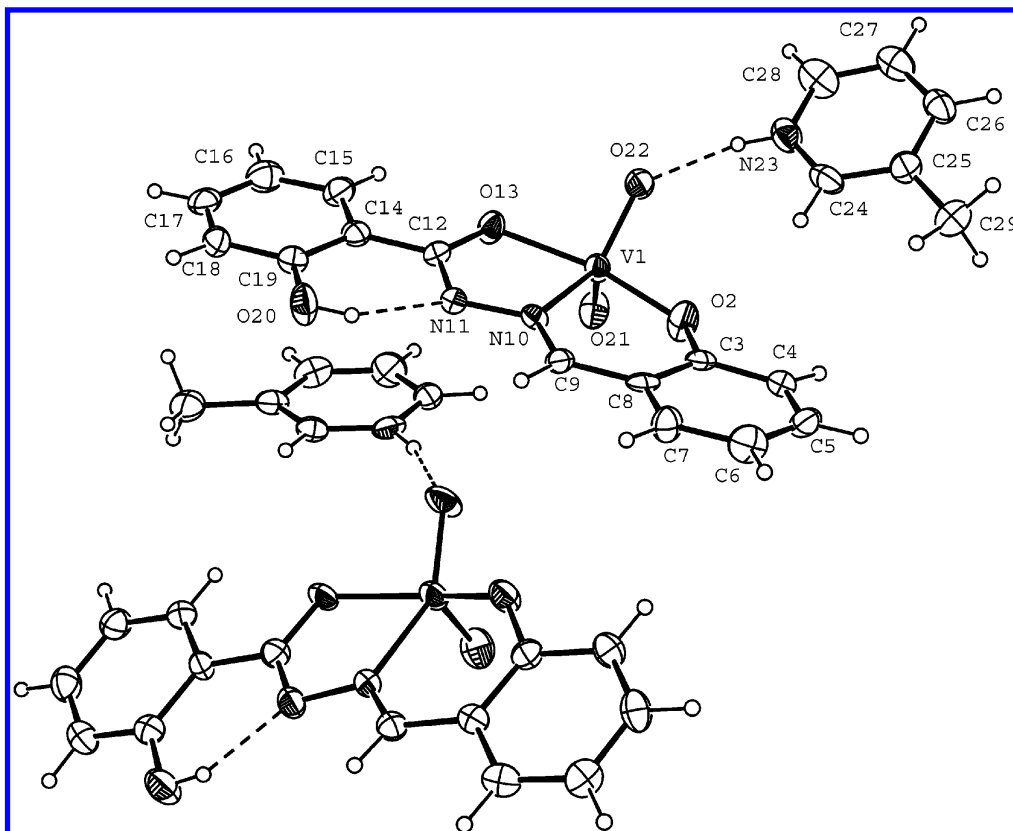


Figure 6. Molecular structure and atom-numbering scheme for complex **8**, with thermal ellipsoids drawn at the 30% probability level. Two equivalent molecules in the asymmetric unit, **8a** and **8b**, are shown. Hydrogen bonds are shown as dotted lines.

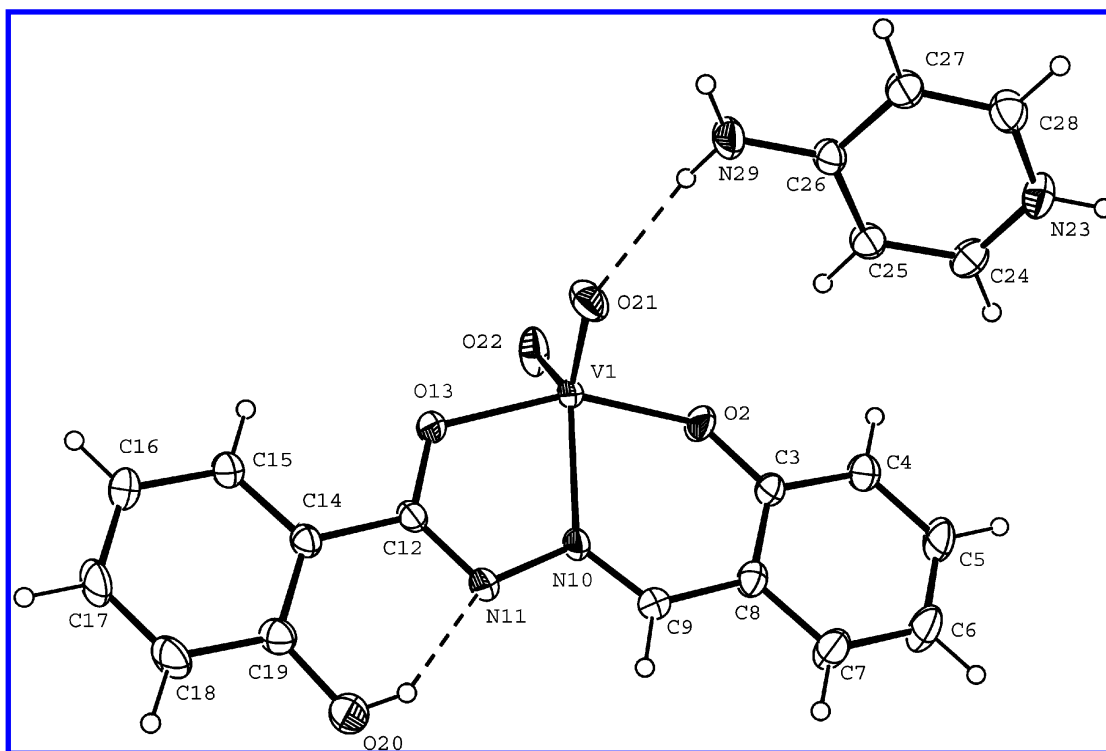


Figure 7. Molecular structure and atom-numbering scheme for complex **10**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen bonds are shown as a dotted line.

In all the dioxo complexes, the V(V)/V(IV) reductions take place in the +0.40–0.45 V region. The $E_{1/2}$ values are close to each other and also close to the $E_{1/2}$ values of the monooxoalkoxo complexes because of the similarity in the

coordination environments of the V(V) center in both the classes. Three representative cyclic voltammograms of the three different types of complexes (**1**, **2**, and **10**) are presented in Figure 8.

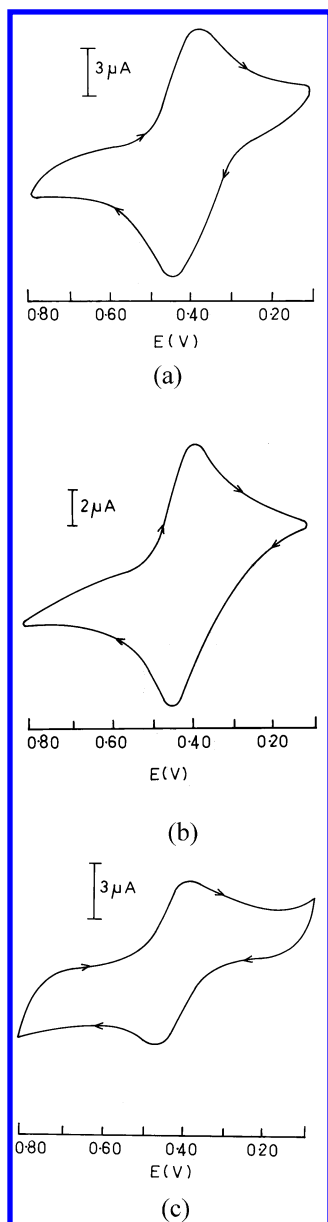


Figure 8. Cyclic voltammograms of (a) complex **1** (b) complex **2** and (c) complex **10** in CH_3CN (0.1 M TEAP) at a platinum electrode with a scan rate of 50 mV s^{-1} ; the potential was recorded vs SCE.

Conclusion

This work reports the preparation and structural characterization of the monooxoalkoxovanadium(V) complex $[\text{VO}(\text{OEt})\text{L}(\text{py})]$ (**1**), which, along with complex $[\text{VO}(\text{OEt})\text{L}]$ (**A**), acted as the precursor of a number of dioxovanadium(V) complexes with the general formula $\text{BH}[\text{VO}_2\text{L}]$, where B is a neutral monodentate Lewis base. It is established that some neutral monodentate donors, such as imidazole, 4-methyl imidazole, 2-picoline, 3-picoline, 4-picoline, and 4-amino pyridine, all of which are stronger bases than pyridine, caused such a transformation. These monomeric dioxovanadium complexes can also be prepared from dinuclear complexes **2–4** by refluxing with excess base B. All the structurally characterized dioxovanadium(V) complexes are found to possess a significantly distorted square pyramidal donor environment. The presence of two asymmetric units in the unit cell of each complex is to be noted. It is also confirmed experimentally that such a transformation is reversed on acidification in an alcohol medium. An interesting aspect of the last reaction is that it serves as a general method for preparing $[\text{VO}(\text{OR})\text{L}]$ type complexes starting from any one of the $\text{BH}[\text{VO}_2\text{L}]$ type complexes using different alcohols. The presence of different alkoxo groups is confirmed from NMR data for the respective complexes. Both **A** and **1** produced the same binuclear complex $[\text{VO}(\text{OEt})\text{L}]_2(\mu\text{-4,4'-bipy})$ (**2**), which we believe to be the first report of a structurally characterized $\mu\text{-4,4'-bipy}$ -bridged binuclear vanadium(V) complex. Two other bridged binuclear vanadium(V) complexes, **3** and **4**, are also reported.

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Supporting Information Available: Crystallographic data for the structural analysis of the complexes (**1**, **2**, **5**, **5A**, **8**, and **10**) have been deposited in the Cambridge Crystallographic Data Centre, with CCDC No. 276166 (**1**), 276167(**2**), 276168(**5**), 276169(**5A**), 276170(**8**) and 276171 (**10**). Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). This material is also available free of charge via the Internet at <http://pubs.acs.org>.

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