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4-Amino- and 4-Nitrodipicolinatovanadium(V) Complexes and Their Hydroxylamido Derivatives: Synthesis, Aqueous, and Solid-State Properties

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A number of 4-substituted, dipicolinatodioxovanadium(V) complexes and their hydroxylamido derivatives were synthesized to characterize the solid state and solution properties of five- and seven-coordinate vanadium(V) complexes. The X-ray crystal structures of $Na[VO_2dipic\text{-}NH_2]\cdot 2H_2O$ (**2**) and $K[VO_2dipic\text{-}NO_2]$ (**3**) show the vanadium adopting a distorted, trigonal-bipyramidal coordination environment similar to the parent coordination complex, $[VO_2dipic]^-$ (**1**), reported previously as the Cs^+ salt. The observed differences in the chemical shifts of the complexes both in the ^1H (ca. 0.7–1.4 ppm) and ^{51}V (ca. 1–11 ppm) NMR spectra were consistent with the electron-donating or electron-withdrawing properties of the substituent groups, respectively. Stoichiometric addition of a series of hydroxylamine ligands (H_2NOH, MeHNOH, Me_2NOH, and Et_2NOH) to complexes **1**–**3** led to the formation of seven-coordinate vanadium(V) complexes. The X-ray crystal structure of $[VO(dipic)(Me_2NO)(H_2O)]\cdot 0.5H_2O$ (**1c**) was found to be similar to the previously characterized complexes $[VO(dipic)(H_2NO)(H_2O)]$ (**1a**) and $[VO(dipic)(OO\text{-}^tBu)(H_2O)]$. While only slight differences in the ^1H NMR spectra were observed upon addition of the hydroxylamido ligand, the signals in the ^{51}V NMR spectra change by up to 100 ppm. The addition of the hydroxylamido ligand increased the complex stability of complexes **2** and **3**. Evidence for a nonstoichiometric redox reaction was found for the monoalkyl hydroxylamine ligand. The reaction of an unsaturated five-coordinate species with a hydroxylamine to form a seven-coordinate vanadium complex will, in general, dramatically increase the amounts of the vanadium compound that remain intact at pH values near neutral.

Introduction

Common coordination numbers of vanadium(V) in the presence of multidentate ligands in aqueous solutions are five, six, and seven.[1–4] Ligands derived from diethanolamine and dipicolinic acid systems favor the five-coordinate coordination geometry.[1,2,5] Because five-coordinate vanadium complexes have geometries similar to the transition states of several enzyme phosphorylation reactions,[6,7] and because the $[VO_2dipic]^-$ ion (**1**) was found to be a potent phosphatase inhibitor,[8,9] we have undertaken a detailed structural and electronic investigation of these five-coordinate complexes

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(1) Crans, D. C.; Smee, J. J. In *Comprehensive Coordination Chemistry*, 2nd ed.; McCleverty, J., Meyer, T. J., Eds.; Elsevier: Oxford, 2003; Vol. 4, 175–239.
(2) Vilas Boas, L. V.; Costa Pessoa, J. In *Comprehensive Coordination Chemistry. The Synthesis, Reactions, Properties & Applications of Coordination Compounds*; Wilkinson, G., Sir, Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 3, pp 453–583.
(3) Rehder, D. *Inorg. Chem. Commun.* **2003**, *6*, 604–617.
(4) Tracey, A. S.; Willsky, G. R.; Takeuchi, E. S. *Vanadium: Chemistry, Biochemistry, Pharmacology and Practical Applications*; CRC Press: Boca Raton, FL, U.S.A., 2007.
(5) Gaetjens, J.; Meier, B.; Kiss, T.; Nagy, E. M.; Buglyo, P.; Sakurai, H.; Kawabe, K.; Rehder, D. *Chem.-Eur. J.* **2003**, *9*, 4924–4935.
(6) Davies, D. R.; Ho, W. G. J. *FEBS Lett.* **2004**, *577*, 315–321.
(7) Borden, J.; Crans, D., C.; Florian, J. *J. Phys. Chem. B* **2006**, *110*, 14988–14999.

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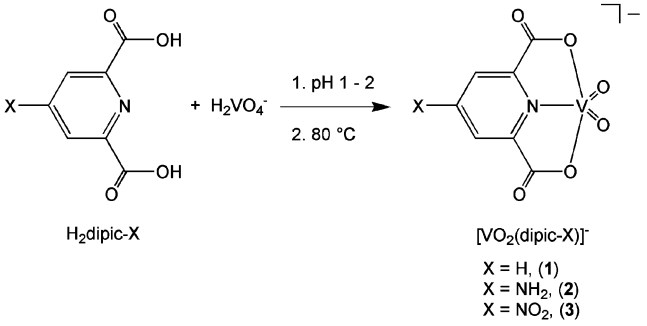
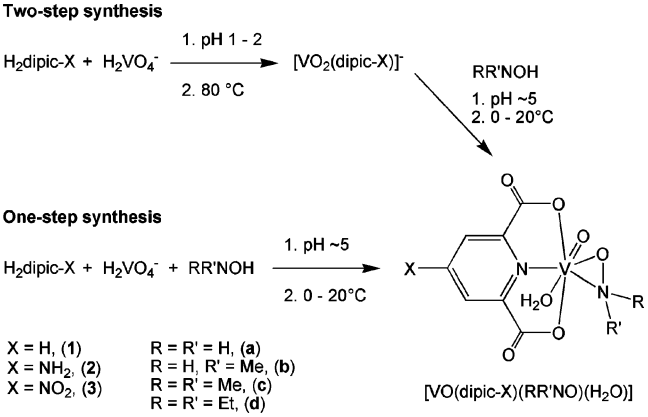
Scheme 1



Scheme 2



and their reaction products with hydroxylamines. The nomenclature for the compounds in this study is shown in Schemes 1 and 2. The parent dipicolinate complexes (**1**−**3**) contain the H_2dipic, H_2dipic-NH_2, and H_2dipic-NO_2 ligands, respectively. The hydroxylamine complexes for each parent complex are denoted with a letter (**a**, **b**, **c**, or **d**) indicating that they are derived from H_2NOH, MeHNOH, Me_2NOH, or Et_2NOH, respectively. In this work we characterize and compare the five-coordinate parent compounds (**1**−**3**) with their respective seven-coordinate hydroxylamido complexes (**1a**−**d**, **2a**−**d**, and **3a**−**d**).

Dipicolinate complexes have been prepared with a wide range of transition metals. The simple complexes are classical inorganic systems[10−13] and are frequently used as starting materials in studies of the self-assembly of supramolecular compounds[14−16] and redox agents.[17−20] The dipicolinatodioxovanadium(V) complex is a potent phosphatase inhibitor[8] and was recently found to be active as a glucose-lowering agent in diabetic rats.[21,22] Further understanding of the properties of these compounds will be important to understand their action in biological systems. Prior to this work some vanadium(V) complexes of dipicolinate and substituted dipicolinate ligands have been structurally characterized.[23−26] With the exception of the vanadium(V) system, most dipicolinate complexes of *d*-block elements are six-coordinate. The V(III) and V(IV) dipicolinate complexes are also six-coordinate.[27−30] A dimeric structure of $[VO_2(dipic)]^-$ was recently reported in which one of the oxo ligands forms a weak interaction with another vanadium to give a pseudo-six-coordinate structure.[26] Additional ligands, such as the hydrazido,[28] peroxo,[31,32] and hydroxylamido[33] groups, have been shown to increase the coordination number of the vanadium(V)-dipicolinate complexes and form ternary complexes.

Vanadium(V)-peroxo[34,35] and -hydroxylamido complexes are often seven-coordinate.[9] Peroxovanadium complexes have been better characterized than hydroxylamido complexes, and the available information suggests that a similarity exists with regard to both structure and reactivity.[36,37] Hydroxylamido and peroxo groups generally coordinate in a side-on fashion,

(8) Crans, D. C.; Keramidas, A. D.; Drouza, C. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *109*−*110*, 245−248.
(9) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849−902.
(10) Hakansson, K.; Lindahl, M.; Svensson, G.; Albertsson, J. *Acta Chem. Scand.* **1993**, *47*, 449−455.
(11) Okabe, N.; Oya, N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*. **2000**, *C56*, 305−307.
(12) Lainé, P.; Gourdon, A.; Launay, J.-P. *Inorg. Chem.* **1995**, *34*, 5138−5149.
(13) Crans, D. C.; Smee, J. J.; Gaidamauskiene, E. G.; Anderson, O. P.; Miller, S. M.; Jin, W.-Z.; Gaidamauskas, E.; Crubellier, E.; Grainda, R.; Chi, L. H.; Willsky, G. R. *J. Inorg. Biochem.* **2004**, *98*, 1837−1850.
(14) MacDonald, J. C.; Luo, T.-J. M.; Palmore, G. T. R. *Cryst. Growth Des.* **2004**, *4*, 1203−1209.
(15) Mukherjee, P. S.; Das, N.; Kryschenko, Y. K.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 2464−2473.
(16) Brayshaw, P. A.; Hall, A. K.; Harrison, W. T. A.; Harrowfield, J. M.; Pearce, D.; Shand, T. M.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Eur. J. Inorg. Chem.* **2005**, 1127−1141.
(17) Sukanya, D.; Prabhakaran, R.; Natarajan, K. *Polyhedron* **2006**, *25*, 2223−2228.
(18) Manohar, T. C.; Rajkumar, M.; Rajagopal, S. *Transition Met. Chem. (Dordrecht, Neth.)* **2006**, *31*, 549−555.
(19) Mauk, A. G.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 7654−7657.
(20) Holder, A. A.; Brown, R. F. G.; Marshall, S. C.; Payne, V. C. R.; Cozier, M. D.; Alleyne, W. A.; Bovell, C. O. *Transition Met. Chem. (Dordrecht, Neth.)* **2000**, *25*, 605−611.
(21) Crans, D. C.; Yang, L.; Jakusch, T.; Kiss, T. *Inorg. Chem.* **2000**, *39*, 4409−4416.
(22) Buglyo, P.; Crans, D. C.; Nagy, E. M.; Lindo, R. L.; Yang, L.; Smee, J. J.; Jin, W.; Chi, L.-H.; Godzala, M. E., III; Willsky, G. R. *Inorg. Chem.* **2005**, *44*, 5416−5427.
(23) Nuber, B.; Weiss, J.; Wieghardt, K. *Z. Naturforsch., B: Chem. Sci.* **1978**, *33B*, 265−267.
(24) Yang, L.; La Cour, A.; Anderson, O. P.; Crans, D. C. *Inorg. Chem.* **2002**, *41*, 6322−6331.
(25) Crans, D.; Mahroof-Tahir, M.; Johnson, M.; Wilkins, P.; Yang, L.; Robbins, K.; Johnson, A.; Alfano, J.; Godzala, M.; Austin, L.; Willsky, G. *Inorg. Chim. Acta* **2003**, *356*, 365−378.
(26) Gonzalez-Baro, A. C.; Castellano, E. E.; Piro, O. E.; Parajon-Costa, B. S. *Polyhedron* **2005**, *24*, 49−55.
(27) Bersted, B. H.; Belford, R. L.; Paul, I. C. *Inorg. Chem.* **1968**, *7*, 1557−1562.
(28) Sundheim, A.; Mattes, R. *Z. Naturforsch., B: Chem. Sci*. **1993**, *48B*, 125−132.
(29) Chatterjee, M.; Ghosh, S.; Nandi, A. *Transition Met. Chem. (Dordrecht, Neth.)* **1999**, *24*, 183−185.
(30) Chatterjee, M.; Maji, M.; Ghosh, S.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 3641−3645.
(31) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1973**, *12*, 829−835.
(32) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L. *Nouv. J. Chim.* **1983**, *7*, 467−475.
(33) Nuber, B.; Weiss, J. *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, *B37*, 947−948.
(34) Slebodnick, C.; Hamstra, B. J.; Pecoraro, V. L. *Struct. Bonding* **1997**, *89*, 51−108.
(35) Rehder, D.; Casny, M.; Grosse, R. *Magn. Reson. Chem.* **2004**, *42*, 745−749.
(36) Butler, A.; Clague, M. J.; Meister, G. *Chem. Rev.* **1994**, *94*, 625−638.
(37) Schwendt, P.; Sivak, M. In *Vanadium Compounds: Biochemistry, Chemistry, and Therapeutic Applications*; Tracey, A. S., Crans, D. C., Eds.; Oxford University Press: 1998; pp 117−125.

but head-on hydroxylamido complexes with transition metals have also been reported.[38] The aqueous chemistry of vanadium complexes containing simple hydroxylamines has been examined in detail by ^{51}V NMR spectroscopy, and several complexes with primarily 1:1 and 1:2 stoichiometric ratios of vanadium to hydroxylamine have been reported.[39,40] Ternary complexes with additional ligands such as amino acids, small peptides, and thiols are also very stable.[41−44] Complexes that have been characterized in the solid state provide a useful benchmark for solution studies and are important to the comparisons described here (**1a**−**d**, **2a**,**b**, **3**, and **3a**−**d**).

In this work we utilized different dipicolinate and hydroxylamine ligands to compare a series of new (**1b, 2a**−**d, 3, 3a**−**d**) and known (**1, 1a,c,d, 2**) complexes. We have prepared the new complexes using strict pH-controlled conditions to overcome the tendency of many of these systems to undergo both redox and/or oligomerization chemistry. The stability and spectroscopic properties of a series of five- and seven-coordinate complexes with an electron-donating ligand and an electron-withdrawing ligand were characterized and compared to the parent system. In general the ternary oxovanadium(V) complexes are more hydrolytically and redox stable than the dioxovanadium(V) parent complexes at higher pH. Thus this work documents the extension of vanadium(V) complex stability at higher pH values via the introduction of hydroxylamine-type ligands.

Experimental Section

Materials and Methods. Fuming sulfuric acid (20% oleum), NH_4VO_3, KVO_3, MeHNOH·HCl, Me_2NOH·HCl, Et_2NOH, and dipicolinic acid (also referred to as pyridine-2,6-dicarboxylic acid or 2,6-pyridinedicarboxylic acid) were purchased from Aldrich; $NaVO_3$ was purchased from Acros; and H_2NOH·HCl was purchased from Fisher Scientific. All chemicals were used as received. Ammonium dipicolinatodioxovanadate(V), $NH_4[VO_2(dipic)]$ (**1**), was prepared as previously described[45] and recrystallized from a hot aqueous solution. $(NH_4)_2$dipic-NH_2 and H_2dipic-NO_2 were prepared using modified versions of previously reported syntheses.[25,46,47] Sodium 4-aminodipicolinatooxovanadate(V) dihydrate, $Na[VO_2(dipic\text{-}NH_2)]\cdot 2H_2O$ (**2**), was prepared similarly to the procedure previously reported for the NH_4^+ salt.[25] Distilled water was used in all of the syntheses. Elemental analyses (C, H, N) were carried out by Desert Analytics in Tucson, AZ.

Aquadipicolinatohydroxylamidooxovanadium(V) [VO(dipic)(H$_2$NO)(H$_2$O)] (**1a**). The compound was prepared as described previously.[33] ^{1}H NMR (D_2O, ppm): 8.63 (t), 8.39 (dd, 2H). ^{51}V NMR (D_2O, ppm): −681.

Aquadipicolinatomethylhydroxylamidooxovanadium(V), [VO(dipic)(MeHNO)(H$_2$O)] (**1b**). Complex **1** (0.26 g, 1.0 mmol) was dissolved in 50 mL of H_2O followed by the addition of MeHNOH·HCl (0.084 g, 1.0 mmol). After 5−10 min of stirring a white precipitate formed. After an additional 30 min of stirring the precipitate was filtered off, washed with 10 mL of H_2O and 2 × 25 mL of EtOH, and dried overnight in a desiccator. Yield 2.59 g (82.5%). ^{1}H NMR (D_2O, ppm): 8.64 (t, 1H), 8.39 (dd, 2H), 3.90 (s, 3H), 3.43 (s, 3H). ^{51}V NMR (D_2O, ppm): −634, −647. Anal. Calcd for $C_8H_9N_2O_7V$: C, 32.45; H, 3.06; N, 9.46. Found: C, 32.50; H, 3.01; N, 9.42.

Aquadipicolinatodimethylhydroxylamidooxovanadium(V)·0.5Hydrate [VO(dipic)(Me$_2$NO)(H$_2$O)]·0.5H$_2$O (**1c**). The compound was prepared in analogous fashion to **1b**. Yield 0.21 g (66%). ^{1}H NMR (D_2O, ppm): 8.62 (t, 1H), 8.38 (dd, 2H), 3.95 (s, 3H), 3.42 (s, 3H). ^{51}V NMR (D_2O, ppm): −614. Anal. Calcd for $C_9H_{12}N_2O_{7.5}V$: C, 33.87; H, 3.79; N, 8.78. Found: C, 33.93; H, 3.59; N, 9.03.

Crystals suitable for X-ray diffraction studies were obtained via an alternate synthesis. $NaVO_3$ (0.15 g, 1.2 mmol) and H_2dipic (0.25 g, 1.5 mmol) were dissolved in 30 mL of water. The pH of the resulting solution was adjusted to 6.0 with 1 M NaOH. To this solution was added KCl (0.5 g). The solution was then cooled to 0 °C in an ice bath, and then Me_2NOH·HCl (0.15 g, 1.5 mmol) was added. The pH was adjusted to 6.5 using 1 M NaOH, and the resulting solution was stirred for 10 min. The solution was stored at 0 °C for several days during which time a white crystalline solid formed. The solid was collected by filtration and washed with cold water. Yield 0.26 g (70%). Anal. Calcd for $C_9H_{12}N_2O_{7.5}V$: C, 33.87; H, 3.79; N, 8.78. Found: C, 34.71; H, 3.57; N, 9.02.

Aquadipicolinatodiethylhydroxylamidooxovanadium(V) [VO(dipic)(Et$_2$NO)(H$_2$O)] (**1d**). The compound was prepared in analogous fashion to **1b**. Yield 0.28 g (83%). ^{1}H NMR (D_2O, ppm): 8.62 (t, 1H), 8.38 (dd, 2H), 3.87 (m, 2H), 3.44 (m, 2H), 1.59 (t, 3H), 1.41 (t, 3H). ^{51}V NMR (D_2O, ppm): −598. Anal. Calcd for $C_{11}H_{15}N_2O_7V$: C, 39.07; H, 4.47; N, 8.28. Found: C, 38.79; H, 4.46; N, 8.13.

Ammonium 4-Aminodipicolinate, (NH$_4$)$_2$(dipic-NH$_2$). To $(NH_4)_2$dipic-Cl (10.0 g, 46.3 mmol)[48] was added 50 mL of concentrated aqueous ammonia. The mixture was placed in a pressure tube and heated to 150 °C in an oil bath with stirring for 9 h during which time the solution took on a clear brownish-yellow color. The mixture was then allowed to cool to room temperature after which time a yellowish-white solid formed which was then filtered off and dissolved in a minimum of water. After an insoluble, sand-colored impurity was removed by filtration, the volume of the clear yellow filtrate was reduced by rotary evaporation until only a thick, white, slurry remained. Ethanol (∼300 mL) was then added to complete the precipitation of the solid, and the mixture was stored overnight in a freezer (−20 °C). The white solid thus obtained was filtered off and washed with 2 × 30 mL of 95% ethanol and then 2 × 30 mL of diethyl ether. The fluffy yellowish-white powder thus obtained was dried in air overnight to give 6.95 g (75.7% yield) of product. ^{1}H NMR (D_2O, pH 7.0, ppm): 7.13 (s, py-*H*, 2H). These properties are similar to those reported previously.[25]

Sodium 4-Aminodipicolinatodioxovanadate Dihydrate, Na[VO$_2$(dipic-NH$_2$)]·2H$_2$O (**2**). A slurry of crude $(NH_4)_2$dipic-NH_2 (1.85 g, 8.56 mmol) and $NaVO_3$ (1.00 g, 8.20 mmol) in 30 mL of water was prepared. The slurry was warmed to 80−90 °C and

(38) Wieghardt, K. *Adv. Inorg. Org. Bioinorg. Mech.* **1984**, *3*, 213−274.
(39) Paul, P. C.; Angus-Dunne, S. J.; Batchelor, R. J.; Einstein, F. W. B.; Tracey, A. S. *Can. J. Chem.* **1997**, *75*, 429−440.
(40) Angus-Dunne, S. J.; Paul, P. C.; Tracey, A. S. *Can. J. Chem.* **1997**, *75*, 1002−1010.
(41) Nxumalo, F.; Tracey, A. S. *J. Biol. Inorg. Chem.* **1998**, *3*, 527−533.
(42) Bhattacharyya, S.; Martinsson, A.; Batchelor, R. J.; Einstein, F. W. B.; Tracey, A. S. *Can. J. Chem.* **2001**, *79*, 938−948.
(43) Paul, P. C.; Angus-Dunne, S. J.; Batchelor, R. J.; Einstein, F. W. B.; Tracey, A. S. *Can. J. Chem.* **1997**, *75*, 183−191.
(44) Keramidas, A. D.; Miller, S. M.; Anderson, O. P.; Crans, D. C. *J. Am. Chem. Soc.* **1997**, *119*, 8901−8915.
(45) Wieghardt, K. *Inorg. Chem.* **1978**, *17*, 57−64.
(46) Bradshaw, J. S.; Maas, G. E.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 467−74.
(47) Lewis, J. C. *J. Biol. Chem.* **1972**, *247*, 1861−1868.
(48) Robison, M. M. *J. Am. Chem. Soc.* **1958**, *80*, 5481−5483.

maintained at that temperature for 1 h. The pH was adjusted to ~2 with 2 M HCl, and the solution was heated for an additional 30 min. The slurry was filtered while still hot to give a bright yellow filtrate which produced an off-white precipitate as it cooled to room temperature. The solid was filtered off, washed with ethanol, and dried in air overnight to give 1.82 g of crude $Na[VO_2(dipic\text{-}NH_2)]\cdot H_2O$ (74.3%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization from a hot aqueous solution. ^1H NMR (D_2O, ppm): 7.1 (s, py-*H*, 2H). ^{51}V NMR (D_2O, ppm): −525. Anal. Calcd for $C_7H_8N_2O_8NaV$: C, 26.10; H, 2.50; N, 8.70. Found: C, 26.43, H, 2.48, N, 8.80.

Aqua-4-aminodipicolinatohydroxylamidooxovanadium(V) [VO(dipic-NH$_2$)(H$_2$NO)(H$_2$O)] (**2a**). Complex **2** (0.32 g, 0.99 mmol) was dissolved in H_2O (50 mL); to this solution was added $H_2NOH\cdot$HCl (0.069 g, 1.0 mmol), and the resulting mixture was allowed to stir until a precipitate formed. The pH was then adjusted to 6 with 1 M NaOH, and the solution was cooled in a refrigerator overnight. The resulting solid was filtered under vacuum and washed with ice cold H_2O (2 × 10 mL). Yield 0.24 g (81%). ^1H NMR (D_2O, ppm): 7.20 (s, 2H). ^{51}V NMR (D_2O, ppm): −688. Anal. Calcd for $C_7H_8N_3O_7V$: C, 28.30; H, 2.71; N, 14.14. Found: C, 28.06; H, 2.65; N, 13.82.

Aqua-4-aminodipicolinatomethylhydroxylamidooxovanadium-(V) [VO(dipic-NH$_2$)(MeHNO)(H$_2$O)] (**2b**). The compound was prepared in analogous fashion to **2a.** Yield 0.30 g (97%). ^1H NMR (D_2O, ppm): 7.21 (d, 1H), 7.19 (d, 1H), 3.76 (s, 3H), 3.29 (s, 3H). ^{51}V NMR (D_2O, ppm): −640, −652. Anal. Calcd for $C_8H_{10}N_3O_7V$: C, 30.88; H, 3.24; N, 13.51. Found: C, 30.92; H, 3.11; N, 13.47.

Aqua-4-aminodipicolinatodimethylhydroxylamidooxovanadium-(V) Monohydrate [VO(dipic-NH$_2$)(Me$_2$NO)(H$_2$O)]·H$_2$O (**2c**). The compound was prepared in analogous fashion to **2a**. Yield 0.28 g (82%). ^1H NMR (D_2O, ppm): 7.22 (d, 1H), 7.19 (d, 1H), 3.81 (s, 3H), 3.28 (s, 3H). ^{51}V NMR (D_2O, ppm): −619. Anal. Calcd for $C_9H_{14}N_3O_8V$: C, 31.50; H, 4.11; N, 12.24. Found: C, 31.55; H, 3.93; N, 12.11.

Aqua-4-aminodipicolinatodiethylhydroxylamidooxovanadium-(V) [VO(dipic-NH$_2$)(Et$_2$NO)(H$_2$O)] (**2d**). The compound was prepared in analogous fashion to **2a**. Yield 0.27 g (76%). ^1H NMR (D_2O, ppm): 7.19 (d, 1H), 7.18 (d, 1H), 3.71 (m, 2H), 3.35 (m, 2H), 1.43 (t, 3H), 1.26 (t, 3H). ^{51}V NMR (D_2O, ppm): −604. Anal. Calcd for $C_{11}H_{16}N_3O_7V$: C, 37.41; H, 4.57; N, 11.90. Found: C, 37.58; H, 4.54; N, 11.86.

4-Nitrodipicolinic Acid (**H$_2$dipic-NO$_2$**). Keeping the temperature below ~10 °C, a mixture of 30 mL of 30% H_2O_2 and 60 mL of fuming sulfuric acid (20% free oleum) is prepared. Then 10.0 g (46.3 mmol) of crude $(NH_4)_2$dipic-NH_2 is dissolved in 17 mL of concentrated H_2SO_4. The second mixture is slowly added to the peroxide/fuming sulfuric acid mixture while keeping the temperature at or below 10 °C in an ice bath. Upon complete addition, the clear, yellow mixture is stirred for 4 h at 10 °C. The ice bath is then allowed to warm to room temperature overnight (failure to allow sufficient warming time may cause the solution to spontaneously erupt). The reaction mixture is removed from the bath and stirred an additional 2 days. The mixture is then carefully diluted with distilled water to give a final volume of ~175 mL, all the while maintaining the temperature at or below 25 °C. Upon dilution the product precipitates out as a pale yellow powder. The crude product was recrystallized from hot water to give pure H$_2$dipic-NO$_2$ (6.87 g, 70%). ^1H NMR (D_2O, pH 7.3, ppm): 8.50 (s, 2H).

Potassium 4-Nitrodipicolinatodioxovanadate(V) K[VO$_2$(dipic-NO$_2$)] (**3**). H$_2$dipic-NO$_2$ (3.00 g, 14.1 mmol) was dissolved in 50 mL of water and heated to 60 °C. Solid KVO_3 (1.99 g, 14.4 mmol) was then added with stirring. Heating and stirring continued for 5 min, or until all of the KVO_3 had dissolved. While still hot, the pH of the solution was adjusted to 1.5 with 1 M HCl (if necessary); immediately afterward the solution was filtered to remove the undesirable solids. The filtrate was placed in a refrigerator overnight during which time the crude product formed as a yellowish solid (3.41 g). The crude product was then recrystallized from a minimum of hot (60 °C) water to give a final yield of 2.86 g (60%) of the product. Crystals of **3** suitable for X-ray diffraction studies were obtained by recrystallization from water. ^1H NMR (D_2O, ppm): 8.89 (s, 2H). ^{51}V NMR (D_2O, ppm): −534 ppm. Anal. Calcd for $C_7H_2N_2O_8KV$: C, 25.31; H, 0.61; N, 8.43. Found: C, 25.28: H, 0.88; N, 8.10.

Aqua-4-nitrodipicolinatohydroxylamidooxovanadium(V) Hydrate [VO(dipic-NO$_2$)(H$_2$NO)(H$_2$O)]·H$_2$O (**3a**). Complex **3** (0.32 g, 0.96 mmol) was dissolved in H_2O (20 mL), and then $H_2NOH\cdot$HCl (0.069 g, 1.0 mmol) was added to the solution which was allowed to stir until a precipitate formed. The pH was then adjusted to 3.5 with 1 M NaOH. The solution was placed in a refrigerator overnight. The resulting solid was filtered under vacuum and washed with cold H_2O (2 × 10 mL). Yield 0.21 g (65%). ^1H NMR (D_2O, ppm): 9.09 (s, 2H). ^{51}V NMR (D_2O, ppm): −671. Anal. Calcd for $C_7H_8N_3O_{10}V$: C, 24.36; H, 2.34; N, 12.18. Found: C, 24.27; H, 2.12; N, 11.91.

Aqua-4-nitrodipicolinatomethylhydroxylamidooxovanadium-(V) Dihydrate [VO(dipic-NO$_2$)(MeHNO)(H$_2$O)]·2H$_2$O (**3b**). The compound was prepared in analogous fashion to **3a**. Yield 0.30 g (90%). ^1H NMR (D_2O, ppm): 9.09 (d, 1H), 9.07 (d, 1H), 3.92 (s, 3H), 3.45 (s, 3H). ^{51}V NMR (D_2O, ppm): −618, −632. Anal. Calcd for $C_8H_{12}N_3O_{11}V$: C, 25.48; H, 3.21; N, 11.14. Found: C, 25.40; H, 3.04; N, 11.14.

Aqua-4-nitrodipicolinatodimethylhydroxylamidooxovanadium-(V)·1.5Hydrate [VO(dipic-NO$_2$)(Me$_2$NO)(H$_2$O)]·1.5H$_2$O (**3c**). The compound was prepared in analogous fashion to **3a**.Yield 0.31 g (85%). ^1H NMR (D_2O, ppm): 9.09 (d, 1H), 9.07 (d, 1H), 3.98 (s, 3H), 3.45 (s, 3H). ^{51}V NMR (D_2O, ppm): −605. Anal. Calcd for $C_9H_{13}N_3O_{10.5}V$: C, 28.29; H, 3.43; N, 11.00. Found C, 28.10; H, 3.33; N, 10.59.

Aqua-4-nitrodipicolinatodiethylhydroxylamidooxovanadium-(V) [VO(dipic-NO$_2$)(Et$_2$NO)(H$_2$O)] (**3d**). The compound was prepared in analogous fashion to **2a**. Yield 0.27 g (73%). ^1H NMR (D_2O, ppm): 9.13 (d, 1H), 9.11 (d, 1H), 3.90 (m, 2H), 3.47 (m, 2H), 1.60 (t, 3H), 1.42 (t, 3H). ^{51}V NMR (D_2O, ppm): −587. Anal. Calcd for $C_{11}H_{19}N_3O_9V$: C, 34.48; H, 3.68; N, 10.97. Found: C, 34.44; H, 3.50; N, 10.55.

NMR Spectroscopy and Sample Preparation. The ^1H and ^{51}V spectra were recorded on a Varian INOVA-300 spectrometer (7.0 T) at 300 MHz for ^1H and 78.9 MHz for ^{51}V. Routine parameters were used for the ^1H NMR spectra, and DSS (3-(trimethylsilyl)-propanesulfonic acid, sodium salt) was used as the external reference for the ^1H chemical shifts. The ^{51}V NMR spectra were generally acquired with a spectral window of 83 600 Hz, a pulse angle of 60°, and an acquisition time of 0.096 s with no relaxation delay. The ^{51}V chemical shifts were obtained using an external reference of $VOCl_3$ (0 ppm).

The spectroscopic studies were carried out using solutions prepared from isolated complexes. Quantitative data were obtained in cases when no reduction had taken place; all the vanadate added was in the form of vanadium(V), and concentrations could be calculated from the mole fractions of the vanadium signals observed in the ^{51}V NMR spectra. The ligand pK_a values were obtained by ^1H NMR spectroscopy titrations and were confirmed by pH titrations. The titrated solutions generally contained 1−5 mM ligand

Table 1. Crystallographic Data for $Na[VO_2dipic\text{-}NH_2]\cdot 2H_2O$ **(2)**, $K[VO_2dipic\text{-}NO_2]$ **(3)**, and $[VO(dipic)(Me_2NO)(H_2O)]\cdot 0.5H_2O$ **(1c)**

identification code	(**2**)	(**3**)	(**1c**)
empirical formula	$C_7H_8N_2NaO_8V$	$C_7H_2KN_2O_8V$	$C_9H_{12}N_2O_{7.50}V$
unit cell dimensions	$a = 5.854(3)$ Å	$a = 8.6161(7)$ Å	$a = 16.5849(5)$ Å
	$b = 7.893(5)$ Å	$b = 10.5474(8)$ Å	$b = 10.5020(3)$ Å
	$c = 12.053(7)$ Å	$c = 11.2200(8)$ Å	$c = 14.3811(2)$ Å
	$\alpha = 90.817(9)°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 96.138(9)°$	$\beta = 97.4230(10)°$	$\beta = 90°$
	$\gamma = 91.890(10)°$	$\gamma = 90°$	$\gamma = 90°$
V, Å^3	553.4(6)	1011.10(13)	2504.82(11)
Z	2	4	8
formula wt, g/mol	322.08	332.15	319.15
space group	$P\bar{1}$	$P2_1/c$	$Pbcn$
temp, K	173(2)	100(1)	165(2)
λ, Å	0.71073	0.71073	0.71073
D_{calcd} g cm^{-3}	1.933	2.182	1.693
final R indices [$I>2\sigma(I)$]	$R1 = 0.0460$	$R1 = 0.0341$	$R1 = 0.0442$
R indices (all data)	$wR2 = 0.1140$	$wR2 = 0.0894$	$wR2 = 0.1090$

in 20% D_2O. The analyses were carried out in triplicate, and the results were analyzed using Microsoft Excel. Since neither electrolytes nor temperature controls were used, the results are only reported to one decimal place.

X-ray Crystallography. X-ray diffraction data were recorded on a Bruker AXS SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Crystallographic results and other details are listed in Table 1. An absorption correction was applied by using SADABS.[49] Structures were solved by direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions. Standard Bruker control (SMART) and integration (SAINT) software was employed, and the Bruker SHELXTL[50] software was used for structure solution, refinement, and graphics.

Results and Discussion

Synthesis and Solubility. 4-Substituted Dipicolinic Acid Complexes of Vanadium(V). Substituted dipicolinate complexes have been investigated to a much lesser degree than the parent system, in part because of the greater synthetic efforts required in derivatizing the dipicolinate unit.[46−48] Although dipicolinate complexes are classical systems, successful isolation typically takes place in the acidic pH range where the reactant dipicolinate derivative is significantly less soluble. Unfortunately, this is a nontrivial issue when the metal ion undergoes complex speciation chemistry, and success in this area demands careful attention to experimental parameters, particularly pH, and the order of adding reaction components.[51] In Scheme 1 we have indicated that, prior to acidification, the predominant vanadium species is $H_2VO_4^-$; however, it is well-known that aqueous VO_2^+ dominates below pH 2 and is the ion which forms a complex with the dipicolinate ligands under our reaction conditions.

The order of solubility for the three dipicolinate ligands is $H_2dipic\text{-}NO_2$ > H_2dipic > $H_2dipic\text{-}NH_2$. The solubility of the complexes follows the same trend as the ligands (**3** > **2** > **1**). The solubility of the complexes can be further modified by a judicious choice of cation. For this series of complexes, the solubility of NH_4^+ complexes is greater than that of the Na^+ and K^+ complexes. Because $H_2dipic\text{-}NO_2$ is very soluble the resulting V(V) complex is the most difficult complex to isolate, and we were only able to readily isolate its potassium salt in useful quantities. In contrast, the NH_4^+, Na^+, and K^+ salts of the H_2dipic and $H_2dipic\text{-}NH_2$ complexes can be more easily isolated.

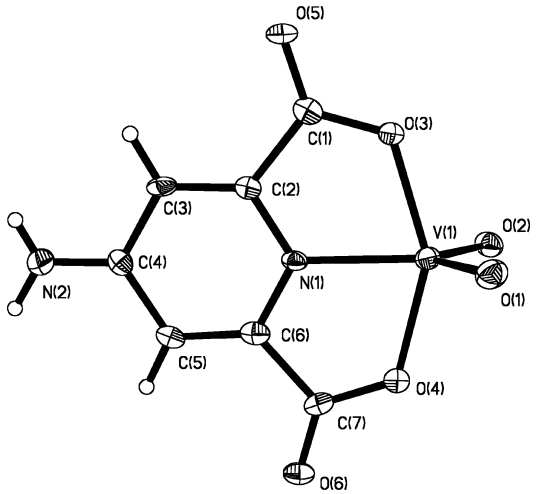


Figure 1. Thermal ellipsoid plot of the anion of $Na[VO_2(dipic\text{-}NH_2)]\cdot 2H_2O$. The two waters of crystallization and the sodium counterion are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Dipicolinatohydroxylamido Complexes of Vanadium(V). Ternary vanadium(V) complexes have been reported with the peroxo and the hydroxylamido moieties.[31−33] Two conceptual methods, depicted in Scheme 2, can be employed to prepare the hydroxylamido complexes. The two-step synthesis requires isolation of the parent dipicolinato complex prior to the addition of the hydroxylamine to isolate the ternary complex. Alternatively, in the one-pot synthesis, the hydroxylamine ligand is added to a mixture prepared by adding metavanadate and a slight excess of the dipic ligand, whereupon the ternary complex can be isolated. Both methods have advantages and disadvantages.

The two-step method is the easier of the two preparative methods because the reagents are pure and the pH of the solution only needs adjustment after the hydroxylamine ligand has been added. However the overall yield is reduced by 10−15% from the one-pot synthesis, and it takes significantly more time. While the one-pot synthesis is

(49) Sheldrick, G. M. *SADABS (a Program for Siemens Area Detection Absorption Correction*); 2000.

(50) Sheldrick, G. M. *SHELXTL, Siemens Analytical X-ray Diffraction*; Siemens: Madison, WI, 1996.

(51) The parent dipicolinate complexes are generally isolated between pH 1 and 2 where they are the most stable. In this pH range vanadate forms decavanadate, and the vanadium(V) is most likely to undergo redox reactions in the presence of hydroxylamines. Furthermore, the dipicolinate ligands are least soluble when protonated. Thus, careful attention to the pH and the order in which reagents are added can be critical for successful isolation of the product. The vanadium(V) complexes can be synthesized directly from metavanadate (NH_4^+, Na^+, or K^+ salts) and the corresponding dipicolinic acid ligand (H_2dipic, $H_2dipic\text{-}NH_2$, and $H_2dipic\text{-}NO_2$) at acidic pH (1−2) at 80 °C as depicted in Scheme 1 to form complexes **1**−**3**. Thus, the increased temperature is necessary to assure that all the dipicolinic acid (or its derivatives) dissolves. Because of the tendency to form decavanadate under the intermittent reaction conditions the preparation of the hydroxylamido complexes is most reliably obtained beginning from the dipicolinate complexes **1**−**3**.

Table 2. Selected Bond Lengths and Angles for $Na[VO_2dipic\text{-}NH_2]\cdot 2H_2O$, $K[VO_2dipic\text{-}NO_2]$, and the Other Known Five-Coordinate Dipicolinato-Vanadium(V) Complexes

	$Cs[VO_2dipic]\cdot H_2O$	$NMe_4[VO_2dipic\text{-}OH]\cdot H_2O$	$Na[VO_2dipic\text{-}OH]\cdot 2H_2O$	$K[VO_2dipic\text{-}OH]\cdot H_2O$	**(2)**	**(3)**
reference	23	24	24	25	this work	this work
V=O	1.610(6), 1.615(6)	1.615(3), 1.626(3)	1.6264(17), 1.6290(17)	1.606(5), 1.616(5)	1.620(3), 1.627(3)	1.6253(15), 1.6293(14)
$V-N_{py}$	2.089(6)	2.077(4)	2.0770(19)	2.089(6)	2.050(3)	2.1019(17)
$V-O_{carb}$	2.001(5), 1.982(5)	1.998(4), 2.022(3)	1.9945(16), 2.0011(16)	2.033(5), 1.990(5)	1.990(3), 1.991(3)	1.9910(14), 1.9953(15)
$O_{carb}-V-O_{carb}$	149.4(2)	148.88(14)	149.42(7)	148.0(2)	149.99(12)	148.81(6)
$O_{oxo}-V-N_{py}$	122.0(3), 128.2(3)	123.37(17), 125.92(18)	124.48(8), 125.71(8)	123.1(3), 127.4(3)	124.92(13), 126.05(13)	118.59(7), 131.85(7)
$O_{carb}-V-N_{py}$	74.6(2), 75.9(2)	74.41(14), 74.48(14)	74.96(7), 74.47(7)	73.3(2), 74.7(2)	75.15(11), 74.85(11)	74.75(6), 74.62(6)

quicker and generally provides for higher yields, the pH of the reaction mixture is critical. Initially, the pH of the mixture of vanadate and dipicolinic acid must be sufficiently low to prevent the formation of decavanadate ($V_{10}O_{28}^{6-}$), which forms between pH 2 and 6.5 and would complicate the formation of the desired dipicolinatodioxovanadium(V) complex. The pH of the solution is then raised to ~5 when the hydroxylamine is added to maintain a significant concentration of the parent dipicolinatodioxovanadium(V) complex while avoiding the possible reduction of vanadium(V) to vanadium(IV) by hydroxylamine (especially with the H_2NOH and MeHNOH ligands). In summary, these solutions require stringent pH control to limit the reduction of V(V) and to favor complex formation over other vanadium(V) species.

X-ray Crystallographic Studies. $Na[VO_2(dipic\text{-}NH_2)]\cdot 2H_2O$ (2). The $Na[VO_2(dipic\text{-}NH_2)]\cdot 2H_2O$ complex (shown in Figure 1) crystallizes as a salt without any required crystallographic symmetry. Selected bond distances and angles are provided in Table 2. The bond angles about the vanadium(V) suggested either a distorted square-pyramidal or trigonal-bipyramidal structure with the latter geometry being emphasized in Figure 1. The two largest angles about the V atom are O3−V1−O4 = 149.99° and O2−V1−N1 = 126.05°. When these angles are used to define τ,[52] then one of the oxo ligands (O1) becomes the 'apical' ligand and $\tau = (149.99 - 126.05)/60 = 0.399$. Since τ is close to 0.5, the coordination geometry for this complex is neither trigonal-bipyramidal nor square-pyramidal. A more detailed comparison of this structure to similar structures is presented in Table 2 and discussed below.[23−25]

In **2** the six-coordinate sodium cation is bound to two symmetry-related O2 oxo ligand atoms (2.418(3), 2.459(3) Å). In addition, symmetry-related oxygen atoms from the C1 carboxylate group (Na−O3 = 2.406(3) Å, Na−O5 = 2.627(3) Å) and both of the lattice water molecules (Na−O7 = 2.405(4) Å, Na−O8 = 2.271(4) Å) are bound to sodium. A long and very weak seventh interaction is also present between sodium and the other oxo oxygen atom (Na−O1 = 3.009(3) Å). The amino substituent forms a weak hydrogen bond to a water molecule (N2···O7 = 2.884(5) Å), as does one of the carboxylate oxygen atoms (O6···O7 = 2.774(4) Å).

$K[VO_2(dipic\text{-}NO_2)]$ (3). The $K[VO_2(dipic\text{-}NO_2)]$ complex (shown in Figure 2) also crystallizes without any required crystallographic symmetry; the pertinent bond angles and distances are listed in Table 2. The bond angles about the vanadium(V) suggested either a distorted square-pyramidal or trigonal-bipyramidal structure shown in Figure 2. The two largest angles about the V atom are O3−V−O4 = 148.81° and O1−V−N1 = 131.85°. Since the O2 atom is not involved in either of these two angles, it becomes the 'apical' ligand, and τ[52] = (148.81 − 131.85)/60 = 0.283. Since the τ value is closer to 0 than to 1, the coordination geometry for this complex is approaching square-pyramidal. The bond distances and angles in these structures may be compared to the corresponding structural features of the $Cs[VO_2(dipic)]$[23] and $Na[VO_2(dipic\text{-}OH)]$[24,25] and the $Na[VO_2(dipic\text{-}NH_2)]$ compounds (see Table 2). From the values in this table it is clear that the V=O and V−O bond lengths are virtually identical, showing that substitution in the 4-position of the pyridine ring does not affect those bonds.

While a majority of the metric parameters in **3** are nearly identical to that of the amino and hydroxyl-substituted dipic complexes, there are two notable differences. The first is the $V-N_{py}$ distance of 2.1019(17) Å, which is significantly longer than those bond lengths in complexes with electron donating substituents (Table 2). The other is the fact that the pyridine ring has a different orientation than in the other substituted dipicolinate complexes (Figure 3). The O(1) atom is oriented in a slightly more trans fashion to the pyridine

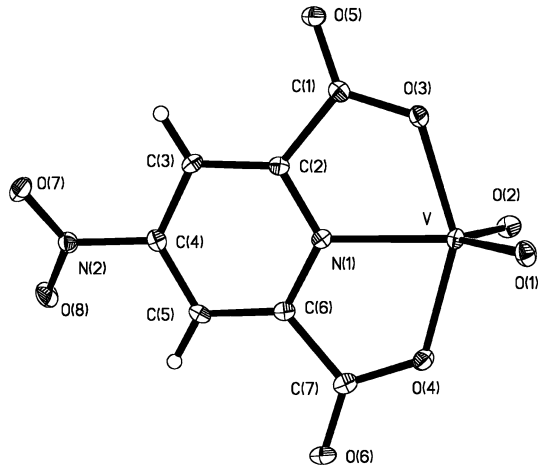


Figure 2. Thermal ellipsoid plot of the anion of $K[VO_2(dipic\text{-}NO_2)]$. The potassium counterion is omitted for clarity. Ellipsoids are shown at the 50% probability level.

(52) Addison, A. W.; Rao, T. N. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

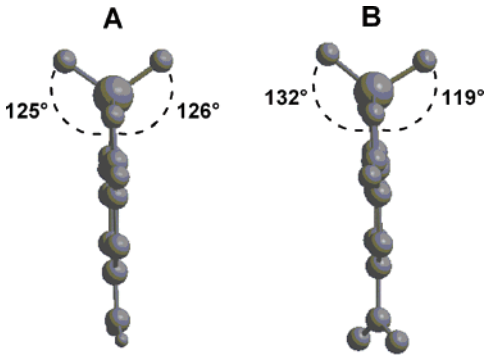


Figure 3. Ball and stick representation of the anions of **2** (A) and **3** (B) that indicates the asymmetry of the N−V−O angle relative to the plane defined by the dipicolinate ligand. The N−V−O angles for both complex anions are depicted and are also listed in Table 2.

nitrogen (∠N−V−O(1) = 131.85(7)°) than the O(2) atom which is in more of a cis orientation (∠N−V−O(2) = 118.59(7)°). This structural modification suggests that, with the appropriate ligand, it may be possible to introduce an additional ligand to form a six-coordinate complex. The N−V−O angles in the other substituted dipicolinate complexes are far more symmetric with respect to the dipicolinate ring, while the unsubstituted dipic structure displays somewhat more asymmetry (Table 2). In addition, the plane defined by the NO_2 group is twisted ∼27° relative to the pyridine ring.

The $V-N_{py}$ bond varies in length as would be expected from the electronic changes in the substituent group. The more electron donating substituent, NH_2, should make the pyridine N-atom a better σ and π donor and shorten the $V-N_{py}$ bond, while the electron-withdrawing NO_2 group should have the opposite effect. Indeed the $V-N_{py}$ bond length in $[VO_2(dipic\text{-}NH_2)]^-$ is 2.050(3) Å compared to the $V-N_{py}$ bond lengths in $[VO_2(dipic\text{-}OH)]^-$ (2.077(4) and 2.0770(19) Å)[24] and in $[VO_2(dipic)]^-$ (2.089(6) Å);[23] the V−N bond length in $[VO_2(dipic\text{-}NO_2)]^-$ is noticeably longer at 2.1019(17) Å.

The eight-coordinate potassium ions knit the structure together tightly by binding to oxygen atoms from seven different symmetry-related complex anions. Five of the K−O bonds are markedly shorter than the other three. Three of these five shortest bonds to potassium involve oxo ligands O1 (2.7395(15) Å) and O2 (2.7495(15), 2.7681(15) Å). The other two short K−O interactions involve oxygen atoms from the nitro substituent (O7, 2.7139(15) Å) and one of the carboxylate groups (O5, 2.7838(16) Å). There is no hydrogen bonding in this structure due to a lack of protic donors.

$[VO(dipic)(Me_2NO)(H_2O)]\cdot 0.5H_2O$. The $[VO(dipic)(Me_2NO)(H_2O)]$ complex (shown in Figure 4) crystallizes as discrete molecules without required crystallographic symmetry. Selected pertinent bond distances and angles are provided in Table 3 along with those of other crystallographically characterized, seven-coordinate vanadium(V)-dipic complexes.[31−33,53] This complex contains seven-

(53) Tinant, B.; Bayot, D.; Devillers, M. *Z. Kristallogr. - New Cryst. Struct.* **2003**, *218*, 477−478.

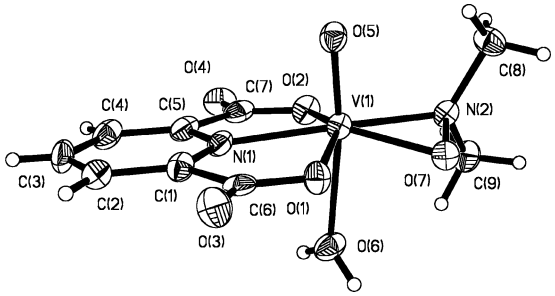


Figure 4. Thermal ellipsoid plot of $[VO(dipic)(Me_2NO)(H_2O)]\cdot 0.5H_2O$. The water molecules of crystallization are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

coordinate vanadium in a pseudo, pentagonal-bipyramidal geometry. Alternatively, if one considers the hydroxylamido group to be a monodentate ligand, then the complex is a distorted, six-coordinate octahedral complex. The geometry of this complex is similar to that of the vanadium(V)-dipicolinato complex reported previously with the corresponding parent hydroxylamine, $[VO(dipic)(H_2NO)(H_2O)]$.[33] Dimethylation of the hydroxylamine unit has no observable effects on the lengths of the $V-O_{H2O}$, $V-O_{R2NO}$, $V-N_{py}$, and the hydroxylamine N−O bonds. However, in the substituted hydroxylamine complex, the $V-N_{R2NO}$ bond length increased from 2.007(3) to 2.028(3) Å, respectively; such an increase would be anticipated based on the extra steric bulk of the two methyl groups. This steric bulk is also apparently sufficient to modify the coordination sphere of the vanadium resulting in a decrease of the $V-O_{carb}$ bond lengths, from 2.031(3) and 2.039(3) Å in **1a** to 2.008(3) and 2.026(3) Å in the substituted complex, **1c**.

Comparing the bond lengths of the hydroxylamido-derivative complexes with those of the parent dipicolinato complexes (Tables 2 and 3) showed several differences. The V=O bonds are significantly shorter in the hydroxylamido complexes perhaps reflecting the need for additional electronic density in the more sterically crowded complexes. The $V-N_{py}$ bonds are shorter, whereas the $V-O_{carb}$ bonds are significantly longer in the hydroxylamido complexes compared to the parent complexes. Because there is little change in the N−C−C and C−C−O angles, the shortening of the $V-O_{carb}$ bonds is primarily attributable to better overlap between the vanadium atom and the pyridine nitrogen donor.

Hydrogen bonding connects the complexes via interactions between the coordinated water molecule (O6) and carbonyl oxygen atoms O3 (2.817(5) Å) and O4 (2.764(5) Å). The disordered water molecule present in the lattice does not form any significant hydrogen bonds (perhaps accounting for its disorder).

Spectroscopic Studies. Solution Chemistry of 4-Substituted Dipicolinato Ligands. The chemical shifts for the ligands $H_2dipic\text{-}NH_2$ (7.08 ppm) and $H_2dipic\text{-}NO_2$ (8.89 ppm) reflect the expected changes in the electron densities of 4-substituted pyridine-2,6-dicarboxylic acids with the H_2-$dipic\text{-}NH_2$ ligand shifting downfield and the $H_2dipic\text{-}NO_2$ ligand upfield compared to the H_2dipic ligand (at 8.32 and

Table 3. Selected Bond Lengths and Angles for $[VO(dipic)(Me_2NO)(H_2O)]\cdot 0.5H_2O$ and the Other Known Seven-Coordinate Dipicolinato-Vanadium(V) Complexes with Ternary Peroxo or Hydroxylamido Ligands

	$[VO(dipic)-(O_2)(H_2O)]$	$[VO(dipic)(O_2)(H_2O)]$	$[VO(dipic)-(OOBu^t)(H_2O)]$	$[VO(dipic)-(H_2NO)(H_2O)]$	**(1c)**
reference	31	53	32	33	this work
$V-O_{oxo}$	1.579(2)	1.588(3)	1.574(3)	1.587(3)	1.588(3)
$V-N_{py}$	2.088(2)	2.080(3)	2.058(4)	2.064(3)	2.067(3)
$V-N_{R_2NO}$				2.007(3)	2.028(3)
$V-O_{carb}$	2.053(2), 2.064(2)	2.041(3), 2.048(3)	1.996(3), 1.983(3)	2.031(3), 2.039(3)	2.026(3), 2.008(3)
$V-O_{R_2NO}$				1.903(3)	1.902(3)
$V-O_{peroxo}$	1.870(2), 1.872(2)	1.869(3), 1.892(3)	1.872(3), 1.999(3)		
$V-O_{H_2O}$	2.211(2)	2.235(3)	2.234(3)	2.240(3)	2.239(4)
$N_{R_2NO}-O_{R_2NO}$				1.371(4)	1.384(4)
$O_{peroxo}-O_{peroxo}$	1.441(3)	1.437(4)	1.436(5)		
$O_{carb}-V-O_{carb}$	147.2 (1)	148.20(12)	149.4[a]	149.5(1)	148.44(12)
$O_{oxo}-V-N_{py}$	92.2 (1)	93.53(16)	95.9(1)	97.2(1)	93.68(14)
$O_{oxo}-V-O_{carb}$	96.2 (1), 94.9 (1)	95.98(16), 94.38(16)	95.2(1), 94.1(1)	93.0(1), 98.9(1)	98.05(14), 95.08(13)
$O_{H_2O}-V-O_{oxo}$	172.1 (1)	169.84(16)	172.8(1)	172.0(1)	172.12(14)

[a] Not reported; calculated from the cif file.

Table 4. ^1H and ^{51}V NMR Data for Compounds **1**−**3**, Their Hydroxylamido Derivatives, and the Known Simple V−Hydroxylamido Complexes

dipic-X	RR′NO	compd	pH	$^1H\ \delta_{dipic-X}$ (ppm)[a]	$^1H\ \delta_{RR'NO}$ (ppm)[a]	$^{51}V\ \delta$ (ppm)[b]	ref
H		**1**	2.6	8.64 (d), 8.32 (t)		−533	21
NH_2		**2**	4.6	7.08 (s)		−525	this work
NO_2		**3**	3.3	8.89 (s)		−534	this work
H	H, H	**1a**	4.9	8.63 (t), 8.39 (dd)	*c*	−681	57
	H, Me	**1b**	5.1	8.64 (t), 8.39 (dd)	3.90 (s), 3.43 (s)	−634, −647	57
	Me, Me	**1c**	5.4	8.62 (t), 8.38 (dd)	3.95 (s), 3.42 (s)	−614	this work
	Et, Et	**1d**	5.2	8.62 (t), 8.38 (dd)	3.87 (dq),[d] 3.44 (dq),[d] 1.59 (t), 1.41 (t)	−598	57
NH_2	H, H	**2a**	4.7	7.20 (s)[e]	*c*	−688	this work
	H, Me	**2b**	4.9	7.21 (d, 1H), 7.19 (d, 1H)	3.76 (s), 3.29 (s)	−640, −652[f]	this work
	Me, Me	**2c**	4.1	7.22 (d, 1H), 7.19 (d, 1H),	3.81 (s), 3.28 (s)	−619	this work
	Et, Et	**2d**	5.2	7.19 (d, 1H), 7.18 (d, 1H)	3.71 (dq),[d] 3.35 (dq), 1.43 (t), 1.26 (t)	−604	this work
NO_2	H, H	**3a**	1.7	9.09 (s, 2H)	*c*	−671	this work
	H, Me	**3b**	1.7	9.09 (d, 1H), 9,07 (d, 1H)	3.92 (s), 3.45(s)	−618, −632	this work
	Me, Me	**3c**	1.7	9.09 (d, 1H), 9,07 (d, 1H)	3.98 (s), 3.45(s)	−605	this work
	Et, Et	**3d**	1.9	9.13 (d, 1H), 9.11 (d, 1H)	3.90 (dq),[d] 3.47 (dq),[d] 1.60 (t), 1.42 (t)	−587	this work
	H, H		7.1		NA	−569,[g] −670,[g] −674,[g] −818,[h] −835,[h] −852,[h] −860[h]	40
	H, Me		7.5		NA	−571,[g] −651,[g] −655,[g] −740 to −815[h]	40
	Me, Me		6.7		NA	−570,[g] −630,[g] −635,[g] −724,[h] −740,[h] −750[h]	39
	Et, Et				NA	−631,[g] −717,[h] −735[h]	this work

[a] Chemical shifts are given in ppm and are reported versus an external standard of DSS in D_2O. Unless otherwise indicated, no changes in the chemical shifts as a function of pH (pH 2−8) were observed. [b] Chemical shifts are given in ppm and are reported versus an external standard of neat $VOCl_3$. [c] Protons are not observable. [d] Multiplets arise from two overlapping quartets. [e] The signal is expected to be a two doublets but is not resolved even at 400 MHz. [f] This signal was only observed on the more sensitive INOVA-400 MHz spectrometer. [g] Signals arising from 1:1 (hydroxylamine:vanadate) species, the chemical shifts vary with pH. [h] Signals arising from 2:1 (hydroxylamine:vanadate) species, the chemical shifts vary with pH.

8.64 ppm[21]). The pK_a values of H_2dipic-NH_2 and H_2dipic-NO_2 were determined by ^1H NMR using eq 1[54] and were found to be 2.9 and 4.3 and 2.5 and 4.2, respectively, and were confirmed by subsequent pH titrations. These values compare to 2.03 (±0.01) and 4.49 (±0.01) for the parent dipic ligand.[21,55]

$$pK_a = pH - \log[(\delta_L-\delta_O)/(\delta_O-\delta_H)] \quad (1)$$

Solution Chemistry of Five-Coordinate Parent Dipicolinatodioxovanadium(V) Complexes. The aqueous chemistry of the complexes was monitored by ^1H and ^{51}V NMR spectroscopy. The spectroscopic similarity of the parent complexes to that of $[VO_2(dipic)]^-$[21] and $[VO_2(dipic-OH)]^-$[24,25] in solution supports the interpretation that the vanadium is five-coordinate as shown above in the solid-state structures of the $[VO_2(dipic-NH_2)]^-$ and $[VO_2(dipic-NO_2)]^-$ complex ions.

From pH 2−8 only one ^1H NMR signal is observed for the two protons on the 4-substituted dipic ligands in compounds **2** and **3**. Table 4 summarizes the ^1H and ^{51}V chemical shifts of compounds **1**,[21] **2**, and **3**. The ^1H chemical shifts of the ligands in the intact $[VO_2(dipic)]^-$, $[VO_2(dipic-NH_2)]^-$, and $[VO_2(dipic-NO_2)]$ complexes were independent of pH; however, the chemical shifts of free ligand are pH dependent (data not shown) and reflect varying degrees of protonation as was previously reported for dipicolinic acid and 4-hydroxypyridine-2,6-dicarboxylic acid.[21,24] In fact, ^{51}V NMR spectroscopy must be employed in some cases to

(54) Tracey, A. S.; Gresser, M. J.; Galeffi, B. *Inorg. Chem.* **1988**, *27*, 157−161.
(55) Funahashi, S.; Haraguchi, K.; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349−1353.

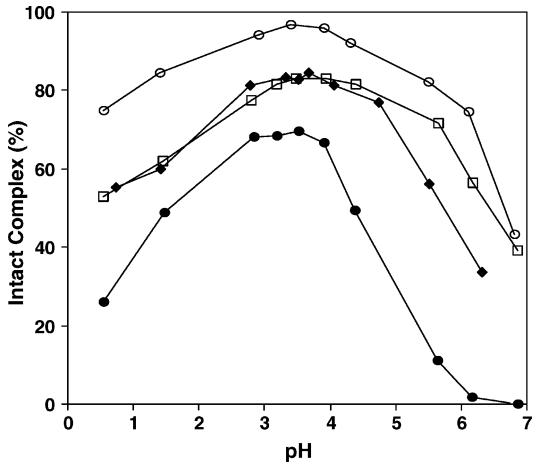


Figure 5. The percentage of intact $[VO_2(dipic\text{-}X)]^-$ as a function of pH. X = H (○); X = OH (◆); X = NH_2 (□); and X = NO_2 (●). Due to the presence of monomeric and oligomeric vanadate species none of the complexes exhibit 100% stability even at the optimal pH of 3.4. The percentages of these other vanadates were omitted for clarity.

distinguish between overlapping ^1H signals arising from the free ligand and the complex at lower pH.

pH Stability of Five-Coordinate Parent Dipicolinatodioxovanadium(V) Complexes. In a comparison between the stability of the $[VO_2dipic]^-$ and the $[VO_2dipic\text{-}OH]^-$ complexes the latter was found to be much more sensitive to pH because of the substituent group.[24] Because of the various protonation forms and existing equilibria a direct comparison is difficult. To provide the reader with some quantitative measure for the relative presence of these complexes we illustrate the effect of electron-donating and -withdrawing substituents by plotting the percentage of the complex present in solutions containing 1.1 mM free ligand ($H_2dipic\text{-}NH_2$ and $H_2dipic\text{-}NO_2$) and 1.7 mM $NaVO_3$ as determined by ^{51}V NMR spectroscopy at various pH values.[56] Figure 5 shows that the percentage of the complex based on the initial ligand concentration varies only slightly when compared with similar data for $[VO_2(dipic)]^-$ and $[VO_2(dipic\text{-}OH)]^-$.[21,24]

All three complexes exhibit a bell-shaped stability curve spanning a range of more than two pH units (Figure 5). The complex generated with the $H_2dipic\text{-}NH_2$ ligand forms in slightly higher amounts than the complex formed with the $H_2dipic\text{-}NO_2$ ligand, while the unsubstituted dipic complex forms the most complex. This observation is consistent with the expectation that an electron-withdrawing substituent should result in a weaker complex and also with previous results with the dipic-OH ligand which showed decreased stability relative to the unsubstitued dipic ligand.[24] Thus, both electron-donating and electron-withdrawing substituents result in less complex formation. Interestingly, when the ratio of the complex to $[V_1]$ is considered, all the complexes show the highest ratio at pH 3.4 (data not shown). Since the pK_a values of the ligands vary, it is possible that aqueous vanadate chemistry is responsible for the similar stability curves for the complexes.

(56) Although formation of V_{10} is a major problem in preparation of these complexes, the concentrations are low, and the binary complexes are sufficiently stable that this species does not significantly impact these studies.

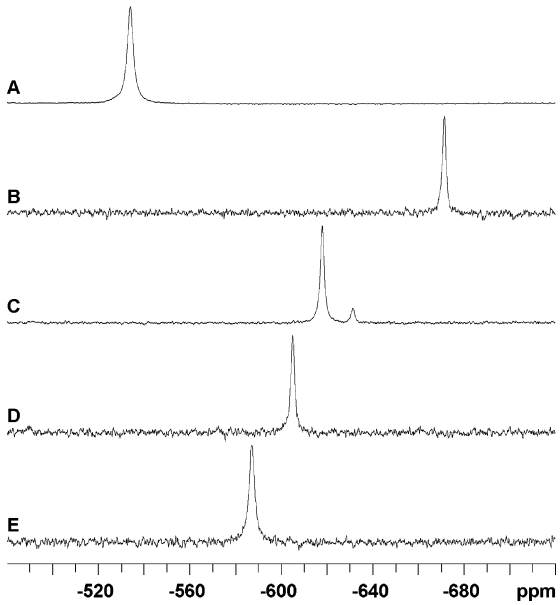


Figure 6. ^{51}V NMR spectra of the parent $[VO_2(dipic\text{-}NO_2)]^-$ ion and its hydroxylamido derivatives: (A) $[VO_2(dipic\text{-}NO_2)]^-$; (B) $[VO(dipic\text{-}NO_2)(H_2NO)(H_2O)]$; (C) $[VO(dipic\text{-}NO_2)(MeHNO)(H_2O)]$; (D) $[VO(dipic\text{-}NO_2)(Me_2NO)(H_2O)]$; and (E) $[VO(dipic\text{-}NO_2)(Et_2NO)(H_2O)]$. The solutions were prepared by dissolving solid complex (3 mM) in D_2O and adjusting the pH to 3.

Solution Chemistry of Seven-Coordinate Dipicolinatohydroxylamidooxovanadium(V) Complexes. The NMR spectroscopic data of aqueous solutions of compounds **3a**−**d** are shown in Figures 6 and 7. The solutions were obtained from solutions of the freshly dissolved complex. The chemical shifts for complexes **1a**−**d**, **2a**−**d**, and **3a**−**d** are listed in Table 4. By ^{51}V NMR spectroscopy, the chemical shifts of the hydroxylamido complexes are found to occur at 50−150 ppm lower resonance than those of the parent complexes (Figure 6). As the alkyl bulk of the hydroxylamido group increases the chemical shift of the V complex decreases, and in fact the V complex with H_2NO^- is observed at the highest resonance, which is consistent with a previous study.[57] Since the pK_a values for these ligands are very similar (H_2NOH, 6.0; MeHNOH, 6.1; Me_2NOH, 5.4; and Et_2NOH, 5.7)[13,58] the variation in the ^{51}V NMR chemical shift cannot be explained by differences in ligand pK_a values.

Although slight structural modifications of a ligand generally do not result in such dramatic changes in chemical shifts,[9,59] precedence for large changes in chemical shifts have been reported for V complexes with catechols.[59] Electron-donating or -withdrawing groups in the hydroxylamido complexes result in the observation of large downfield chemical shift changes. In contrast to the upfield effects reported for the "noninnocent" catechol ligands, both systems show large chemical shift changes in response to subtle

(57) Rehder, D.; Wieghardt, K. *Z. Naturforsch., B: Chem. Sci.* **1981**, *36b*, 1251−1254.
(58) Bissot, T. C.; Parry, R. W.; Campbell, D. H. *J. Am. Chem. Soc.* **1957**, *79*, 796−800.
(59) Cornman, C. R.; Colpas, G. J.; Hoeschele, J. D.; Kampf, J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1992**, *114*, 9925−9933.

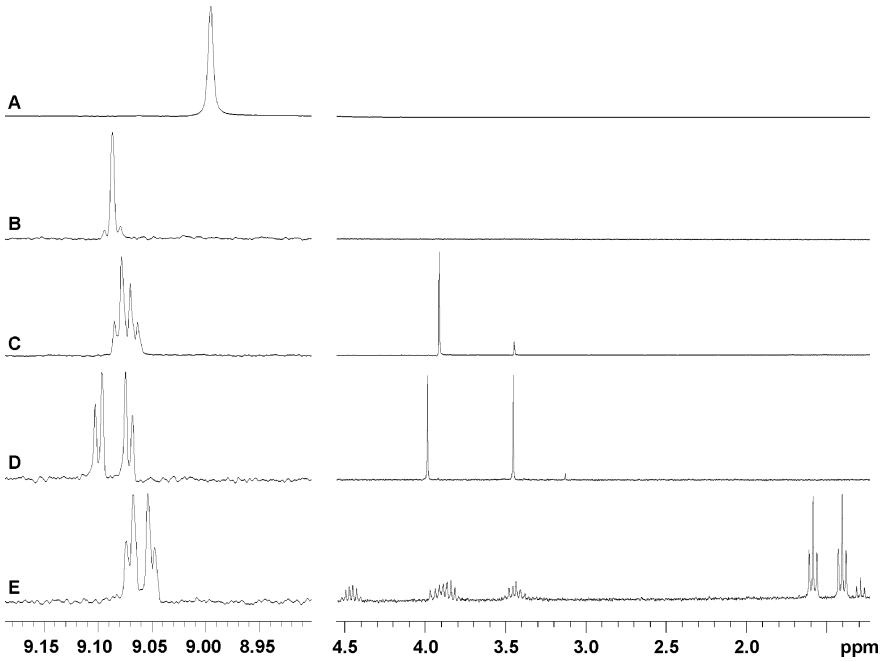


Figure 7. The ^{1}H NMR spectra of the parent $[VO_2(dipic\text{-}NO_2)]^-$ ion and its hydroxylamido derivatives. Shown on the left is the 'dipic-NO_2' region (scale is enlarged to indicate splitting) and on the right side is the 'hydroxylamido' region: (A) $[VO_2(dipic\text{-}NO_2)]^-$; (B) $[VO(dipic\text{-}NO_2)(H_2NO)(H_2O)]$; (C) $[VO(dipic\text{-}NO_2)(MeHNO)(H_2O)]$; (D) $[VO(dipic\text{-}NO_2)(Me_2NO)(H_2O)]$; and (E) $[VO(dipic\text{-}NO_2)(Et_2NO)(H_2O)]$. The small signals at ~3.1 ppm in (D) and ~4.5 and 1.3 ppm in (E) are assigned to free ligand. The solutions were prepared by dissolving solid complex (3 mM) in D_2O and adjusting the pH to 3.

electronic differences in the ligands. Because the pK_a values are very similar for the simple hydroxylamine ligands, the large chemical shift differences for the series of hydroxylamido compounds described here are not likely to be explained solely in terms of the electronic differences of the ligands. The side-on coordination of the N−O ligand to the vanadium atom presumably also contributes to the chemical shift changes in the vanadium since similar changes were not observed with ligand substitution on the dipic moiety.[39,41,43]

Studies were carried out on solutions containing added vanadate, H_2dipic, H_2dipic-NH_2, or H_2dipic-NO_2 and a systematic variation of the hydroxylamines from the unsubstitued hydroxylamine to the mono- and dialkylated hydroxylamines. The stoichiometry of the new complexes was deduced from the known solution species,[39,40] their ^{51}V NMR chemical shifts, and the solution composition. Monomeric vanadate ($H_2VO_4^-/HVO_4^{2-}$) at −560 ppm is converted to complex **3** at −534 ppm upon addition of dipic-NO_2 in acidic solution. This species converts to a hydroxylamido complex upon addition of any of the four hydroxylamines used in this study; this process has been described in detail previously for the simple vanadate/hydroxylamido system.[39,40] For example, addition of the unsubstituted hydroxylamine forms a new species at −671 ppm. The complexes formed between vanadate and H_2NO^- have chemical shifts at −569, −670, and −674 ppm for a 1:1 species and −818, −835, −852, and −860 ppm for a 2:1 (H_2NO:V) species (Table 4).[39,40] Because the new species is different than the $[VO_2dipic\text{-}NO_2]^-$ complex, the signal at −671 ppm arises from a species consisting of vanadium(V), hydroxylamine, and H_2dipic-NO_2. Furthermore, considering that the chemical shift of the new complex is between that of the 1:1 vanadium(V)-hydroxylamine complex and the $[VO_2dipic\text{-}NO_2]^-$ complex, a likely stoichiometry for the new species is 1:1:1 (H_2NO^-:V(V):dipic-NO_2^{2-}). A study of a series of spectra at different ratios of reactants supports this expectation (data not shown).

Structural diversity is also observed in these ternary complexes. While the parent and dialkylhydroxylamido complexes give rise to only one ^{51}V NMR signal, the *N*-methylhydroxylamido complex shows two distinct signals 14 ppm apart (Figure 6).[39,40] The ratio of the signals in these complexes is about 9:1 with the downfield signal being the predominant species. We attribute these two signals to coordination isomers that have previously been reported in related V-hydroxylamido complexes.[44]

The ^{1}H NMR chemical shifts for the simple hydroxylamido (H_2NO^-) complexes with H_2dipic-NH_2 and H_2dipic-NO_2 are 7.20 and 9.09 ppm, respectively (Table 4). This compares to the chemical shifts of 8.63 and 8.39 ppm for the corresponding dipic derivative. The electron-withdrawing nitro group results in a downfield shift, while the electron-donating amino group results in an upfield shift compared to the parent complexes (summarized in Table 4). Only a small change in the ^{1}H NMR chemical shift on the order of 0.2 ppm is observed between the hydroxylamido complexes and the parent complexes.

Correspondingly, the chemical shifts for the ^{1}H NMR signals arising from the protons in the 3 and 5 positions in the dipic ligands in the series of the hydroxylamido complexes $[VO(dipic\text{-}NH_2)(RR'NO)(H_2O)]$ and $[VO_2(dipic\text{-}NO_2)(RR'NO)(H_2O)]$ are similar to those described for the parent dipicolinatodioxovanadium(V) systems (ca. 7.2 and 9.1 ppm for each series, respectively, Table 4). However, these signals are split into two doublets, rather than the singlet observed for H_2dipic-NH_2 and H_2dipic-NO_2. The fact that

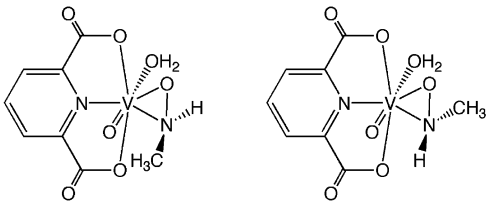


Figure 8. Two possible isomeric structures for [VO(dipic)(MeHNO)-(H_2O)].

such a coupling pattern is observed shows that these protons are different, which requires geometric restrictions in these complexes. Hydroxylamido-vanadium(V) complexes were previously found to be much more labile.[39,40]

The signals arising from the alkylhydroxylamido protons on the α-carbons show little variation in chemical shifts (3.8−4.0 ppm), Table 4. These signals are split into two groups of signals reflecting the different environments of the *N*-substituted groups in the complex. Since only one ^{51}V NMR signal was observed for the hydroxylamido complexes formed from the unsubstituted and disubstituted hydroxylamines, the two environments for the alkyl groups reflect two different coordination modes. This interpretation is supported by the observation of the monoalkylated hydroxylamine complexes that show two ^{51}V NMR signals with different intensities (approximately 9:1). Two possible structures for these complexes are illustrated in Figure 8.

pH Stability of Dipicolinatohydroxylamidooxovanadium(V) Complexes. The stability of the hydroxylamido complexes was examined with ^{51}V and ^{1}H NMR spectroscopy over a wide pH range (2−8) in H_2O. The spectra for complex **1b** are shown in Figure 9; the other hydroxylamido compounds in this series (including those with substituted dipicolinate ligands) also showed increased stability toward the neutral pH region. All the solutions were prepared from freshly dissolved complex in H_2O. The pH of the solutions were adjusted with NaOH or HCl.[60] In solutions below pH 8, the solution color changes from yellow to green over a period of a few hours with the lowest pH samples showing the fastest changes. This color change is indicative of the reduction of V(V) (presumably in the form of oxovanadates) to V(IV) by the hydroxylamine ligands. However, the ^{1}H and ^{51}V NMR spectra of these solutions show that the vanadate-dipic-hydroxylamido complexes persist even after a few days indicating that significant amounts of the complexed V(V) remain in solution. An alternative complication can be the formation of the decavanadate species. If the dipic ligand is added to the vanadate solutions at pH values where the yellow/orange decavanadate is the major species in solution (pH 3−6), the decavanadate ion can prevail and thus delay formation of even thermodynamically favorable vanadium(V) complexes for weeks.

(60) The order of mixing is very important, and we caution that any deviation from this order can lead to the formation of undesirable side products. For example, at acidic pH values unless the vanadate−dipic complex is formed prior to addition of the hydroxylamine, the hydroxylamines will reduce the oxovanadates present in solution. The pH of the $NaVO_3$ stock solution should not be adjusted below ~7 prior to mixing, or else the reaction will be seriously compromised.

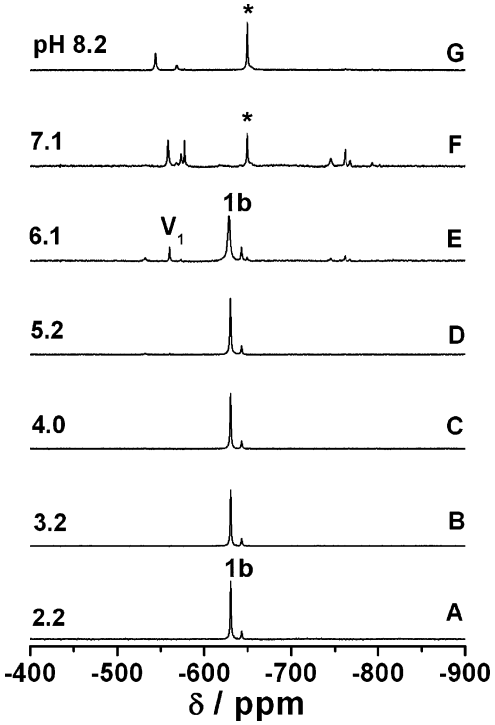


Figure 9. The ^{51}V NMR spectra of [VO(dipic)(MeHNO)(H_2O)] recorded as the pH was varied from 2−8 (A−G). Each spectrum was recorded from a separate sample with an initial concentration of 2 mM complex. Monomeric vanadate and the predominant hydroxylamido:V species are labeled as V_1 and *, respectively.

The ternary complexes formed from vanadate, H_2dipic, H_2dipic-NH_2, H_2dipic-NO_2, and the unsubstituted hydroxylamines had ^{51}V chemical shifts of −681, −688, and −671 ppm, respectively. This order lies in contrast to that of the parent dipicolinatooxovanadium(V) series (dipic^{2-}, −533; dipic-NH_2^{2-}, −528; and dipic-NO_2^{2-}, −534 ppm). The two methylhydroxylamido-dipic-NO_2 complexes (**3b**) are at −618 and −632 ppm, while the 1:1 and 2:1 methylhydroxylamido-V complexes arise at −636 (1:1), −738 (2:1), and −745 (2:1) ppm, respectively. Once formed, the complexes persist over most of the pH range examined (Figure 9), albeit with some reduction and hydrolysis during complex formation. Hydrolysis is indicated by the appearance of signals in the ^{51}V NMR spectrum at −508, −528, and −424 ppm (decavanadate) at acidic pH and at −533 (**1**), −749, and −766 (2:1 methylhydroxylamido-V complex) at neutral pH. Reduction is also readily observed by the solution color changing from pale-yellow to a yellow-green; this observation was confirmed by spectroscopic methods. The high stability of complexes **1a**−**d** stands in contrast to V(V)-hydroxylamido complexes reported containing amino acids and dipeptides.[41−44] Similar stability patterns were observed for complexes **2a** and **3a**.

From pH 2−7 the new species, formed from solutions of prepared from freshly dissolved complex, is present in solution (Figure 9 for **1b** and Figure 10 for **3c**). Figure 10 was included with the purpose of illustrating the comparative stability between the parent and hydroxylamido complexes (complex **3** versus **3c** series). Below pH 6 decavanadate signals can appear at −508, −528, and −424 ppm in the ^{51}V NMR spectrum and demonstrate that complex formation

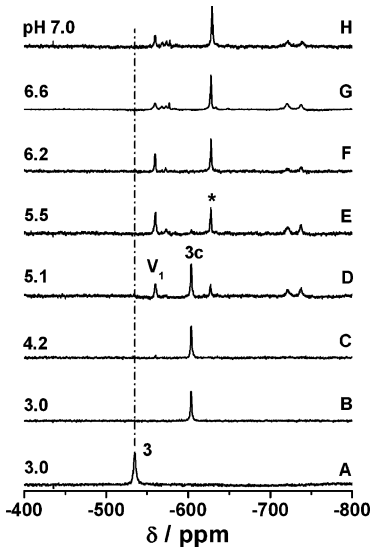


Figure 10. ^{51}V NMR spectra of $[VO_2(dipic\text{-}NO_2)]^-$ at pH 3 (A) and $[VO(dipic\text{-}NO_2)(Me_2NO)(H_2O)]$ from pH 3 to pH 7 (B−H). Monomeric vanadate and the predominant 1:1 hydroxylamido:V species are labeled as V_1 and *, respectively.

is not complete. At higher pH values the signals at −803, −812, and −817 ppm are attributed to the formation of 2:1 (H_2NOH:V) complexes,[40] but for the dipic series one of the 1:1 complex has a chemical shift only 1 ppm from the ternary complex. For this reason we chose to include Figure 10 of **3** and **3c** because the difference in the chemical shift for the H_2NOH:V complexes and that of the ternary dipic-NO_2 complex is 20 ppm and the nature of the complexes are easily distinguished. As shown in Figure 10 complexes **3** and **3c** were both intact at pH 3 when both complexes were dissolved. Since no complex **3** (indicated by broken line) forms in solutions containing added complex **3c** the ternary complex is more stable than the parent complex. Above pH 5 complex **3c** hydrolyzes and since the resulting complexes formed are those formed from hydroxylamine and vanadate[40] with no evidence for complex **3**, this observation demonstrates that both the ternary complex and the hydroxylamine-vanadate complexes are more stable than the binary parent complex **3** over the entire pH range 3−7. Overall, the spectra shown in Figures 9 and 10 show that the addition of the hydroxylamine led to the formation of the ternary complex **3c** which extended the pH stability of complex **3** closer to the neutral pH range.

The pH stability studies with the dipic system showed that as the hydroxylamine is methylated, the complex's stability increases toward acidic pH values and decreases near neutral pH. This observation was made because less decavanadate was observed at low pH in the samples at low pH. In contrast, above pH 5, slightly more hydrolysis to oligomers and the 2:1 hydroxylamido complexes was observed as indicated by the presence of signals arising from $[VO_2dipic]^-$, oligomeric vanadate species, the 2:1 methylhydroxylamido species (at −739 and −765 ppm),[40] and the dimethylhydroxylamido species (at −724 and −739 ppm).[39] Thus these spectra showed greater amounts of oligomeric vanadates at neutral pH and more vanadium(V)-hydroxylamine complexes at pH 8. The diethylhydroxylamido complex showed a similar pattern but was not characterized in as much detail due to its decreased solubility (data not shown). Since the hydroxylamines have similar pK_a values, it is possible that the steric bulk of the diethylhydroxylamine ligand facilitates the hydrolysis of the complex which would lead to its decreased stability

Solution Chemistry of Nonstoichiometric Solutions of the MeHNOH/H_2dipic-NO_2/V(V) System. The reaction of vanadate and H_2dipic-NO_2 in the presence of excess MeHNOH, under mildly acidic conditions, takes a very different course. The reaction was investigated under a variety of conditions: differing reagent stoichiometries, varying the hydroxylamine and dipic derivatives, altering the initial pH of the solution, and excluding oxygen. As expected, vanadium(V) is completely reduced to vanadium(IV) in the presence of excess hydroxylamine; however, the reaction with H_2dipic-NO_2 results in the formation of additional vanadium(V) products. Unbuffered solutions containing 3.0 mM vanadate, 3.0 mM H_2dipic-NO_2, and 30 mM MeHNOH at approximately pH 5 were monitored as a function of time using ^{51}V NMR spectroscopy. The resulting spectra indicated the formation of complex **3b** and two new signals of similar intensity (at −588 and −592 ppm), Figure 11A. Unexpectedly one or two new species are observed in these solutions after 24 h. The signal intensities of the new species were found to increase until 72 h at which point the species persist in solution for several weeks. The pH of the reaction mixture slowly decreased to about 2.5 after 72 h. These new species were not detected by ^{1}H NMR spectroscopy presumably, because the signals of these new species overlap with the signals arising from complex **3b**. The course of this reaction was investigated as a function of starting pH, and as shown in Figure 10B these two species were only observed when the initial pH was near 5. When the initial pH was below pH 3.5 and above pH 6, these new species were not observed even though the reaction mixtures approached the same pH after 3 days. The additional signals appearing at −738 and −745 ppm in these solutions are assigned to the formation of the two isomers of the 2:1 complex $[VO(OH)(MeHNO)_2]$ and a 1:1 (V:MeHNOH) complex at −636 ppm (Figure 11B).[39,40,61] Attempts to systematically determine the stoichiometry of the new complexes were abandoned due to the formation of side products. The observation of this reaction demonstrates that more unusual products such as a few described in the literature[38] are prime candidates for exploration in the future.

Comparison of Five- and Seven-Coordinate Vanadium(V) Complexes. Can a five-coordinate near trigonal-bipyramidal complex convert to a seven-coordinate near pentagonal-bipyramidal structure? To explore the bonding of the hydroxylamido ligand in the seven-coordinate complexes, B3LYP/6-31G* DFT calculations using Spartan '06[62] were done on compound **1a**. The bonding of the hydroxylamido ligand to the vanadium clearly implicates ligand orbitals localized on the nitrogen and oxygen atoms, strongly suggesting that the hydroxylamido ligand is behaving as a

(61) Nxumalo, F.; Tracey, A. S. *J. Biol. Inorg. Chem.* **1998**, *3*, 527−533.
(62) Wavefunction, Inc.: Irvine, CA, 2006.

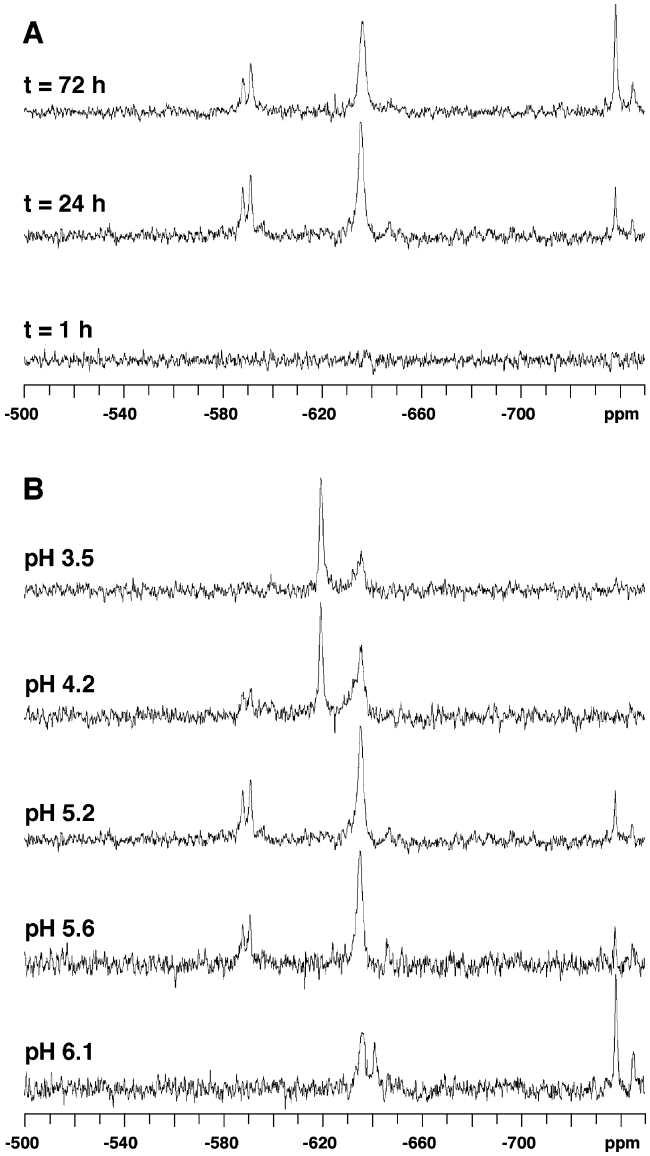


Figure 11. The ^{51}V NMR spectra of nonstoichiometric solutions of *N*-methylhydroxylamine, 4-nitrodipicolinate, and sodium metavandate as a function of time (A) and of initial pH (B). The reaction mixtures were comprised of 3 mM $NaVO_3$, 3 mM H_2dipic-NO_2, and 30 mM MeHNOH·HCl in H_2O. 1 M HCl or 1 M NaOH was used to adjust the pH. The initial pH of the spectra in A was 5.2.

bidentate donor. No σ interactions between the N−O bonding pair and the metal ion were observed near the HOMO−LUMO gap, which would have been consistent with the hydroxylamide ligand acting as a monodentate, η^2-donor. Thus, there are no interactions that could lead to a six-coordinate complex in these systems, which explains why the addition of the hydroxylamido ligand results in a seven-coordinate species. A structural comparison shows that if the complexes are viewed in this manner, the incoming hydroxylamido ligand must approach the dipicolinatodioxovanadium complex between the dioxo groups. The conversion between the structures would then render one oxo group untouched, with the other receiving both protons from the hydroxylamine. The steps required in the preparation of these complexes suggests that this formal reaction does take place and that prior formation of the parent complex in many cases is required in order to prevent or diminish the amount of reduction that takes place.

Detailed DFT calculations on this and two other hydroxylamido complexes are described elsewhere, which explored the effects of ligand substitution on the solid-state ^{51}V NMR chemical shift and quadrupolar coupling parameters.[63] These calculations suggest that the primary contributor to the magnetic shielding of the complexes are the molecular orbitals involved in the V═O bonding. The bonding interactions involving the dipicolinate ligands have little if any density on the vanadium which can explain why substitution on the dipicolinate ring does not dramatically affect the vanadium chemical shift. Changes on the hydroxylamido ligand, however, are more likely to impact the V═O bond and hence the vanadium chemical shift, due to the nature of the V−O−N metallocycle moiety.

The structures of the parent dipicolinatodioxovanadium(V) complexes are sensitive to changes in the electron-donating properties of the dipicolinato ligand and structural parameters such as the $V-N_{py}$ bond length change (e.g., the $V-N_{py}$ is longest in complex **3** and shortest in complex **2**). This structural sensitivity stands in direct contrast to the hydroxylamido complexes **1a** and **1c** where there was no observed change in the $V-N_{py}$ bond length. Accordingly, the structural changes in the hydroxylamido complexes of a particular dipicolinate ligand are most likely dictated by the hydroxylamido ligand. The only observed structural difference between the five-coordinate complexes **1**−**3** was a slight twisting of the VO_2-moiety of the complex in **1** and **2** relative to that of **3**. We conclude that the five-coordinate complexes are more sensitive to substituent effects compared to the seven-coordinate complexes and that this response can be directly observed in the structural parameters of the complexes.

How do the general properties of the five-coordinate and seven-coordinate complexes of these classes of compounds compare? The most important difference is the fact that ternary complex formation significantly increases the amount of complex that is intact in the near-neutral pH range. Some properties of the complexes such as color trace with the compound class and are similar between the two classes of compounds. The colors of the parent dipicolinato complexes are white or yellow as are the hydroxylamidooxovanadium(V) complexes. These complexes stand in direct contrast to the deep red dipicolinatoperoxovanadium(V) complexes,[64] which have LMCT transfer bands in the visible region rather than in the UV region. The compounds' characteristics as described by ^{1}H NMR spectroscopy of the dipic-type ligands are also very similar between the two classes of compounds as summarized in Table 4 and illustrated in Figure 7. This observation suggests that ternary complexes may arise from dipicolinatodioxovanadium(V) without significantly changing the nature of the dipic ligand-vanadium interaction.

Other properties are very different between the two classes of compounds. For example, the parent dipicolinatodioxo-

(63) Ooms, K. J.; Bolte, S. E.; Smee, J. J.; Baruah, B.; Crans, D. C.; Polenova, T. *Inorg. Chem.* **2007**, *46*, in press.
(64) Hartkamp, H. *Angew. Chem.* **1959**, *71*, 553.

vanadium(V) complexes in general are very soluble, whereas the dipicolinatohydroxylamidooxovanadium(V) complexes are much less soluble. Within the classes of compounds, the nitro-substituted compounds were the most soluble while the amino-substituted compounds were the least soluble. The ^{51}V NMR chemical shift changes 50−150 ppm for the hydroxylamido complexes (see Figure 6), whereas much smaller differences were observed for the series of parent complexes. The aqueous complex stability profiles of the parent dipicolinato complexes have bell curve shapes with an optimum complex:V_1 ratio centered around pH 3.4. The corresponding dipicolinatohydroxylamidooxovanadium(V) complexes have pH optima at much higher pH values (ca. 4.5). The parent complex at acidic pH will undergo redox chemistry, whereas the preformed hydroxylamido complexes are relatively inert. Presumably the differences can be attributed to an empty coordination site in these complexes that facilitates hydrolytic and/or redox chemistry. The exceptional stability of the ternary complexes could be an important factor in the protein-vanadium(V) complexes that have been structurally characterized.[6]

Conclusions

Five-coordinate vanadium(V) complexes generally form with a ligand such as dipicolinate that structurally and electronically favors the five-coordinate complex over other coordination geometries. In the case of the small vanadium(V) ion, the ligand should have a bite angle that is small and structurally favors V−O and V−N single bonds on the order of 1.9−2.0 Å and 2.0−2.1 Å, respectively. Small structural changes were observed in the coordination geometry when electron-donating and -withdrawing substituents were added. Addition of a ternary ligand such as hydroxylamine results in seven-coordinate dipicolinatohydroxylamidooxovanadium(V) complexes with the oxo and aqua ligands occupying the axial positions. The coordination geometry governs the complex's properties, and the properties of these complexes have been examined using a range of methods.

Both series of coordination complexes were investigated in detail using NMR spectroscopy. The similar ^{1}H NMR chemical shifts in the spectra showed that the protons on the dipic units had very similar electronic environments in both the five- and seven-coordinate geometries although the subtle changes in the ^{1}H chemical shifts do suggest a fine-tuning of complexes with changes in substituent. Small changes were also observed in the ^{51}V NMR shifts of the parent complexes. These subtle shifts stand in contrast to the very different ^{51}V NMR data that showed the hydroxylamido complexes were significantly impacted when the hydroxylamido ligand was varied. The different nature of effect of these ligands is noteworthy considering that both ligands are coordinated to the vanadium in the same plane in the seven-coordinate complexes.

The parent dipicolinatodioxovanadium(V) and the dipicolinatohydroxylamidooxovanadium(V) complexes exhibit bell curve stability patterns. The parent series of complexes have pH optima near 3.4 regardless of the substituent on the dipicolinato-ligand. The corresponding dipicolinatohydroxylamidooxovanadium(V) complexes have a wider bell curve with optimum stability at ∼4.5 thereby extending the stability of the parent complex into the near-neutral pH range.

The five-coordinate trigonal-bipyramidal geometry is typical for a transition state in enzymatic phosphoryl group transfer reactions. The studies described in this work demonstrate that five-coordinate vanadium complexes exhibit some inherent stability and that the proper ternary groups in an enzyme active site could interact and potentially enhance the stability of a vanadium complex. However, the subtleties in such stabilization may explain why only a limited number of proteins form stable complexes with vanadium-containing transition analogs.

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