Vanadium(V) Hydroxylamido Complexes: Solid State and Solution Properties[1]

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Abstract: A novel series of vanadium(V) hydroxylamido complexes with weak ligands including glycine, [VO-$(NH_2O)_2$(Glycine)]·H_2O (**1**); serine, [$VO(NH_2O)_2$(Serine)]·H_2O (**2**); glycylglycine, [$VO(NH_2O)_2$(GlyGly)]·H_2O (**3**); and imidazole, [$VO(NH_2O)_2$(imidazole)$_2$]Cl (**4**) were prepared and characterized both in solution and in the solid state. All complexes were prepared in aqueous solution at neutral pH at ambient temperature and as crystalline solids. The vanadium atom in these four complexes is seven-coordinate with pentagonal bipyramidal geometry. In complexes **1**−**3** the hydroxylamido groups are coordinated side-on with the hydroxylamido nitrogen cis to the organic ligand in the equatorial plane. In complex **4**, the hydroxylamido groups are coordinated side-on with the hydroxylamido nitrogen trans to the imidazole ligand in the equatorial plane. The UV/vis spectra of these complexes were also examined, and the absorbance peaks show similarities between the properties of the vanadium(V) hydroxylamido complexes and known side-on peroxovanadium complexes. Multinuclear NMR studies were conducted to characterize the solution structure and properties of compounds **1**−**4**. A particularly detailed study of compound **4** was carried out since the analogous vanadium(V) peroxo complex could also be prepared. Complex **4** was less labile and more stable than the corresponding diperoxovanadium(V)−imidazole complex, H[$VO(O_2)_2$(imidazole)] (**5**). In solution the inherent asymmetry of the hydroxylamido ligand has facilitated an in-depth study of ligand exchange. Upon dissolution, compound **4** forms three isomeric complexes, all of which have one of the original two-coordinated imidazole groups in the complex dissociated. 1D and 2D EXSY and multinuclear NMR spectroscopies were used to examine the stoichiometry of the isomers, their structures, and the dynamics of their ligand exchanges. Specifically, both inter- and intramolecular exchanges were observed for the dihydroxylamine−vanadium(V)−imidazole involving both the coordinated imidazole and the coordinated hydroxylamido groups. The intramolecular exchange of the coordinated imidazole in **5** was compared to the exchange in the hydroxylamido complex, and the hydroxylamido compounds were found to have some properties that may be advantageous over those of the diperoxovanadium(V) complexes. In summary, evidence was generated to support the existence of a novel and unprecedented asymmetric hydroxylamido−metal complex as well as the first isolation and characterization of a vanadium(V)−imidazole complex not enjoying stabilization by other organic ligands.

Introduction

Vanadyl sulfate, vanadate, and peroxovanadium compounds are capable of inducing an insulin-mimetic response *in vitro* and *in vivo*.[2,3] However, due to the complex chemistry of these compounds under physiological conditions, the active species has remained elusive. We have been examining the chemistry of vanadium compounds under physiological conditions[4] and have been exploring new families of vanadium compounds with three ultimate goals: understanding the chemistry and biological properties of the simple vanadium compounds and developing new compounds with improved insulin-mimetic properties over those already known. The present paper concerns a novel series of vanadium−amino acid−hydroxylamido derivatives.

There has been an increased interest in studying the vanadium−amino acid complexes mainly fueled by the recent elegant work with halogenases and nitrogenases (reviewed in refs 5−7). Spectroscopic and X-ray crystallographic studies[8] of the vanadium-containing halogenase has been accompanied by rich model chemistry probing both the structure and catalytic properties of the vanadium(V) protein adduct.[9−14] Particular attention has been paid to vanadium−imidazole complexes due

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(1) Abbreviations: 2,3-acetpic, 3-acetatoxypicolinate; bipy, bipyridine; dipic, 2,5-dipicolinic acid; EDDA, ethylenediamine diacetic acid; EXSY, homonuclear exchange spectroscopy; Gly, glycine; GlyGly, glycylglycine; Hpycan, *N*-(2-nitrophenyl)pyridine-2-carboxamide; im, imidazole; OHpic, 3-hydroxypyridine-2-carboxylic acid; oxal, oxalic acid; 2,4-pdc, 2,4-pyridinedicarboxylic acid; pic, picolinic acid; py, pyridine; Ser, serine.

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to the presumed axial coordination of histidine to the vanadium center in haloperoxidase.[10,13−16] Despite much effort, little progress has been made in structurally characterizing the vanadium−amino acid complexes in the absence of other organic ligands. Most of the efforts in this area have focused on either stabilizing the amino acid complex with another organic ligand[9,10,14,15,17] or solution studies in which spectroscopic studies have been employed to characterize the vanadium−amino acid adduct.[18−22] The former approach has led to several reports on a variety of new families of compounds using various supporting ligand groups such as thiocyanate[23] or Shiff-bases of the amino acid with salicylaldehyde to stabilize the vanadium−amino acid complex.[10,15,17,24] Although, there are several reports on other oxidation states of vanadium, including the vanadium(IV)−1-vinylimidazole complex,[25] the corresponding vanadium(V) complexes have remained elusive.

Vanadium peroxo compounds have been of interest not only to the insulin-mimetic community[26−28] but also to the synthetic organic community, since these compounds have potent and very desirable properties as catalysts.[29,30] As a result, much work has been carried out preparing, characterizing, and analyzing the properties of these complexes, and the subject has been a target of several recent reviews.[29−31] Peroxo complexes are interesting not only because of their chemical and biological properties but these complexes are also structurally interesting because of the variety of geometries the peroxo ligand and the metal ion have been shown to adopt. The hydroxylamido group is an analog of the peroxo group and thus is expected to form similar complexes, although the replacement of one oxygen atom with a nitrogen atom breaks the symmetry of the ligand and introduces the possibility of structural isomers. Thus, characterization of vanadium hydroxylamido complexes is of interest with respect to the properties of such complexes as well as with respect to their specific geometries.

Previous studies of vanadium hydroxylamido complexes have shown that the hydroxylamido ligand coordinates in a side-on manner[32−34] as does the peroxo functionality.[31] Not many examples of vanadium hydroxylamido complexes are known, although interest in mainly the solution chemistry of the complexes has recently emerged.[35,36] Much more work has been carried out with the related hydroxamic acid systems because of the occurrence of this functionality in the siderophores and both vanadium(IV) and -(V) complexes of this type have been reported.[31] In addition, the only known vanadium-containing natural product, amavadine, is a vanadium complex with the *N*-hydroxyliminodiacetate group.[37−39] This complex is the only known eight-coordinate vanadium(IV) complex in a dodecahedral structure[37,38] and is extraordinarily stable.[39] The interesting chemistry of these related systems bodes well for the properties of vanadium hydroxylamido complexes.

In this paper, we describe the synthesis, solution characterization, and the solid state characterization of these compounds. We used X-ray crystallography and IR spectroscopy for the solid state characterization and UV/vis and NMR spectroscopies for characterization of the solution properties of these compounds. We show that the hydroxylamido ligands can adopt different orientations in the complexes and that in solution such isomers interconvert. The solid state and solution properties of the hydroxylamido and peroxovanadium(V) imidazole complexes have been directly compared since we were able to obtain and characterize both imidazole complexes. The hydroxylamido−vanadium(V)−imidazole complex distinguishes itself from other vanadium(V)-imidazole derivatives in that the imidazole residue remains coordinated to the vanadium in aqueous solution.

Experimental Section

Materials and Methods. All chemicals were obtained from Sigma or Aldrich, were reagent grade, and were used without further purification. UV/vis spectra were recorded on a Perkin-Elmer Lamda 4B spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer in KBr pellets. Microanalyses were performed by Desert Analytics, Tucson, AR.

Preparation of $[VO(NH_2O)_2(Gly)]\cdot H_2O$ (1). NH_4VO_3 (1.00 g, 8.20 mmol), NaOH (1.20 g, 30.0 mmol), and glycine (1.80 g, 21.6 mmol) were dissolved in H_2O (35 mL). The solution was cooled to 4 °C, and solid $NH_2OH\cdot HCl$ (3.00 g, 43.2 mmol) was added. The mixture was stirred until dissolution was complete. The resulting clear solution was held at 4 °C for 4 days, at which time colorless crystals had formed. The precipitate was filtered from the solution, washed with cold H_2O (5 mL) and acetone (3 × 10 mL), and dried under vacuum. The isolated yield was 1.0 g (55%). For **1**: ^{51}V NMR δ (D_2O) −843, −854 ppm (major peaks); ^1H NMR δ (D_2O) 3.65 (s), 3.56 (s); IR (KBr) 3426 (s), 3217 (s), 3052 (s), 1606 (s), 1438 (m), 1403 (s), 1326 (m), 1275 (w), 1140 (s), 1110 (s), 971 (s), 922 (s), 732 (w), 638 (s), 586 (m), 511 (m), 480 (m); UV/vis (H_2O) (λ/nm, ϵ/(cm^2 mol^{-1})) 308 sh, 780; 257 sh, 2500; 207, 10 300. Anal. Calcd for $C_2H_{10}N_3O_6V$: C, 10.76; H, 4.52; N, 18.83; Found: C, 11.02; H, 4.59; N, 18.63.

Preparation of $[VO(NH_2O)_2(Ser)]$ (2). NH_4VO_3 (0.50 g, 4.1 mmol), NaOH (0.90 g, 23 mmol), and serine (1.30 g, 12.4 mmol) were dissolved in H_2O (30 mL). The solution was cooled to 4 °C, and solid $NH_2OH\cdot HCl$ (1.50 g, 21.6 mmol) was added. The mixture was stirred until dissolution was complete. The resulting clear solution was held

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Table 1. Crystallographic Details for $[VO(NH_2O)_2(Gly)]\cdot H_2O$ (**1**), $[VO(NH_2O)_2(Ser)]\cdot H_2O$ (**2**), $[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (**3**), $[VO(NH_2O)_2(imidazole)_2]Cl$ (**4**), and the Diperoxovanadium(V)−Imidazole Complex, Imidazole $H[VO(O_2)_2(imidazole)]$ (**5**)

	1	**2**	**3**	**4**	**5**
empirical formula	$C_2H_8N_3O_6V$	$C_3H_{10}N_3O_6V$	$C_4H_{13}N_4O_7V$	$C_6H_{12}ClN_6O_3V$	$C_6H_{11}N_4O_6V$
cryst color, habit	colorless plates	colorless prisms	colorless prisms	colorless thin plates	yellow irregular
cryst size (mm^{-3})	0.44 × 0.44 × 0.20	0.20 × 0.18 × 0.30	0.40 × 0.26 × 0.24	0.40 × 0.25 × 0.04	0.54 × 0.34 × 0.32
formula weight	221.1	235.1	280.1	302.6	286.1
temp (K)	173(2)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	0.7107	0.7107	0.7107	0.7107	0.7107
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/n$	Cc	$Pbca$	$P2_1$
a (Å)	5.670(2)	5.587(1)	9.126(2)	9.198(2)	6.454(3)
b (Å)	7.384(2)	14.581(3)	16.304(3)	12.542(3)	13.083(6)
c (Å)	18.603(4)	10.117(2)	7.104(2)	21.779(4)	6.513(1)
β (deg)	97.83(3)	92.86(3)	102.61(3)		100.46(3)
vol. ($Å^3$)	771.5(4)	823.2(4)	1031.5(5)	2512.5(9)	540.8(3)
Z	4	4	4	8	2
ρ_{calcd} Mg/m^3	1.903	1.897	1.804	1.600	1.757
abs coeff (mm^{-1})	1.287	1.212	0.993	1.009	0.943
2θ range for data collection (deg)	4.0−60.0	1.9−55.0	5.0−60.0	3.7−55.0	6.0−55.0
index range	$-1 \le h \le 6, -9 \le k \le 9, -14 \le l \le 19$	$-1 \le h \le 7, -1 \le k \le 18, -13 \le l \le 13$	$-1 \le h \le 12, -1 \le k \le 22, -9 \le l \le 9$	$-1 \le h \le 10, -1 \le k \le 16, -1 \le l \le 28$	$-1 \le h \le 10, -1 \le k \le 16, -1 \le l \le 28$
no. of obsd reflns	1591	1517	1688	1956	1302
no. of ind reflns	1765	1890	1755	2830	1406
data/parameters	14.6	11.9	12.1	12.7	9.1
min/max Δp ($eÅ^{-3}$)	0.82, −0.65	1.48, −0.71	1.13, −1.04	1.12, −0.46	1.90, −2.03
R, wR^a	0.038, 0.056	0.061, 0.189	0.050, 0.131	0.056, 0.170	0.023, 0.071

[a] For **1**, refinement on F using observed data; R and wR on observed data only. For **2**−**5**, refinement on F^2 using all data; R on observed data, wR on all data.

at 4 °C for 2−4 days, after which time colorless crystals had formed. The precipitate was filtered from the solution, washed with cold H_2O (5 mL) and acetone (3 × 10 mL), and dried under vacuum. The isolated yield was 0.60 g (63%). For **2**: ^{51}V NMR δ (D_2O) −847, −850, −861 ppm; ^1H NMR δ (D_2O) 3.82 (m), 3.68 (t), 3.64 (m); IR (KBr) 3390 (s), 3329 (s), 3245 (s), 3065 (s), 1651 (s), 1548 (s), 1450 (m), 1400 (s), 1365 (m), 1344 (m), 1298 (m), 1280 (m), 1231 (m), 1139 (s), 1094 (s), 1043 (s), 962 (s), 928 (s), 862 (m), 802 (m), 590 (m), 523 (m), 487 (m), 416 (w); UV/vis (H_2O) (λ/nm, ϵ/(cm^2 mol^{-1})) 320 sh, 370; 254 sh, 2400; 206, 9200. Anal. Calcd for $C_3H_9N_3O_6V$: C, 15.32; H, 4.29; N, 17.87; Found: C,15.21; H, 4.32; N, 17.41.

Preparation of $[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (3). NH_4VO_3 (0.50 g, 4.1 mmol), NaOH (0.70 g, 18 mmol), and GlyGly·HCl (0.90 g, 5.3 mmol) were dissolved in H_2O (25 mL). The solution was cooled to 4 °C, and solid $NH_2OH\cdot HCl$ (1.50 g, 21.6 mmol) was added. The mixture was shaken until dissolution was complete. The resulting clear solution was held at 4 °C for 4 days, after which time colorless crystals had formed. The precipitate was filtered from the solution, washed with cold H_2O (5 mL) and acetone (3 × 10 mL), and dried under vacuum. The isolated yield was 0.86 g (75%). For **3**: ^{51}V NMR δ (D_2O) −834, −844 ppm (major peaks); ^1H NMR δ(D_2O) 3.82 (s), 3.68 (s),3.64 (s), 3.40 (s), 3.38 (s), 3.34 (s); IR (KBr) 3190 (s), 1605 (s), 1409 (s), 1373 (m), 1319 (m), 1264 (m), 1221 (m), 1122 (s), 1051 (m), 1017 (w), 963 (s), 934 (s), 802 (w), 685 (m), 642 (m), 593 (m), 548 (w), 516 (w), 494 (m); UV/vis (H_2O) (λ/nm, ϵ/(cm^2 mol^{-1})) 255 sh, 2000; 198, 11 800. Anal. Calcd for $C_4H_{13}N_4O_7V$: C, 17.15; H, 4.68; N, 20.00; Found: C,16.87; H, 4.88; N, 19.75.

Preparation of $[VO(NH_2O)_2(imidazole)_2]Cl$ (4). NH_4VO_3 (1.00 g, 8.20 mmol) and imidazole (1.80 g, 26.4 mmol) were dissolved in H_2O (20 mL). The solution was cooled to 4 °C, and solid $NH_2OH\cdot$HCl (1.50 g, 21.6 mmol) was added. The mixture was stirred until dissolution was complete. The resulting clear solution was kept at 4 °C for 60−90 min, after which time colorless crystals had formed. The precipitate was filtered from the solution, washed with cold H_2O (3 mL) and acetone (3 × 10 mL), and dried under vacuum. The isolated yield was 0.80 g (30%). For **4**: ^{51}V NMR δ (D_2O) −850, −856, −868 ppm; ^1H NMR δ(D_2O) 7.23 (2H, s), 8.03 (1H, s), 7.44 (1H, s), 7.65 (1H, s), 8.47 (1H, s); IR (KBr) 3218 (s), 3032 (s), 2081 (w), 1890 (w), 1590 (m), 1540 (m), 1508 (m), 1431 (m), 1327 (m), 1259 (m), 1139 (s), 1097 (s), 1068 (s), 953 (s), 838(w), 779 (m), 749 (m), 649 (s), 613 (m), 586(w), 506 (s), 402 (w); UV/vis (H_2O) (λ/nm, ϵ/(cm^2 $mole^{-1}$)) 308 sh, 2100; 259 sh, 5800; 206, 16 700. Anal. Calcd for $C_6H_{12}N_6ClO_3V$: C, 23.82; H, 4.00; N, 27.77. Found: C, 24.13; H, 3.98; N, 27.67.

Preparation of Imidazole $H[VO(O_2)_2(imidazole)]$ (5). Complex **5** was prepared as described elsewhere.[40] We note, however, that unless H_2O_2 is added to a carefully stirred solution, the yields will be reduced.

X-ray Structure Determination of Compounds 1−5. Crystals suitable for X-ray diffraction studies were obtained directly from the reaction mixtures for **1**−**5**. Experimental data for these studies are listed in Table 1. The intensity data for all five crystals were collected on a Siemens P4 diffractometer using Mo Kα (λ = 0.7107 Å) radiation. In each case, the unit cell constants reported were determined from a least-squares fit to the setting angles of 25 centered reflections. The intensities of three standard reflections were examined every 97 reflections; no significant changes were noted in any case. All five structures were solved by using the direct methods routine TREF in the Siemens SHELXTL PLUS program library.[41] All non-hydrogen atoms were refined with anisotropic displacement parameters. Neutral atom scattering factors and anomalous dispersion corrections were used.[42] Additional details of the crystallographic procedures vary for the five structures and are summarized in Table 1.

Preparation of NMR Samples. The samples were prepared from crystalline compounds in D_2O or in CD_3OD or in mixtures of DMSO-d_6 and CD_3CN at 4 °C or in DMSO-d_6 at 18 °C. Samples used to measure the NMR parameters in variable-temperature (VT) experiments were prepared in triplicate, typically at concentrations of 0.5−10 mM complex.

NMR Spectroscopy. NMR spectra were recorded on a Bruker ACP-300 spectrometer operating at 300 MHz for ^1H, 75 MHz for ^{13}C, and 79 MHz for ^{51}V. Routine parameters were used when recording the ^1H and ^{13}C NMR spectra. DSS (sodium 3-(trimethylsilyl)-1-propanesulfonate) was used as an external reference in these spectra. Particularly in the mixed solvent experiments, the chemical shifts were variable and very sensitive to temperature. The ratio of the three different isomers was determined by integration of one, two, or all three

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imidazole protons in the ^{1}H NMR spectra (dependent on solvent). In the case of overlapping signals, the integrations were determined by manual integrations; in addition, the spectra were simulated using Glinfit and/or Brüker software. The accuracy in quantitation by ^{1}H NMR spectroscopy was significantly higher than the accuracy obtained by quantitation using ^{51}V NMR spectroscopy due to the overlap of signals. However, in all cases, the results obtained by both methods were in close agreement. As described in the results section, the isomer ratio varied significantly with solvent but only insignificant changes were observed in the temperature range from 0 to 10 °C.

The ^{51}V NMR spectra were recorded using a sweep width of about 50 000 Hz, an accumulation time of 0.1 s, a pulse angle of 90°, a relaxation delay of 0.0 s, and approximately 1000 scans. No significant changes were observed when an increased relaxation delay was used during accumulation of the spectra. The ^{51}V NMR spectra are referenced to external $VOCl_3$. An exponential line broadening of 15 Hz was imposed on the accumulated data before Fourier transformation, at which point each ^{51}V NMR spectrum was phased, base line corrected, and integrated. Using the known total vanadium concentration (assuming all vanadium atoms are present in oxidation state V), the mole fraction for each vanadium species can be determined by integration of the ^{51}V NMR spectra (assuming that the species in solution have similar relaxation times so that ^{51}V NMR spectral integrations are quantitative). The concentration of each of the isomers and other oxovanadate species can be calculated from the integration results.

The low-temperature NMR experiments required that the NMR spectrometer be calibrated to within ±1 °C using a methanol sample. The NMR spectrometer was equilibrated for 10 min at each temperature before the first spectrum was recorded. To assure that the temperature had stabilized, a second NMR spectrum was acquired and compared to the first spectrum. The NMR spectra were first recorded at lower temperatures and then spectra were recorded at gradually increasing temperatures. At the end of each temperature series, the sample was cooled back down to the first temperature and reacquired to ensure that the sample had not significantly decomposed during the VT experiment. This control is important with these compounds since the compounds readily decompose (also evidenced by coloring of the solution).

T_1 measurements were obtained by using the inversion recovery method. Since these compounds showed a large variation in T_1 value with variations in concentration, the T_1 values were determined prior to each 2D experiment in order to determine the conditions required for accurate spectral accumulation. The phase-sensitive ^{1}H 2D COSY experiments were obtained using 256 or 512 increments (each consisting of a range of 16−40 scans) covering approximately 2000 Hz in both dimensions. The 2D COSY spectra were used to assign the complex, free ligand, and hydroxylamido and imidazole proton signals. The data were processed with the Bruker software using routine parameters. The 2D ^{1}H EXSY measurements were recorded using 256 or 512 increments of size 1 K (with 24−32 scans each) covering approximately 2000 Hz in both dimensions. The delay time used in these experiments was based on the measured T_1 values; the delay time was set at 2−3 times longer than the largest T_1 value in the spectrum. Variable mixing times ranging from 0.1 to 0.7 s were used. Specific parameters are given in the figure captions. The data were processed with the Bruker software using routine parameters.

Results and Discussion

Preparation and Reactions of 1−4 in Aqueous Solution. Compounds **1**−**4** were prepared by mixing vanadate with appropriate ratios of hydroxylamine and ligands at 4 °C. The reaction yield was not particularly sensitive to the ratio of the components; however, the reaction pH and temperature were found to be critical to obtaining high yields and pure products. The optimum pH for all of these reactions are in the neutral pH range. Bengtsson has previously shown that the presence of hydroxylamine at low pH reduces vanadium(V) to vanadium(IV) coupled with oxidation of hydroxylamine to molecular N_2.[43,44] We also observed that the vanadium(V) was reduced at acidic pH and the colorless solution turned blue. In addition, we observed formation of red solutions at alkaline pH, presumably reflecting the formation of NO^- which will react with the lower oxidation states of vanadium to form the products reported previously.[33,45]

Even at the optimal pH (neutral pH), the solutions of compounds **1**−**4** are unstable at higher temperatures. At ambient temperature the decomposition of compounds **1**−**4** presumably takes place by oxidation of the hydroxylamido ligand to other species as reported previously.[33] Compound **4** is less stable than compounds **1**−**3**; a 10 mM solution of **4** at pH 7.8 decomposes within 1 h, and at higher concentrations the decomposition rates are even faster. However, the greater solubility of compound **4** in aqueous solutions made this compound the target of our most detailed studies. The vanadium hydroxylamido complexes decompose by a different mechanism than the corresponding peroxovanadium complexes. At high concentrations, the vanadium(V) hydroxylamido complex rapidly undergoes redox chemistry, and this appears to begin by reduction of the entire complex. The peroxovanadium compound also undergoes redox chemistry; however, this reaction is a second-order radical reaction involving substrate (which may be free H_2O_2) and vanadate or a vanadium monoperoxo complex.[46,47] This reaction shows the characteristic induction period for autocatalytic reactions and formation of both intermediate vanadium(IV) and vanadium(V) species. Though peroxovanadium and vanadium hydroxylamido complexes are more hydrolytically stable than the simple VO_2 parent vanadium compounds, such reactions are still rapid at ambient temperature in aqueous solution. Thus, at low (micromolar) concentrations of peroxovanadium compounds when the hydrolytic processes are followed by redox chemistry, an increased rate of decomposition is observed. Even though the vanadium hydroxylamido complexes undergo similar hydrolytic reactions as the peroxovanadium compounds, the vanadium hydroxylamido compounds enjoy greater stability at lower concentrations. This observation supports the possibility that the redox chemistry of these hydroxylamido complexes is due to the intact vanadium complex. In summary, hydroxylamido complexes are most stable in aqueous solution at pH 6−7, at low temperature, and at low concentrations. Well-dried solid samples of compounds **1**−**4** are stable for more than 3 months at −20 °C, although solid materials containing residual water can decompose within 1 week.

One decomposition product in the reaction mixture of complex **1** at ambient temperature was isolated as large dark-green hexagonal crystals and found to be the pentadecavanadate mixed-valent complex $(NH_4)_3Na_7[V_{15}O_{36}Cl]\cdot 30H_2O$ which has been described previously.[34] The decomposition products from reaction mixtures of both **2** and **3** maintained at ambient temperature were also consistent with the presence of this oxometalate anion, although the elemental analyses of these products showed that the crystals contained equal amounts of NH_4^+ and Na^+ counterions. Molybdenum nitrosyl compounds such as $Mo(NO)(NH_2O)^{2+}$ at pH 5.7−6 are converted to oxomolybdate oligomers coupled with the release of N_2O and NH_3.[48] It is therefore reasonable to suggest that the vanadium(V) hydroxylamido complexes described here first decom-

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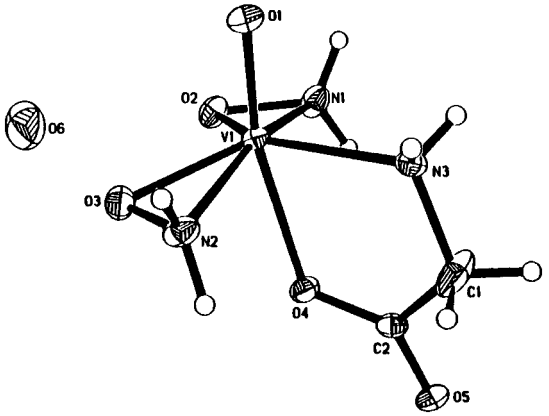

Figure 1. Molecular structure and numbering scheme for complex $[VO(NH_2O)_2(Gly)]\cdot H_2O$, **1**.

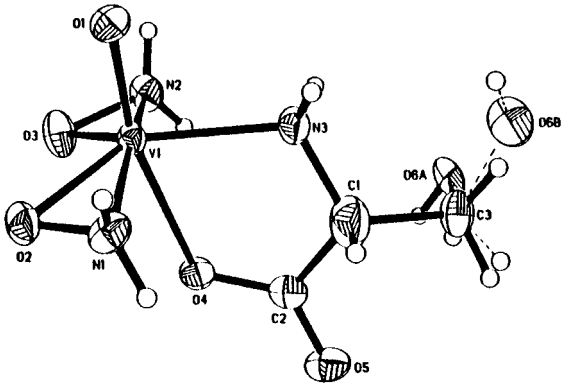

Figure 2. Molecular structure and numbering scheme for complex $[VO(NH_2O)_2(Ser)]$, **2**. The O6A and O6B represent the 70% and 30% occupancies for these atoms.

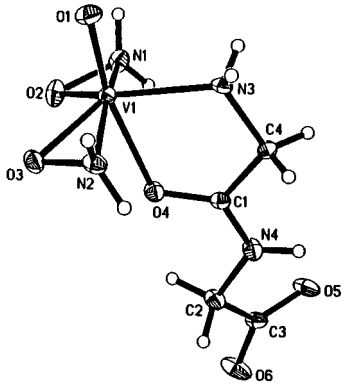

Figure 3. Molecular structure and numbering scheme for complex $[VO(NH_2O)_2(GlyGly)]\cdot H_2O$, **3**.

pose to form nitrosyl complexes followed by further decomposition to the polyoxometalate anion isolated from these reactions. This suggestion is supported by the formation at alkaline pH of red-orange solutions of other vanadium nitrosyl complexes and the evolution of gas from these solutions.

X-ray Crystallographic Results. Figures 1−5 show the molecular structures and the labeling schemes of compounds **1**−**5**. Tables 2 and 3 in the Supporting Information list the atomic coordinates and bond lengths and angles. Selected bond lengths and angles are listed in Table 2. The results for compounds **1**−**3** add to the relatively few structural results for vanadium−amino acid or vanadium−peptide complexes.[23,49−53]

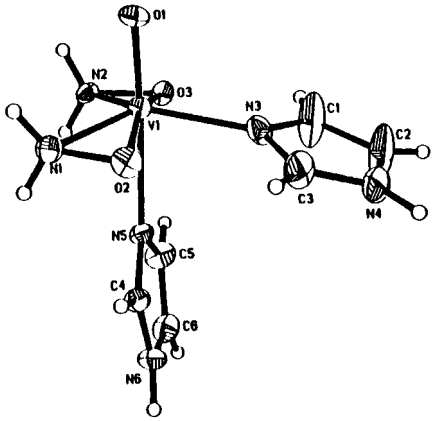

Figure 4. Molecular structure and numbering scheme for complex $[VO(NH_2O)_2(imidazole)_2]Cl$, **4**.

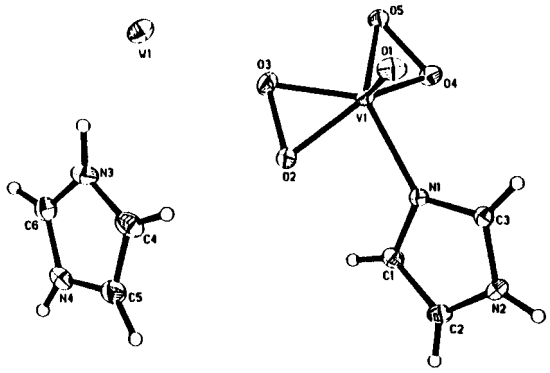

Figure 5. Molecular structure and numbering scheme for complex imidazole $H[VO(O_2)_2(imidazole)]\cdot H_2O$, **5**.

Complexes **4** and **5** are of interest, since there has been only one structural characterization of a vanadium(IV)−imidazole complex[25] and no vanadium(V) complex.

The vanadium(V) centers in complexes **1**−**4** are seven-coordinate in pentagonal bipyramidal geometry containing two bidentate hydroxylamido ligands, one oxo ligand, and the organic ligand. The two hydroxylamido ligands and the imidazole, or amine, nitrogen atom define an equatorial plane perpendicular to the V═O bond. The V═O bond lengths are very similar for all five complexes. The V−N and V−O bond lengths to the hydroxylamido ligands in **1**−**4** are similar (1.991−2.022 and 1.892−1.929 Å, respectively) and correspond to the bonds in the other vanadium(V) hydroxylamido compounds that have been structurally characterized.[32,34,49,54] The V−N(eq) (where eq = equatorial) bond length in **1** (2.122(2) Å) is slightly less than that in **2** (2.142(4) Å), but is indistinguishable from the corresponding distance in **3** (2.123(3) Å) within experimental error. The V−N(eq) bond length to the imidazole nitrogen atom in **4** is shorter than the V−N(amine) bond length. The carboxylate or peptide oxygen atoms are coordinated trans to the oxo group in **1**−**3** and as expected those V−O bonds are relatively long. The V−O(peptide) bond in **3** (2.188(3) Å) is shorter than the V−O(amide) bonds in *mer*-$[VOCl_3(Hpycan)]$ and $[VOCl_2(CH_3CN)(Hpycan)]$ (2.214(1) and 2.206(1) Å),

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Table 2. Bond Lengths (Å) and Angles (deg) for $[VO(NH_2O)_2(Gly)\cdot H_2O$ (**1**), $[VO(NH_2O)_2(Ser)]\cdot H_2O$ (**2**), $[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (**3**), $[VO(NH_2O)_2(imidazole)_2]Cl$ (**4**), and the Diperoxovanadium(V)−Imidazole Complex, Imidazole $H[VO(O_2)_2(imidazole)]$ (**5**)

		For **1**	
V1−O1	1.603(2)	V1−O2	1.898(2)
V1−O3	1.901(2)	V1−N2	2.008(2)
V1−N1	2.021(2)	V1−N3	2.121(2)
V1−O4	2.1888(14)	N1−O2	1.401(2)
O1−V1−O2	101.08(8)	O2−V1−N1	41.75(7)
O2−V1−O3	88.43(7)	N2−V1−N1	160.24(8)
O1−V1−N1	99.42(8)	O1−V1−O4	166.11(6)
N1−V1−N3	93.29(7)	O3−V1−N1	128.24(8)
N3−V1−O4	75.57(6)	O1−V1−N3	90.68(7)
		For **2**	
V1−O2	1.899(3)	V1−O3	1.892(3)
V1−N1	2.011(4)	V1−N2	2.004(4)
V1−O4	2.183(3)	V1−N3	2.139(4)
O3−V1−O2	88.7(2)	O1−V1−O2	102.3(2)
O1−V1−N1	98.5(2)	O3−V1−N1	129.5(2)
O2−V1−N1	41.9(2)	N2−V1−N1	164.4(2)
O1−V1−N3	91.9(2)	O1−V1−O4	165.85(14)
N1−V1−N3	93.5(2)	N3−V1−O4	74.00(13)
		For **3**	
V1−N1	2.022(4)	V1−O2	1.892(3)
V1−O4	2.188(3)	V1−N3	2.123(3)
O1−V1−O2	102.8(2)	O2−V1−N1	41.90(14)
O2−V1−O3	89.00(14)	O1−V1−O4	168.04(14)
O1−V1−N1	96.7(2)	N2−V1−N1	163.6(2)
O1−V1−N3	92.7(2)	N1−V1−N3	92.54(13)
		For **4**	
V1−O1	1.606(3)	V1−O3	1.916(3)
V1−O2	1.927(3)	V1−N1	1.992(4)
V1−N2	1.993(3)	V1−N3	2.079(4)
V1−N5	2.333(4)	O2−N1	1.400(5)
O1−V1−O3	100.1(2)	O1−V1−O2	98.8(2)
O2−V1−N1	41.82(14)	O3−V1−N2	41.59(13)
O3−V1−O2	160.31(14)	N1−V1−N2	100.8(2)
O1−V1−N2	96.3(2)	O3−V1−N3	85.57(14)
O1−V1−N3	101.1(2)	O1−V1−N5	177.43(14)
O2−V1−N3	85.37(14)	O2−V1−N5	80.57(13)
N3−V1−N5	81.38(14)	N1−O2−V1	71.5(2)
		For **5**	
V1−O1	1.603(2)	V1−O4	1.865(2)
V1−O2	1.866(2)	V1−O3	1.884(2)
V1−O5	1.922(2)	V1−N1	2.092(2)
O2−O3	1.467(3)	O4−O5	1.475(2)
O4−V1−O2	137.90(9)	O1−V1−O2	110.19(10)
O1−V1−N1	95.49(9)	O1−V1−O3	108.38(10)
O2−V1−N1	81.28(9)	O2−V1−O3	46.04(8)
O2−O3−V1	66.31(10)	O3−V1−O5	89.18(8)
C1−N1−V1	126.4(2)	O3−O2−V1	67.64

respectively.[55] The only other example of a vanadium−GlyGly complex is $[NEt_4][VO(O_2)(GlyGly)$, 1.58 H_2O, where the deprotonated amide is coordinated to the vanadium.[49] In complex **3**, it is the carboxyl oxygen atom that is coordinated to the vanadium atom trans to the oxo group.[49] In **4**, the position trans to the oxo group is occupied by an imidazole nitrogen atom. This V−N bond is much longer than the V−N(eq) bond in **4** even though both bonds are to imidazole ligands.

The hydroxylamido ligands in **1**−**3** are coordinated with the nitrogen atoms cis to the remaining equatorial ligand. However, in **4** the hydroxylamido oxygen atoms are cis to the equatorial ligand as is the case in $[VO(NH_2O)_2(NH_3O)(H_2O)]Cl$.[34] The differences in the orientation of the side-on coordinated hydroxylamido ligands in these complexes demonstrate that potentially both isomers can be prepared and isolated. The organic ligands in complexes **1**−**3** are bidentate and are presumably less sterically demanding than the imidazole ligand in **4**. It is possible that the steric requirements of the other equatorial ligand dictate the orientation of the hydroxylamido ligands.

Comparison of the V−N(eq) distances for several dihydroxylamido complexes (see Table 3)[26,28,32,40,56−63] shows that the bond lengths are influenced by the remaining equatorial nitrogen ligand atom. Bond lengths decrease in the following order: V−N(py) > N(primary amine) > N(ammonia) ≈ N(imidazole). It is interesting that the replacement of a hydrogen atom on the carbon atom next to the primary amine in **1** with a hydroxymethyl group (**2**) increases the V−N bond length 0.020(6) Å. Although one can argue that this difference may be barely significant, these compounds do illustrate the trend that the ligand that is the strongest base forms the shortest V−N bond. However, this pattern is not confirmed in complexes **1**−**4** or for other complexes listed in Table 4. Neither the pK_a nor the hybridization of the amine nitrogen atom can by themselves account for the observed V−N bond lengths. Presumably, a combination of these factors, in addition to other factors such as crystal packing forces, could explain the observed changes in V−N bond length.

In order to compare our hydroxylamido complexes with peroxo complexes, we prepared and characterized complex **5**.[40] In this compound the vanadium atom is six-coordinate, its geometry approximating a pentagonal pyramid (Figure 5). The oxo group is in the apical position and the basal positions are occupied by the imidazole nitrogen atom and the two peroxo groups. The V═O, V−O(peroxo), and V−N bond lengths are similar to those in related vanadium complexes.[26,27,59,60] The most unusual feature of this complex is its six-coordinate nature, since vanadium atoms are typically seven-coordinate in peroxovanadium complexes.[31] Only one peroxovanadium compound exhibiting similar coordination has been reported, in the anion of $((NH_4)[VO(O_2)_2NH_3])$.[59]

The V═O bond length in **5** (1.603(2) Å) is indistinguishable from that of the corresponding bond in **4** (1.606(3) Å) in spite of the many observed differences between these complexes. The V−N bond length in the equatorial plane in **4** (V1−N3 = 2.079(4) Å) is slightly shorter than the bond in **5** (V1−N1 = 2.092(2) Å). The vanadium atom is raised approximately 0.5 Å above the basal pentagon in **5** and $(NH_4)[VO(O_2)_2NH_3]$[59] compared to a displacement toward to the oxo ligand of 0.3 Å in typical seven-coordinate diperoxo complexes.[64,65] The four hydroxylamido complexes (**1**−**4**) all have displacements similar to the seven-coordinate peroxovanadium complexes.

In complexes **1**−**3**, the NH_2 groups of the hydroxylamido ligands are cis to the coordinated nitrogen atom in the amino

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Table 3. Comparison of Structural Parameters (V−O, V−N, V−S, O−O, S−S, and O−N bonds and O−V−N, O−V−O, and S−V−S angles) in Vanadium(V) Hydroxylamido and Related Complexes

hydroxylamine compounds	V−O (Å)	V−N (Å)	O−N (Å)	O−V−N (deg)	ref
NH_2OH			1.47		57
$[VO(NH_2O)_2(Gly)]\cdot H_2O$ (**1**)	1.898(2)	2.018(2)	1.405(2)	41.9(1)	this work
	1.902(2)	2.010(2)	1.402(3)	41.9(1)	
$[VO(NH_2O)_2(Ser)]$ (**2**)	1.899(4)	2.010(4)	1.398(5)	41.8(2)	this work
	1.894(3)	2.004(4)	1.386(5)	41.6(2)	
$[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (**3**)	1.892(3)	2.022(4)	1.404(5)	41.90(14)	this work
	1.908(3)	2.007(3)	1.397(5)	41.71(13)	
	1.8961(14)	2.0046(16)	1.3974(25)	41.87(7)	ref 35
	1.8886(20)	2.0160(19)	1.3957(23)	41.73(7)	
$[VO(NH_2O)_2(imidazole)_2]Cl$ (**4**)	1.929(3)	1.991(4)	1.403(5)	41.9(2)	this work
	1.913(3)	1.994(4)	1.391(5)	41.6(1)	
$[VO(NH_2O)(dipic)(H_2O)]$	1.903(3)	2.007(3)	1.371(4)	40.9(1)	32
$[VO(NH_2O)_2(NH_3O)(H_2O)]Cl$	1.929(9)	1.965(10)	1.390(13)	41.8(4)	34
	1.892(9)	1.955(11)	1.405(13)	42.8(4)	
$[O(VO((C_2H_5)_2NO)_2)_2]$	1.851(3)	2.029(4)	1.398(5)	41.1(1)	54
	1.873(3)	2.061(4)	1.400(5)	41.3(1)	
	1.864(3)	2.094(4)	1.409(5)	41.2(1)	
	1.866(3)	2.079(4)	1.402(5)	41.2(1)	
mean values	1.894 ± 0.043	2.016 ± 0.078	1.397 ± 0.026	41.6 ± 1.2	

peroxo compounds	V−O (Å)	V−O (Å)	O−O (Å)	O−V−O (deg)	ref
O_2^-			1.49		58
$[VO(O_2)_2(imidazole)_2]\cdot H_2O$ (**5**)	1.866(2)	1.865(2)	1.467(3)	46.04(8)	this work
	1.884(2)	1.922(2)	1.475(2)	45.82(7)	
$K_2[VO(O_2)_2(pic)]\cdot 2H_2O$	1.881(4)	1.895(4)	1.464(5)	45.6(2)	26
	1.899(4)	1.917(4)	1.458(6)	45.0(2)	
$K_2[VO(O_2)_2(HOpic)]\cdot 2H_2O$	1.924(2)	1.877(2)	1.463(2)	44.95(7)	26
	1.902(2)	1.908(2)	1.461(2)	45.40(7)	
$(NH_4)[VO(O_2)_2(NH_3)]$	1.871(3)	1.872(3)	1.463(4)	46.0(1)	59
$(NH_4)[VO(O_2)_2(bipy)]$	1.880(3)	1.909(3)	1.471(4)	45.7(1)	60
	1.883(3)	1.911(3)	1.465(4)	45.4(1)	
$K_3[VO(O_2)_2(oxal)]$	1.923(3)	1.876(3)	1.466(4)		61
$K_3[VO(O_2)_2(2,4\text{-pdc})]\cdot 3.25H_2O$	1.894(9)	1.862(10)	1.460(14)	45.3(4)	27
	1.894(9)	1.909(10)	1.452(13)	45.3(4)	
$K_3[VO(O_2)_2(2,3\text{-acetpic})]\cdot 2H_2O$	1.917(4)	1.878(4)	1.461(5)	45.41(15)	27
	1.866(4)	1.941(4)	1.480(5)	45.46(4)	
mean values	1.894 ± 0.047	1.465 ± 0.015	45.49 ± 0.55		

bisulfide compounds	V−S (Å)	V−S (Å)	S−S (Å)	S−V−S (deg)	ref
S_2^-			2.06 Å		62
$(NEt_4)[VO(S_2)_2(bipy)]$	2.3686(13)	2.4403(13)	2.0549(13)	50.57(4)	63
	2.3437(11)	2.4251(12)	2.0531(15)	50.97(4)	
mean values	2.394	2.054	50.77		

acid and dipeptide, whereas in **4** the NH_2 groups of the hydroxylamido groups are trans to the equatorial imidazole (Figures 1−4). It is possible that the orientation of the hydroxylamido groups in **4** reflect the greater steric requirements of the imidazole ligand in the equatorial plane. To this end, comparison of the rotation of the imidazole groups in complexes **4** and **5** may be informative. In **4** the equatorial imidazole is perpendicular to the V═O group and coplanar with the two hydroxylamido groups (Figures 4 and 6). The bond angles between the two groups adjacent to the variable ligand in compounds **1**−**3** (N2−V1−N2 about 160°) are very similar to the corresponding bond angle in compound **4** (O2−V1−O3) 160.31(14)°). This would suggest that the substitution of one bidentate ligand with two monodentate ligand sterically supports imidazole ring rotation in the equatorial plane. However, when the orientation of the equatorial imidazole in compounds **4** and **5**, is compared directly, a difference is observed in the imidazole rotation. Compound **5** has a longer V−N bond than **4**, supporting the interpretation that the imidazole could have been planar but preferred to be rotated out of the plane. The more pyramidal nature of the vanadium in compound **5**, than the vanadium in **4**, provides additional space which supports the interpretation that the rotation of the imidazole in **4** may be the unusual geometry.

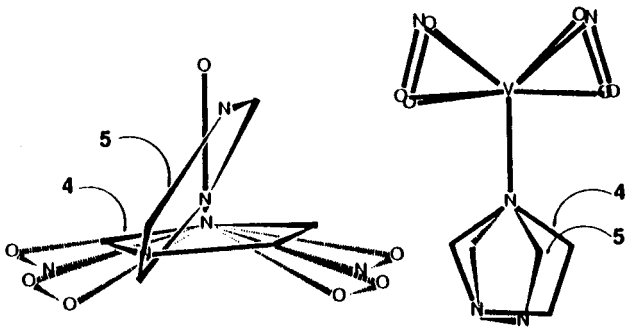

Figure 6. The steric requirements in compounds **4** and **5** are illustrated by drawing the two molecular geometries obtained by X-ray crystallography superimposing the V═O bonds and the O═V−N(imidazole) planes in the two molecules.

A series of six- and seven-coordinate vanadium(V) compounds and selected bond lengths and angles for the three-membered rings that vanadium forms with hydroxylamido, peroxo, and disulfido groups are listed in Table 4.[26,28,40,59,60,63] The V−N bond in **4** is indeed the shortest V−N bond in the equatorial plane reported in seven-coordinate complexes (Table 4). The mean N−O bond length is 1.397 ± 0.026 Å in the vanadium complexes, which is significantly shorter than 1.47 Å for free hydroxylamine.[57] However, the mean O−O bond

Table 4. Comparison of the V−N Bond Distance for Seven-Coordinated Vanadium(V) Complexes That Are Coordinated with Two Peroxo, Two Hydroxylamido, or Two Sulfido Groups with the Nitrogen Atom in the Same Equatorial Plane

compounds	N-type	V−N (Å)	pK_a	ref
$[VO(NH_2O)_2(Gly)]\cdot H_2O$ (**1**)	primary amine	2.122(2)	9.70	this work
$[VO(NH_2O)_2(Ser)]$ (**2**)	primary amine	2.142(4)	9.21	this work
$[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (**3**)	primary amine	2.123(3)	8.25	this work
		2.1211(19)		35
$[VO(NH_2O)_2(imidazole)_2]Cl$ (**4**)	imidazole	2.079(4)	6.99	this work
$[VO(O_2)_2(imidazole)_2]\cdot H_2O$ (**5**)	imidazole	2.092(2)	6.99	this work
$(NH_4)[VO(O_2)_2NH_3]$	ammonia	2.098(4)	9.25	59
$K_2[VO(O_2)_2(pic)]\cdot 2H_2O$	pyridine	2.123(5)	5.29	26
$K_2[VO(O_2)_2(HOpic)]\cdot 2H_2O$	pyridine	2.137(2)		26
$(NH_4)[VO(O_2)_2(bipy)]$	pyridine	2.149(4)	4.35	60
$K_3[VO(O_2)_2(2,4\text{-pdc})]\cdot 3.25H_2O$	pyridine	2.144(11)	7.02	27
$K_3[VO(O_2)_2(2,4\text{-acetpic})]\cdot 2H_2O$	pyridine	2.179(4)		27
$(NEt_4)[VO(S_2)_2(bpy)]$	pyridine	2.139(3)	4.35	63

length is 1.465 ± 0.015 Å in the peroxo groups in vanadium complexes, which is only 0.025 shorter than in free hydrogen peroxide. The bond increase in O−O bonds is attributed to the partial withdrawal of electron density from the antibonding π^*2p_y orbitals of the peroxo group to the empty d_{xy} and $d_{x^2-y^2}$ orbitals of vanadium atom.[59] Consequently, the much greater bond length change in hydroxylamido groups probably indicates larger charge transfer from ligand to metal in metal hydroxylamido complexes than in the related peroxo complexes. Corresponding structural changes have also been observed in other metal hydroxylamido complexes.[54,66−69] Thus, we predict solution characterization of vanadium hydroxylamido complexes will demonstrate a larger charge transfer from ligand to metal than peroxo complexes.

IR and UV/Vis Spectroscopy. The characteristic absorptions due to the V═O bond (970−950 cm^{-1}) and the coordinated hydroxylamido (950−860 and 610−510 cm^{-1}) all appear in of the IR spectra for **1**−**4**.[69] The V═O stretches of compounds **1**−**4** are 971, 962, 963, and 953 cm^{-1}, respectively. The frequencies of the V═O stretch vary up to 20 cm^{-1} despite the fact that the V═O bond lengths for all of these complexes are indistinguishable by X-ray crystallography. No hydrogen bonds or other structural differences can explain this variation in the V═O bond stretch frequencies. We have previously encountered variations in V═O bond stretch frequencies which were not correlated with corresponding structural changes[70] and were presumably a result of packing effects in the solid state. The orientation of the hydroxylamido groups in compound **4** is interestingly different from the hydroxylamido groups in complexes **1**−**3**, which may explain, in part, why the V═O stretch for **4** is 10 cm^{-1} lower than the V═O stretch for **2** and **3** and 20 cm^{-1} lower than in **1**. The IR absorption of the V═O bond for compound **5** is at 950 cm^{-1}, which is only 3 cm^{-1} different than the corresponding hydroxylamido complex. The observations suggest that the V═O bond vibration in these complexes is affected significantly by the ligands and their orientation in the equatorial plane.

The UV/vis spectra for complexes **1**−**4** are very similar; the spectrum for compound **4** is shown in Figure 7. In addition, we show the UV/vis spectrum for complex **5** in Figure 7 as well as 5-fold enlargement of the spectra for compounds **4** and **5** above 250 nm. Two bands were expected for **5**, one low-intensity band at 325 nm and one high-intensity band at 203 nm, which have previously been assigned as the $\pi^*_v \rightarrow d\sigma^*$ and the $(\sigma)\pi^*_v \rightarrow d\sigma^*$ transitions (from the side-on peroxo group to the vanadium) in other peroxo complexes.[71,72] The higher energy peak is also expected to contain the $\pi \rightarrow \pi^*$ transition of the imidazole and the n → d, $\pi^* \rightarrow$ d transitions from the imidazole to the metal ion.[73−75] When the absorbance spectra of complexes **4** and **5** are compared, it is clear that the band at 320 nm in the peroxo complex is replaced by the shoulders in **4** beyond 300 nm. Although other metal ion imidazole complexes have shown transitions from the imidazole to the metal ion in the region of 250−300 nm,[74] this assignment for the transition in complex **4** can be ruled out. Such assignment is made because no similar transition in the spectrum for complex **5** is observed. Accordingly, we conclude that the shoulders beyond 300 nm are due to in the transitions from the hydroxylamido ligands to the metal.

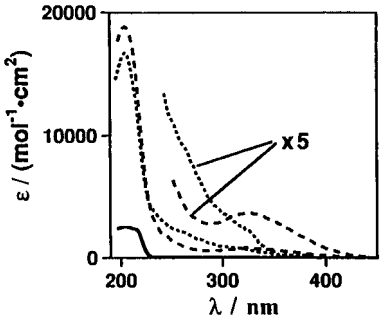

Figure 7. UV/vis spectra of compounds **4** (0.156 mM, pH 7.8 in water; dotted line), **5** (0.140 mM, pH 6.8 in water; broken line), and free imidazole (1.18 mM, pH 8.0 in water; solid line). The 5-fold enhancements of the high wavelength region of the spectra for compound **4** and **5** are also given.

The X-ray studies described above suggest that compounds **1**−**5** are monomeric in the solid state, and multinuclear NMR solution studies described below support the hypothesis that these complexes remain monomeric in solution. Accordingly, we make the following points concerning the binding modes of hydroxylamido ligand to the vanadium atom that can be extracted from the UV/vis spectra. Since no previous information is available on the UV/vis spectra of vanadium hydroxyl-

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amido complexes, we rely on the structural analog given above and expect that the analogy extends to spectroscopic properties between the hydroxylamido and peroxo complexes. Thus, we make the following interpretations based on the known absorbances of peroxovanadium complexes. The side-on metal peroxo complexes show a characteristic weak low-energy charge-transfer absorbance which is absent in head-on complexes.[71] Although head-on vanadium peroxo complexes have been prepared,[31] detailed UV/vis spectroscopic information is not yet available for these complexes. In other metal complexes with head-on peroxo ligand(s), such as Co(III), there are two ligand−metal charge-transfer (LMCT) transitions (one weak, one strong).[71] This type of absorption pattern is not observed in complexes **1**−**5**. The hydroxylamido complexes we have prepared also have a low intensity charge transfer absorbance which we tentatively assign to the charge transfer of a side-on bound hydroxylamido ligand to the vanadium.

^{51}V NMR Spectroscopy. The ^{51}V NMR spectra of the four hydroxylamido complexes (**1**−**4**) each gave two or three resonances upfield of −830 ppm in D_2O.[76] Complexes **1**−**4** have chemical shifts in the same range as VF_5 (−875 ppm),[77] which is the highest chemical shift reported for vanadium(V) compounds. All of the hydroxylamido complexes have chemical shifts higher than peroxovanadium complexes.[78] In Figures 8A and B, the spectra of compound **4** at 10 °C and 0 °C are given. Figure 8 shows that at 10 °C the signals for two of the three isomers overlap strongly and that the situation does not improve as the temperature is decreased due to the quadrupolar character of the ^{51}V nucleus.

In the present study, the NMR spectra were recorded on solutions prepared from isolated compound; observed multiplicities thus reflect the conversion of the solid state compound to other vanadium species upon dissolution of the crystalline material. No differences in the ratios of the isomers were observed upon dissolution to give different concentrations of compounds **1**−**4**. The nature of the isomers was examined by the addition of excess hydroxylamine and ligands to solutions containing isolated compound and examining these solutions using ^{51}V NMR spectroscopy. The addition of excess free ligand or free hydroxylamine did not change the ratio of the peaks, consistent with the interpretation that the species giving rise to these signals have the same stoichiometry. In order to reach this conclusion, we examined solutions of pure compounds ranging from 0.5 to 100 mM and in the presence of up to 10-fold excess of free ligand. We carried out the most extensive studies on compound **4** due to the higher solubility of **4** in both aqueous and organic solvents, even though compound **4** is less stable than compounds **1**−**3**. However, some studies were carried out with compounds **1**−**3** so that most of the observations reported above also include these complexes. In view of the overlapping signals, the quantitation of these spectra were mostly carried out at 10 °C given the better signal resolution and complex stability at this temperature. In addition, we used both manual and simulated fits (Glinfit and/or Brüker software) of the ^{51}V NMR signals to integrate the spectra. Using these experiments and precautions, we did not observe any significant changes in the ratios of isomers. Thus, we conclude that each of the signals represents a species containing two hydroxylamido groups, an oxo group, and an organic ligand and thus is an isomeric form of the material isolated and characterized by X-ray crystallography in the solid state.

In contrast to complex **4**, the peroxovanadium complex **5**, shows only one signal at −744 ppm. Given the asymmetry of the hydroxylamido ligand, this ligand has the possibility of forming structural isomers, which the symmetric peroxo ligand does not. The precedence of such asymmetry was demonstrated in this work in the X-ray structures of compounds **1**−**4** (see Figures 1−4). Examination of the ^{1}H NMR spectra gave more information about the nature of the three isomers observed in the ^{51}V NMR spectra.

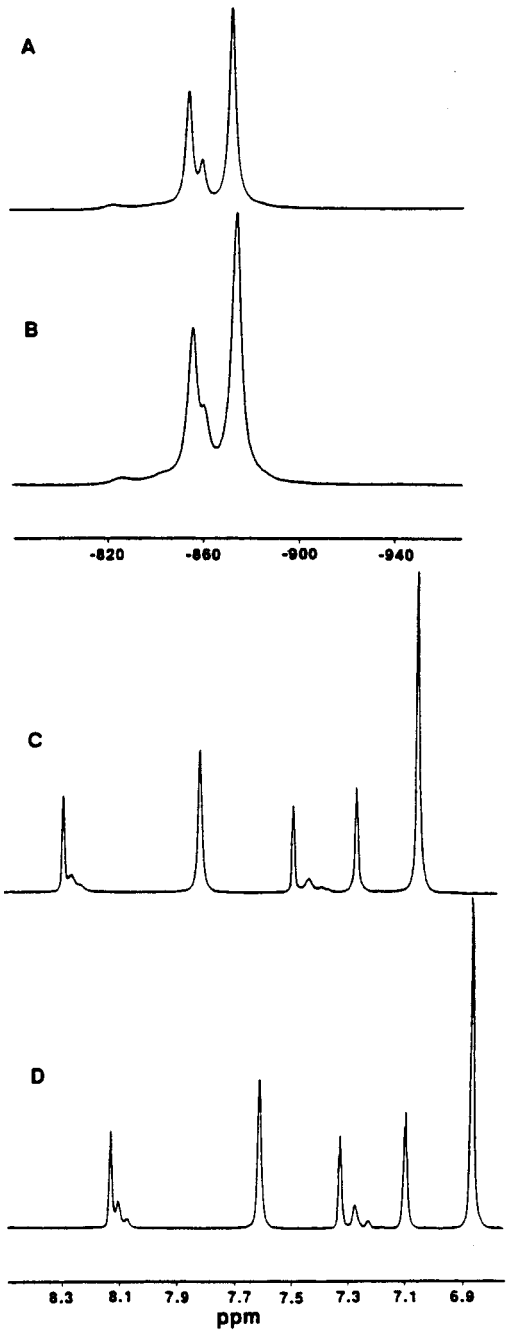

Figure 8. ^{51}V (79 MHz) and ^{1}H (300 MHz) NMR spectra of compound **4** (50 mM and pH 7.8 in D_2O); ^{1}H NMR spectra of **4** (A) ^{51}V NMR at 10 °C, (B) ^{51}V NMR at 0 °C, (C) ^{1}H NMR at 10 °C, and (D) ^{1}H NMR at 0 °C.

^{1}H NMR Spectroscopy. The ^{1}H NMR spectra of the vanadium hydroxylamido complexes (**1**−**4**) show two or three species in solution (see Figures 8C and D for compound **4**) in agreement with the ^{51}V NMR spectra shown for compound **4** (Figure 8A and 8B). The ^{1}H NMR spectra of **4** in D_2O, CD_3OD, and DMSO-d_6 all show signals from three different coordinated imidazoles and from free imidazole (Table 5). From the integration of the imidazole signals, it is clear that one of

(76) The ^{51}V spectrum of **4** in CD_3OD gave three resonances at −830, −839, and −851 ppm with a significantly different ratio of 5.4:1.0:7.4.

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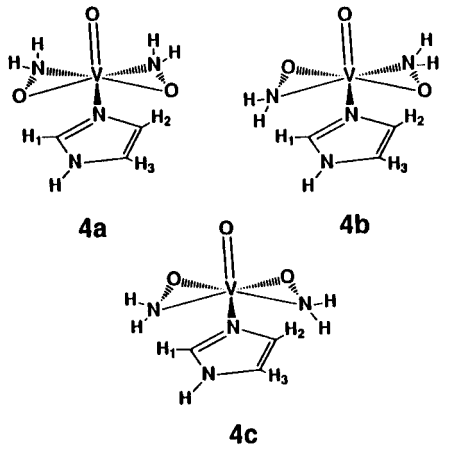

Figure 9. Three structural proposals for the isomers formed in aqueous solution upon dissolution of crystalline compound **4** (**4a**−**4c**).

Table 5. ^{1}H NMR Chemical Shifts for the Coordinated Imidazole Group in $[VO(NH_2O)_2(Gly)]\cdot H_2O$ (**1**), $[VO(NH_2O)_2(Ser)]\cdot H_2O$ (**2**), $[VO(NH_2O)_2(GlyGly)]\cdot H_2O$ (**3**), $[VO(NH_2O)_2(imidazole)_2]Cl$ (**4**), and the Diperoxovanadium(V)−Imidazole Complex, $H[VO(O_2)_2(imidazole)]$ (**5**)

compound	solvent	temp (°C)	H_1 (ppm)	H_2 (ppm)	H_3 (ppm)
imidazole	D_2O	0	7.60	6.86	6.86
4a	D_2O	0	8.16	7.34	7.11
4b	D_2O	0	8.13	7.29	7.11
4c	D_2O	0	8.10	7.25	7.11
imidazole	CD_3OD	−40	7.74	7.07	7.07
4a	CD_3OD	−40	8.55	7.74	7.43
4b	CD_3OD	−40	8.54	7.68	7.46
4c	CD_3OD	−40	8.43	7.60	7.49
5	D_2O	0	8.11	7.30	7.22

the two imidazole ligands is completely dissociated from the complex and generated free imidazole. Thus, dissolution of complex **4** generates three different isomeric vanadium complexes containing one coordinated imidazole and 1 equiv of free imidazole. Given the limited stability of the complex and the limited resolution of the spectra, we find that the best determination of the isomer ratios by ^{1}H NMR is obtained at 0 °C, as illustrated in Figures 8C and D. As mentioned above the limited solubility of compounds **1**−**3** in aqueous solution has led us to focus our studies on compound **4**.

Chemical expectations would infer that the imidazole group in the axial position would most readily be lost leaving a six-coordinate complex with the structure shown as **4a** in Figure 9. An axial imidazole is a weaker ligand than an equatorial imidazole ligand, and different chemical shifts would be expected. The chemical shifts that are observed in the ^{1}H NMR spectra for all three isomers of **4** are not particularly close to the signals for the free imidazole. Furthermore, when the ^{1}H NMR spectra of compounds **4** and **5** are compared (Table 6), the chemical shifts are very similar, and the solid state characterization of compound **5** placed the imidazole group in the equatorial plane. In addition, the structural precedence from related compounds including $[Mo(O)(O_2)_2(imidazole)(H_2O)]$,[79] and $[V(O)(NH_2O)_2(NH_2OH)(H_2O)]Cl$[34] place the coordinated imidazole cis to the oxo group. Furthermore, an argument can be made against a seven-coordinate species where a solvent molecule is occupying the seventh coordination site since only small chemical shift changes are observed between different solvents (Table 5). We conclude that the ^{1}H NMR spectroscopic data confirm the possibility that the coordinated imidazole is in the equatorial plane (see below, Figure 9).

As observed by ^{51}V NMR spectroscopy (Figures 8A and B), three different isomers of identical stoichiometry are present, but the structure referred to as **4a** in Figure 9 accounts for only one of these isomers. What are the structures of the two other isomers observed in the ^{51}V and ^{1}H NMR spectra? The hydroxylamido groups are coordinated side-on (through the N,O functionalities) to the vanadium with the nitrogen atoms trans to the organic ligand in compound **4**; however, in compounds **1**−**3**, the hydroxylamido groups coordinated with the nitrogen atoms cis to the amine-N of the organic ligand. An isomer of **4a** such as **4c** is thus a reasonable proposal for an isomer. Both **4a** and **4c** are symmetrical isomers, and although no solid state structural precedence is currently available to support an unsymmetrical isomer, such an isomer illustrated in **4b** can be envisioned. Alternative structures involving head-on isomers cannot be ruled out at this time. However, such isomers would not only be expected to be less stable, but are likely to have different charges since the head-on hydroxylamido functionality may not be deprotonated. A complex with a different charge would not be consistent with the similar chemical shifts for the three isomers in both the ^{51}V and ^{1}H NMR spectra but also would be less consistent with the observed UV/vis spectra described above. The possibilities involving isomers of different nuclearities were ruled out since the NMR studies of compound **4** over a wide range of concentrations (from 0.5 to 100 mM) and with added imidazole (from 0.5 to 1000 mM; 10-fold excess), and hydroxylamine (from 0.5 to 500 mM; 5-fold excess) show no evidence for concentration dependence in isomer ratios. Thus, on the basis of chemical considerations and the studies described so far, three likely isomers, even in the absence of structural precedence for an unsymmetric isomer, are the structures shown in Figure 9.

Chemical shift considerations concerning the protons in the coordinated imidazole (Table 5) provide a vehicle to test the three structural proposals for the isomers **4a**−**4c** (Figure 9). The chemical shifts of the two protons adjacent to the ligated nitrogen atom (H_1 and H2 in Figure 9) will, if coordinated to the metal atom, shift significantly downfield, indicative of σ donation from the ligand to the metal.[80] On the other hand, the chemical shift of a proton remote from the metal (H_3 in Figure 9) is a sensitive indicator of the π back donation from metal to ligand.[80] Assuming that the three isomers have the structures shown in Figure 9, the assignments of the signals would be as follows. The hydroxylamido nitrogen atoms are weaker ligands than the hydroxylamido oxygen atom which translates to a smaller trans effect on an equatorial imidazole group. That is, the imidazole nitrogen will be coordinated more tightly to the metal ion (it will be a stronger σ donor) if it is trans to the hydroxylamido nitrogen atoms. Thus, H_1 and H_2 in **4a** will be at lower field than the corresponding protons in **4b** or **4c**. For the identical reasons H_1 and H_2 in isomer **4b** will be at lower field than the corresponding protons in **4c**. Accordingly, the three isomeric structures suggested in Figure 9 are consistent with the ^{1}H NMR spectroscopic properties observed and furthermore show that the major isomer is **4a** in aqueous solution. In aqueous solution, the resonances of the H_3 proton overlap for the three isomers showing only small, if any, difference in the π back donation in water as expected for a vanadium(V) complex (Table 5). In CD_3OD we were able to record the spectrum at −40 °C, and at this temperature the H_3 resonances do separate. Although vanadium(V) complexes are not expected to accept much π back donation, the observations in chemical shift changes reported in Table 6 are consistent with π back donation (**4c** > **4b** > **4a**). However, as illustrated

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in Figure 8C and 8D, chemical shifts are sensitive to temperature, suggesting that structural conclusions based on chemical shifts alone be treated cautiously.

^{1}H NMR spectra of **4** in DMSO-d_6 also contain signals for the protons on the hydroxylamido and imidazole nitrogen atoms and are more complicated and informative than the spectra in either deuterated water or methanol. The signals for the hydroxylamido protons and N−H imidazole protons were assigned using both titration studies (the addition of incremental amounts of CD_3OD to a solution of **4** in DMSO-d_6 and observing the disappearance of signals) and by 2D-COSY spectroscopy, since both chemical shift and stability of the isomers vary in different solvents. The addition of DMSO to an aqueous solution of the vanadium(V)−EDDA complex was found to change the stability ratio of the α-*cis*-$NH_4[VO_2$-(EDDA)] and *β*-*cis*-$NH_4[VO_2$(EDDA)] isomers.[70] Thus, the observation that **4c** is the most stable isomer in DMSO-d_6 in contrast to its stability in D_2O and CD_3OD, where **4a** is the major isomer, has precedence in observations of the stabilities of $NH_4[VO_2$(EDDA)] complexes.[70] Furthermore, as anticipated the stability ratio changes as the polarity of the solvent changes; in CD_3OD, the stability of **4a** is less than that in D_2O solution. The addition of less than 20% of CD_3OD to the DMSO-d_6 solution of **4** does not significantly affect the equilibrium ratio of isomers. At 20% of CD_3OD in DMSO-d_6, the equilibrium ratio changes. We infer that the observed changes perhaps involve hydrogen bonding, polarity of the solvent, other solvation effects, or most likely a combination of such effects.

Free imidazole yields signals that are singlets in protic solvents; however, in organic solvents the peaks of the coordinated imidazole are broad singlets, and at ambient temperature these resonances are very broad and difficult to observe since they are almost lost in the base line. The broadness of these signals reflects dynamic processes since in a DMSO-d_6−CD_3CN solution, these broad imidazole proton signals become resolved triplets (doublet of doublets) at 0 °C. Thus, there is no doubt that dynamic processes are occurring in these systems and that application of 2D NMR techniques will allow us to obtain further information on the complex−imidazole exchange, complex−hydroxylamido ligand exchange, and isomer interconversion and any other dynamic processes occurring in this system.

Dynamic Processes. The lability of complexes **4** and **5** were examined using homonuclear ^{1}H 2D-EXSY spectroscopy. We examined the dynamic properties of these compounds both in aqueous and CD_3CN−DMSO-d_6 solutions (from 2:3 to 3:4 ratio). Because of proton exchange, chemical shift separation, relaxation times, solvent effects, lability, and stability of the complexes, the conditions required to obtain interpretable spectra precluded investigation of this system under a single set of conditions. We show the exchange between free imidazole and dissolved complex **4** and compare this to the exchange between free imidazole and complex **5**, Figure 10 (bottom) and 10 (top), respectively. In addition, we show the exchange among the **4a**−**4c** isomers (intermolecular) in a partial ^{1}H 2D-EXSY spectrum (Figure 11) as well as intramolecular exchange patterns between **4a**−**4c** in a partial ^{1}H 2D-EXSY spectrum (Figure 11). Although **4c** is the least stable isomer of the three in water and the most stable isomer in DMSO-d_6, the stability of **4a** and **4c** are similar and higher than the stability of **4b** in the CD_3CN−DMSO-d_6 (3:4) solvent mixture. The protons on the imidazole ring H_1, H_2 and H_3 in these structures are defined in Figure 9 and shown in Figures 10 and 11.

Imidazole-Complex Exchange. With respect to intermolecular dynamic processes, the hydrogen atoms on the coordinated imidazole group exchange with hydrogen atoms on the free imidazole in both **4** and **5**. The ^{1}H 2D EXSY spectra were recorded in water at 4 °C for both complexes to optimize the complex stability and spectral quality (Figure 10). The conver-

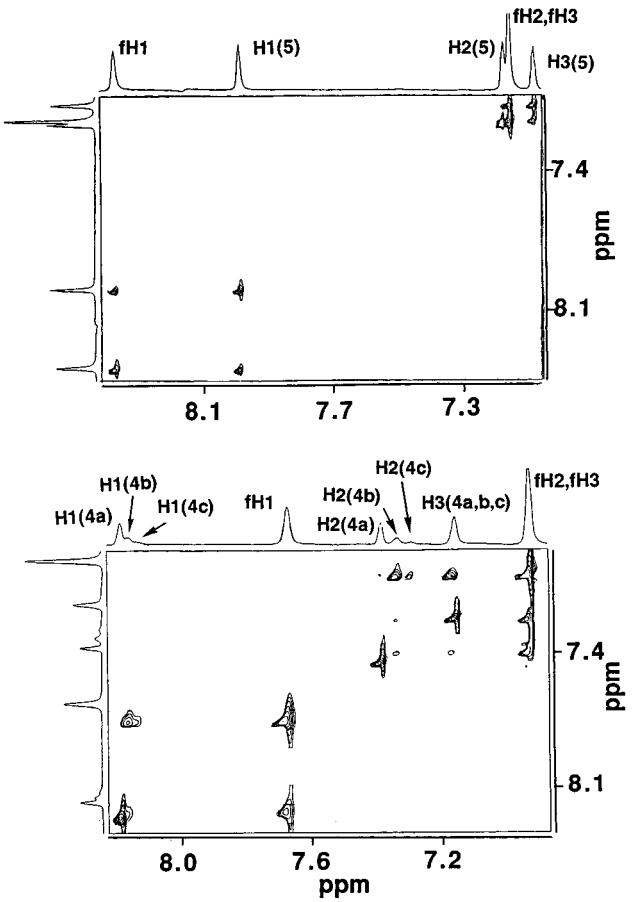


Figure 10. Partial 2D ^{1}H-EXSY spectra of compounds **4** and **5** in D_2O. The spectrum (bottom) was recorded of 100 mM **4** at pH 7.8 and 4 °C, and key accumulation parameters were a sweep width of 1500 Hz, accumulation time of 0.47 s, a delay time of 5 s, a mixing time of 0.7 s, and 512 increments of each 32 scans. The spectrum (top) was recorded of 100 mM **5** at pH 6.5 and 4 °C, and key accumulation parameters were a sweep width of 1500 Hz, accumulation time of 0.29 s, a delay time of 12 s, a mixing time of 0.7 s, and 256 increments each of 32 scans.

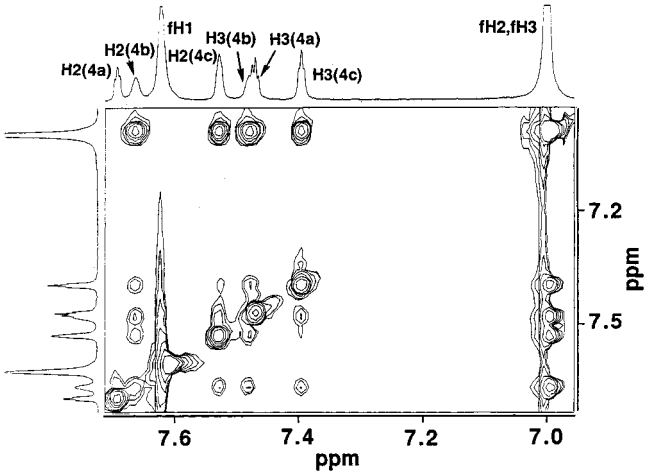


Figure 11. Partial 2D ^{1}H-EXSY spectra of compound **4** in a mixture of CD_3CN−DMSO-d_6 (3:4). The spectrum was recorded of 100 mM **4** and at 5 °C, and key accumulation parameters were a sweep width of 1250 Hz, accumulation time of 0.21 s, a delay time of 5 s, mixing time of 0.7, and 256 increments each of 32 scans.

sions H1/fH1, H2/fH2, and H3/fH3 (where f refers to the free imidazole) are observed for all three isomers in complex **4**. The cross peaks quantitating the exchange of the imidazole protons for isomers **4c** and **4b** are much larger than the cross peaks for the imidazole protons of isomer **4a**. As a matter of fact, the cross signals for the **4a** isomer are very weak and only clearly observed when examining the 2D-EXSY spectrum recorded in $CD_3CN-DMSO-d_6$; however, this exchange is more evident in the spectrum recorded in water (Figure 10). Here, it is interesting to note that the exchange between **4b** and **4c** is observed, but the exchanges between **4a** and other isomers were not observed. On the basis of these studies it is clear that the coordinated imidazole in complex **4** is labile and exchanges rapidly with free imidazole even at 0−10 °C. As illustrated in Figure 10, the exchange between the free imidazole and the coordinated imidazole in complex **5** in water is also rapid. As a matter of fact this exchange is faster than that observed for compound **4**. On the basis of these data, the lability of the vanadium hydroxylamido complex is clearly lower than that of the corresponding peroxo compound.

In contrast to our observations with compound **5**, diperoxo complexes are commonly considered as more inert compounds with respect to chemical exchange.[31,81] Perhaps the observations made here are related to the unusual structural characteristics of compound **5**; that is, the lability of compound **5** may be due to the free coordination site trans to the oxo group in the complex.

Inter- and Intramolecular Exchange in Complex 4. We will now discuss the intramolecular exchange patterns observed for the coordinated imidazole and hydroxylamido residues. Most of these exchange patterns can be observed in organic solvents. Organic solvents were preferred in these studies in part because of the greater thermal and redox stability of the complex in these media making longer accumulation times possible and in part because of the greater resolution of the spectra providing more unambiguous exchange patterns. We show the data that we obtained in a 3:4 mixture of $CD_3CN-DMSO-d_6$ at 5 °C. The partial 2D ^1H EXSY spectrum illustrated in Figure 11 shows that H_2 exchanges with H_3 and that H_3 exchanges with H_2 in the imidazole residue. This exchange pattern is observed for both isomers **4b** and **4c**, with **4b** showing the largest cross peak even though it is the less stable isomer. This type of exchange is observed when the coordinated imidazole is dissociated and after rotation of the imidazole recoordinated so that the original H_2 becomes H_3. An alternative mechanism will be discussed below.

Exchange pathways between isomers include the exchange of H_1 in **4c** with H_1 in **4b**, H_2 in **4c** with H_2 in **4b**, and H_3 in **4c** with H_3 in **4b**. In $CD_3CN-DMSO-d_6$, we do not see the corresponding exchange with the **4a** isomer. Given our experimental difficulties with acquiring the spectra in aqueous solution, further information on the exchange of the **4a** isomer was not obtained even though larger exchange rates were expected in water. However, two additional sets of cross peaks were identified. H_2 in **4c** was found to exchange with H_3 in **4b**, and H_2 in **4b** was found to exchange with H_3 in **4c** as well as the corresponding reverse pathways. The conversion of isomer **4b** to **4c** and vice versa could take place by several plausible mechanisms. The simplest and seemingly most reasonable mechanism would involve loss of the hydroxylamido ligand followed by recoordination to the vanadium atom. Our attention is now turned to the question of exchange among hydroxylamido protons.

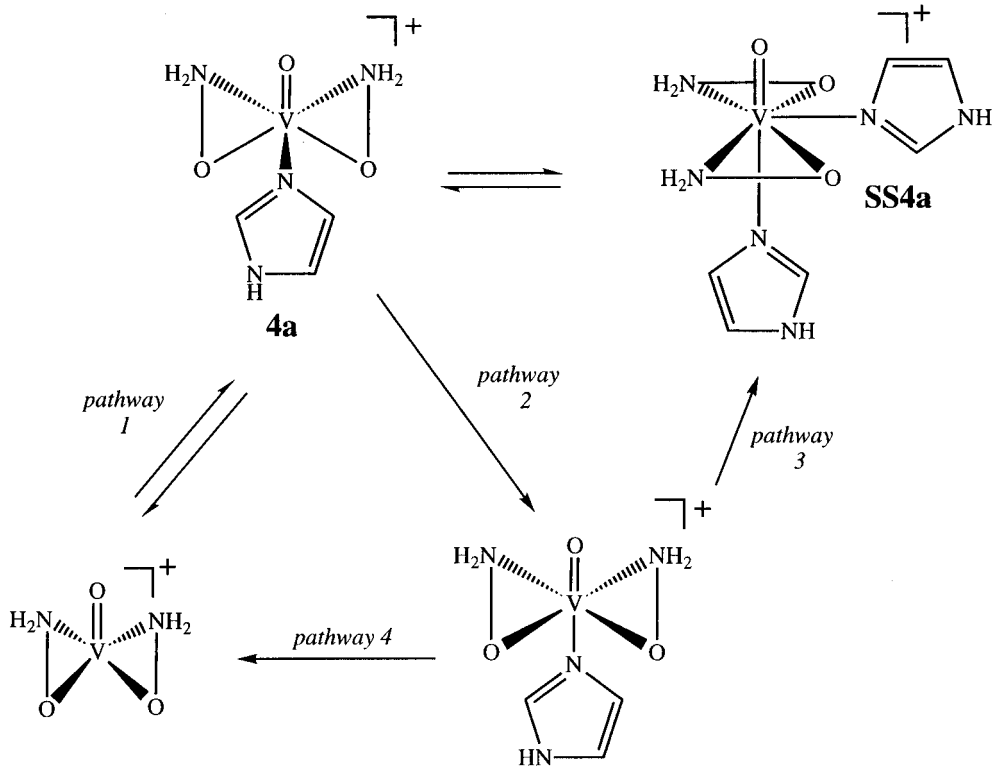
(81) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1990**, *29*, 4457−4461.

In D_2O solution the coordinated hydroxylamido protons rapidly exchange and become invisible by ^1H NMR. The dynamic processes of the coordinated hydroxylamido protons must therefore be examined in an aprotic mixture organic solvent. We found that a 3:4 mixture of CD_3CN and DMSO-d_6 was a good solvent since it allowed observation of the coordinated hydroxylamido protons and its temperature could be reduced below 20 °C. However, even in the temperature range of 0−10 °C, the signals for the hydroxylamido protons are very broad. Unfortunately, the experimental conditions used for observation of the inter- and intramolecular exchange processes involving the coordinated imidazole protons (Figure 11) were not appropriate for observation of the exchange processes among the hydroxylamido protons. The partial ^1H 2D EXSY spectra shown in Figure 11 in fact did not even have any diagonal signals (part of spectrum not shown) for the hydroxylamido protons indicative that these processes are not appropriately evaluated on the time scale of this experiment. Indeed, the broad signal for the hydroxylamido protons suggest short T_1 values, and when measured, we found that the T_1 values for the coordinated hydroxylamido protons are 5−10-fold less than the T_1 values for the imidazole protons. Thus, in order to observe the exchange pattern for the hydroxylamido protons, we needed to increase the T_1 values for the hydroxylamido protons and decrease the time we were observing the intermolecular processes in the complex, τ_{mix}. This was accomplished by decreasing the concentration of compound **4** until further reduction would jeopardize the signal-to-noise ratio. Recording the spectrum of **4** at 6 mM allowed us to use a τ_{mix} of 0.1 s. Recording the ^1H EXSY spectrum at 5 °C allowed us to observe some (weak) exchange between the hydroxylamido protons in **4a** and **4b**, **4a** and **4c**, and **4b** and **4c** (data not shown). We point out that under these conditions **4a** exchanges with the two isomers (presumably by dissociating the hydroxylamido ligand), whereas the exchange among isomers by loss of coordinated imidazole cannot be observed. Nonetheless, the exchange processes (described above) among the coordinated and free imidazole protons are observed under these conditions; given the lower compound concentration and shorter τ_{mix}, the overall quality of this spectrum is much poorer than that shown above in Figure 11. This result supports the interpretation that both the hydroxylamido ligand and the imidazole ligand readily fall off the complexes.

On the basis of these 2D EXSY studies, we conclude that exchange between isomeric hydroxylamido protons is observed. However, the fact that no free hydroxylamine is observed upon dissociation of compound **4** would be consistent with the first hydroxylamido ligand dissociating from the complex and recoordinating to the same or a different isomer. NMR studies carried out on complex **4** in the presence of excess hydroxylamine (data not shown) confirm these conclusions since the observed line broadening of free and coordinated hydroxylamido amine proton signals was observed.

Exchange Pathways: Mechanistic Interpretations. What do these exchange processes mean with respect to the chemistry of these complexes? The rapid exchange of the imidazole in the diperoxovanadium compound **5** is perhaps unexpected when considering the slower ligand exchange observed in the more common seven-coordinate diperoxovanadium compounds. It is reasonable to suggest that the difference in complex−ligand reactivity originates from the unusual coordination geometry of the six-coordinate peroxo complex, particularly in light of the characterization of the solution properties of the related hydroxylamido complex **4** carried out in this work. In the solid state, compound **4** contains two imidazole residues (**SS4a**,

Scheme 1. Coordinated Imidazole Exchange in Complex **4a**



Scheme 1); however, in aqueous and organic solvents, the one imidazole residue dissociates to generate the three isomers (**4a**−**4c**) and 1 equiv of free imidazole as shown by ^{1}H NMR and discussed above. Thus, compound **4** upon dissolution becomes a six-coordinate complex with a free coordination site. The rich intermolecular exchange processes described above probably take place because of this open coordination site. At this time, we cannot rule out the possibility that the conversion among isomers are due to intramolecular reorganization processes akin to the "Berry pseudorotation" that occurs in five-coordinate phosphorus complexes with an open coordination site. At this time there is no reported precedence for "Berry pseudorotation" type processes in vanadium complexes. We conclude that observed intermolecular molecular exchange between free imidazole ligand and vanadium coordinated imidazole, combined with the different exchange rates among isomers, supports the interpretation that the observed exchange among isomers is not simply an intramolecular reorganization. Evidence has previously been summarized pointing at a dissociative types of reaction mechanisms for a variety of five- and six-coordinate vanadium(V) compounds exhibiting complex-free ligand exchange[82] and consistent with the observations made in this work.

Direct comparison of the exchange processes for complexes **4** and **5** reveal that complex **5** is more labile than complex **4**. On the basis of the structural information now available we feel the following points should be made. First, compound **5** does not coordinate a second imidazole ligand in the solid state. Although several reasonable explanations can be offered, no evidence for coordination of a second imidazole even at large excesses of imidazole are seen in the NMR spectra. X-ray data show that the V−N bond is longer for the peroxo complex than for the hydroxylamido complex, thus supporting a weaker bond that is more readily cleaved. In addition, the imidazole residue is rotated out of plane in the peroxo complex thus precluding the π interaction of the imidazole orbitals with the appropriate d orbital on the vanadium atom. On the other hand, the orientation of the imidazole residue in the hydroxylamido complex is optimal for this type of interaction, supporting the observation that the peroxo complex is more labile than the hydroxylamido complex.

The hydroxylamido complexes, with their inherent structural asymmetry, are likely to become informative models for diperoxo complexes. Analogous studies are not possible with the diperoxo complex, given the symmetry of the complex. However, the potential that mechanistic insight may be important for understanding the properties of both families of compounds as insulin mimics and catalysts makes such studies important. In Scheme 1, we show an equilibrium between **4a** and the solid state form of **4a** (**SS4a**). Although some of these considerations at this time only are supported by NMR experiments, the combination of chemical shift, EXSY experiments, and structural information allows evaluation of the possibilities for exchange processes in these vanadium(V) complexes. In Scheme 1, we have illustrated the conversions for **SS4a** beginning with the loss of one imidazole residue to form isomer **4a**. The second coordinated imidazole can be lost in a dissociative manner from the pentagonal pyramidal complex geometry in isomer **4a** (Scheme 1, reaction 1) or, via a structural rearrangement, through an octahedral complex (product of reaction 2). Should the octahedral complex form, a nucleophilic attack by free imidazole with or without concomitant structural rearrangement will lead to **SS4a** (reaction 3). Alternatively, the sequential loss of two imidazole residues (reaction 4) via intermediate formation of **4a** can lead to formation of **SS4a**. Thus, the solid state structure of the hydroxylamido complex could, in the presence of 1 equiv of free imidazole, be an intermediate on the exchange pathway between monodentate complexes. Although Scheme 1 only shows this type of pathway for **4a** and **SS4a**, the outlined equilibria and pathways are presumably equally possible for **4b** and **4c** even though we have not isolated and structurally

(82) Crans, D. C.; Ehde, P. M.; Shin, P. K.; Pettersson, L. *J. Am. Chem. Soc.* **1991**, *113*, 3728−3736.

characterized their respective complexes containing two imidazole ligands.

In addition to considering the rearrangements and exchanges within one complex, the observation of exchange processes documents the need to consider conversion among isomers. By what mechanism would a symmetric isomer convert to an unsymmetric isomer? A reasonable mechanism would involve the loss of one hydroxylamido ligand and the reorientation and recoordination of a hydroxylamido group in another orientation. Indeed, we were able to demonstrate that even though the hydroxylamido ligands are coordinated to the vanadium in solution and no signals are observed for free hydroxylamine in solutions of dissolved complex, the hydroxylamido ligands do exchange. This exchange is also a rapid process. Several exchange processes including H_1 in **4c** to H_1 in **4b**, H_2 in **4c** to H_2 in **4b**, and H_3 in **4c** to H_3 in **4b** are consistent with hydroxylamido exchange even though we have only directly demonstrated that the hydroxylamido ligand exchanges under some conditions. An alternative interesting pathway would involve a head-on hydroxylamido complex, and this process would not require the presence of low concentrations of free hydroxylamine.

However, simple hydroxylamido ligand exchange cannot explain All of the observed exchange patterns shown in Figure 11. The conversion of H_2 in **4c** to H_3 in **4b** or the conversion of H_3 in **4c** to H_2 in **4b** cannot be explained by simple hydroxylamido or imidazole exchange. These processes are indicative of multistep processes or a more complex exchange pathway. When the fact that the exchange between complex and both free ligands are fast is considered, a major exchange path to explain this process exists. One possible mechanism accounting for the cross peak between H_2 in **4c** and H_3 in **4b** is the dissociation of the imidazole from complex **4c** and reassociation in a rotated manner to a different vanadium atom to form complex **4b**. This mechanism is an intermolecular process in which two vanadium atoms are involved. Since we see no evidence for even low concentrations of either species and some concentration of intermediate vanadium species and free hydroxylamine is required, this process seems less likely. An alternative and perhaps more credible two-step process would involve both hydroxylamido exchange and imidazole exchange in one complex within the time of the experiment (τ_{mix}). By this mechanism, the vanadium complex is originally a type **4c** complex and after the hydroxylamido exchange becomes a type **4b** complex. In view of the fact the hydroxylamido exchange is very rapid, and that the imidazole exchange between isomers is also observable on the time scale of this experiment, this type of mechanism seems more likely. This conclusion is supported by the fact that the size of the respective cross peaks for the various processes such as H_2 in **4b** converting to H_2 in **4c** are of about the same magnitude as the cross peaks for the conversion of H_2 in **4b** to H_3 in **4c** or the conversion of H_3 in **4b** to H_2 in **4c**. In addition, this type of mechanism is consistent with only observing this type of exchange between the two most reactive isomers. This type of process is not observed with the **4a** isomer where the individual processes also are slower.

Biological Relevance. The hydroxylamido group in the natural product *Amavadine* has fascinated chemists for some time, and various model systems and spectroscopic characterizations have been carried out.[37,39,83] The structure of the vanadium(IV) complex still remains a curiosity since it is the only naturally occurring example of a "bare" vanadium(IV) (a vanadium(IV) complex without a V=O). Furthermore, the exceedingly high stability of this complex is very unusual.[39]

Coordination of the hydroxylamido group to vanadium, as for the coordination of the peroxo groups to vanadium, changes the properties of the central metal ion. Specifically, the $VO(NH_2O)_2^+$ and $VO(O_2)_2^-$ units have greater affinities for weak ligands in aqueous solution so that complexes of such ligands can form in significant concentrations. Prime examples of such weak ligands are imidazole, amino acids, and dipeptides. These are the types of ligands investigated in this work, and our studies with imidazole complexes are particularly thought-provoking. We show that the imidazole functionality, in both the peroxo and hydroxylamido complexes, is quite labile, in contrast to the general belief that the peroxo groups significantly increase complex stability and decrease complex lability.[31,81] When the properties of the amino acid or dipeptide complexes are compared with those of the imidazole complex, the former are less labile than the latter, consistent with the interpretation that the lability is likely to be closely associated with the mono- or bidentate nature of the ligand. Fine-tuning the properties of a specific compound by selection of functionalities in catalytic and biological systems will thus depend on the specific role of the vanadium atom in each case. Peroxovanadium picolinate is a useful catalyst in organic synthesis;[30] the pyridine and the carboxylate functionalities are presumably essential in tuning the properties of the complex to facilitate the dynamic exchanges required in catalytic oxidations. When the roles of the imidazole and carboxylate functionalities in the haloperoxidases[8] are considered and the organic catalysts carrying out oxidative processes are compared, some interesting differences are apparent. For the haloperoxidase, only the histidine group is coordinated to the vanadium atom, making the corresponding complex a monodentate complex (the carboxylates are involved through H-bonding). The X-ray characterization of the vanadate−prostatic acid phosphatase from rat liver complex also reveals axial coordination of a histidine,[84] illustrating the structural analogy between these two types of enzymes.[85] There is no doubt that the vanadium complex is an excellent structural analog of one or more transition state or intermediate species along the hydrolytic reaction pathway of phosphoester hydrolysis. Furthermore, the fact that the enzyme is only coordinated in monodentate manner is consistent with the much more labile nature of such a complex compared to that observed for the complexes coordinated to bidentate ligands. Perhaps, this general pattern will continue to develop as more structural characterizations of enzyme−vanadium complexes are reported.[86]

The increased stability of complexes when a weak ligand is complexed to $VO(NH_2O)_2^+$ and $VO(O_2)_2^-$ units could potentially be taken advantage of for preparation of complexes from weak ligands with larger biomolecules including proteins. Although the rich redox chemistry of the $VO(O_2)_2^-$ unit may limit applications of this type, there is no doubt that pH and biomolecule functionality can reduce undesirable redox chemistry, and indeed, a large number of complexes have been characterized as the peroxovanadium complex,[31] whereas the vanadium(V) parent compound remains elusive. Similar applications of the $VO(NH_2O)_2^+$ unit have not been examined. As we show in this work, the rates of hydrolytic reactions have been decreased in this family of compounds; however, we still

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(84) Lindqvist, Y.; Schneider, G.; Vihko, P. *Eur. J. Biochem.* **1994**, *221*, 139−142.

(85) Hemrika, W.; Renirie, R.; Dekker, H. L.; Barnett, P.; Wever, R. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 2145−2149.

(86) Zhang, M.; Zhou, M.; Van Etten, R. L.; Stauffacher, C. V. *Biochemistry* **1997**, in press.

observe redox reactions under mild conditions, therefore, the general applicability of the hydroxylamido unit for stabilizing other biomolecule complexes may be limited. However, the remarkable stability of the Amavadine complex still has not been matched in other systems and remains a formidable challenge. One obvious direction such work can take is to decrease the sources of decomposition in the hydroxylamido complexes; that is, decrease the concentration of free NH_2OH in aqueous solution. Indeed, we have already carried out some preliminary studies substituting R_2NOH or RNHOH for NH_2-OH (Crans and Keramidas, unpublished results). These alkyl hydroxylamido derivatives are more stable in aqueous solution than NH_2OH and also form more stable complexes with vanadium(V). Perhaps these compounds will provide more useful analogs of peroxovanadium complexes in the future, if the parent NH_2OH compounds described in this work fail in this endeavor.

At this time no information has been reported on whether hydroxylamido complexes are merely structural analogs of peroxovanadium compounds. Work in our laboratory suggests that indeed the structural analogy may be developed into useful probes of peroxovanadium compound activities in biological systems (Crans et al., unpublished results). There is no doubt that such studies will provide not only novel chemistry but also information of the mechanisms by which vanadium compounds act in biological systems and as catalysts.

Conclusions

In the pursuit of vanadium compounds with specific structure, chemical and biological properties a new series of vanadium(V) compounds analogous to the peroxovanadium(V) compounds has been prepared and characterized in solution and solid state. This series of compounds provide not only access to further in depth studies of complexes with weak ligands such as amino acids, peptides, and derivatives but also provide a rare opportunity to probe the lability of this type and peroxovanadium compounds. Solution studies are carried out and probe the analogy of these vanadium(V) hydroxylamido complexes with peroxovanadium(V) complexes. The following general conclusions and comparisons can be made at this time:

Vanadium(V) hydroxylamido complexes are structurally similar to the seven-coordinate diperoxovanadium(V) complexes in the solid state. The hydroxylamido ligands are coordinated in a bidentate manner with the vanadium atom placed in a pentagonal bipyramidal-like geometry. The vanadium atom is displaced slightly out of the plane in direction of the oxo group as commonly observed for peroxovanadium complexes.

Vanadium(V)-hydroxylamido complexes exhibit structural isomerism presumably determined by a combination of the σ donation of the equatorial amine ligand and the steric requirements of the ligand. Complexes have been structurally characterized with N,O side-on coordination to the vanadium atom in both orientations in the solid state.

Aqueous and organic solvent studies demonstrate that the properties of these complexes vary significantly depending on the nature of the organic ligand. In all cases, the complexes are extremely sensitive to redox chemistry outside the neutral pH range. For, bidentate amino acid ligands, the complexes show a smaller degree of lability in solution. Complexes of a monodentate ligand such as imidazole show a greater level of lability and instability.

UV/vis spectra were recorded and the characteristic bands at 320 nm in peroxo complexes are replaced by shoulders at lower wavelengths ($<$300 nm) in all complexes prepared in this work. These absorbance shoulders are attributed to transitions from the hydroxylamido ligands to the metal. The hydroxylamido complexes show a low-intensity charge-transfer absorbance which can tentatively be assigned as the charge transfer of a side-on hydroxylamido group to vanadium in analogy with the low-energy charge-transfer weak absorbance (such a band is absent in head-on peroxo complexes).

Crystalline materials generate isomeric hydroxylamido complexes in solution. The stability of the isomers are very sensitive to specific conditions of solvent and temperature. Solution studies suggest that the isomers formed upon dissolution are of identical stoichiometry and are consistent with side-on hydroxylamido coordination. Detailed EXSY NMR spectroscopic studies have characterized the exchange processes in the vanadium(V)−hydroxylamido−imidazole complex and show both intermolecular and intramolecular processes.

In a detailed comparison of the peroxo and the hydroxylamido imidazole complexes using 1D and 2D multinuclear NMR spectroscopy, the aqueous solution structures of both systems are consistent with a six-coordinate vanadium atom. The hydroxylamido complex shows rapid hydroxylamido and organic ligand exchange; however, the level of exchange is less than that observed for the related peroxovanadium compound.

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Supporting Information Available: The full tables listing crystal data and experimental results for compounds **1**−**5** are provided (32 pages). See any current masthead page for ordering and Internet access instructions.

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