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Dinuclear Oxovanadium(IV) *N*-(Phosphonomethyl)iminodiacetate Complexes: $Na_4[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]\cdot 10H_2O$ and $Na_8[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]_2\cdot 16H_2O$[1]

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The dioxovanadium(IV) complexes with pida^{4-} ligands (H_4pida) = *N*-(phosphonomethyl)iminodiacetic acid), $Na_4[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]\cdot 10H_2O$ (**1**) and $Na_8[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]_2\cdot 16H_2O$ (**2**), were isolated from reactions of H_4pida with either oxovanadium(V) (i.e., $NaVO_3$) or oxovanadium(IV) precursors within the pH range of 2−8. The structures of complexes **1** and **2** were investigated by X-ray diffraction methods and in contrast to expectation were both found to be dinuclear. Complex **1** crystallized in the monoclinic system: $P2_1/n$, $a = 10.5632(1)$ Å, $b = 11.1868(1)$ Å, $c = 12.6921(1)$ Å, $\beta = 106.45°$, $V = 1438.44(2)$ Å^3, $Z = 4$, and R (w$R2$) = 0.0781 (0.2017). Complex **2** crystallized in the monoclinic system $P2_1/c$: $a = 13.9822(2)$ Å, $b = 11.1888(2)$ Å, $c = 18.6519(3)$ Å, $\beta = 100.88°$, $V = 2865.51(8)$ Å^3, $Z = 4$, and R (w$R2$) = 0.046 (0.125). Both complexes **1** and **2** have similar dimeric frameworks where two vanadium centers are linked by two phosphonate groups of two pida^{4-} ligands (quadridentate binucleating), bridging through their four oxygen atoms to form a $V_2O_4P_2$ eight-membered ring which possesses a crystallographic inversion center. In contrast to their solid-state features, in aqueous solution both dinuclear crystalline compounds immediately dissociate to monomeric species, as observed by EPR and UV/vis spectroscopy. Both solution-state EPR and NMR spectroscopy confirmed that redox chemistry is involved in the reaction between vanadate and H_4pida. Studies in mixed solvent systems showed that the dinuclear complex would remain intact in the presence of sufficient organic solvent. In the absence of oxygen the mononuclear and the dinuclear complexes will reversibly interconvert, whereas, in the presence of oxygen, the complexes will oxidize. These studies document the existence of higher oligomeric vanadium compounds and surprisingly, in general, lend credibility to several emerging mechanistic proposals involving oligomeric species of vanadium compounds in catalytic processes.

Introduction

Vanadium(IV) and vanadium(V) form complexes with polydentate ligands with N, O donors, resulting in complexes of varied stoichiometries depending on ligand design. Simple and flexible tetradentate ligands such as nitrilotriacetic acid, triethanolamine, *N*-(2-pyridylmethyl)iminodiacetic acid,[1] and N-(hydroxyethyl)iminodiacetic acid[1] tend to form stable mononuclear or single oxo-bridging dinuclear complexes containing six-coordinate vanadium atoms.[2−9] A series of such complexes with ligands that include *N*-(2-aminoethyl)iminodiacetic acid, *N*-(carbamoylmethyl)iminodiacetic acid, *N*-(hydroxylalkyl)salicylideneamines, and tris(pyrazolyl)borate has recently been examined as a model for bromoperoxidase and its activity.[10−16] The V(IV) complex, V(IV)−pida, formed from *N*-(phosphonomethyl)iminodiacetic acid (H_4pida) has been studied in detail in solution with respect to ligand substitution and redox chemistry.[17,18] This complex was found to oxidize, and the major product generated is *N*-(phosphonomethyl)glycine. *N*-(phosphonomethyl)glycine is the herbicide commercially sold as PMG, and the vanadium-catalyzed oxidation of H_4pida was investigated as an alternative to the process currently used.[17] Accord-

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(1) Abbreviations: H_4pida, *N*-(phosphonomethyl)iminodiacetic acid; IR, infrared spectroscopy; NMR, nuclear magnetic resonance; DMF, dimethylformamide; THF, tetrahydrofuran; nta, nitrilotriacetate; tea, triethanolaminate; pmida, *N*-(2-pyridylmethyl)iminodiacetate; hida, *N*-(hydroxyethyl)iminodiacetate; pida^{4-}, *N*-(phosphonomethyl)iminodiacetate tetraanion.

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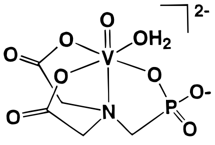

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Figure 1. Structure of the V(IV)−pida complex.

ingly, the V(IV)−pida complex (Figure 1) may be identified as one of the complexes that is best understood from the perspective of aqueous chemistry. However, despite several detailed studies, no solid-state structural information was available. Given our interests in the stability and lability of vanadium complexes in general, and the effects the phosphonic acid group could have on such properties, we wanted to explore not only the solid-state but also solution properties of this type of complex.

Vanadium oxides mixed with phosphate and other transition metal oxides are used as catalysts for commodity chemical production or manufacture[19] and as ion exchangers.[20] In addition, the vanadium phosphate materials that have recently been structurally characterized and the cagelike vanadium phosphate clusters that have been shown to form around template ions document the structural diversity of this group of complexes.[21−24] Phosphates coordinate to vanadium in a bidentate manner, and this includes complexes of simple phosphates and phosphonates[25] as well as vanadium peroxo complexes.[26] Spectroscopic and potentiometric studies of V(IV) with a series of simple phosphonates showed that the alkylphosphonates coordinate in a monodentate manner in contrast to phosphates that chelate in a bidentate manner in solution.[27] In addition, the Carrano group has recently developed vanadium complexes that show specific interactions with simple phosphates and phosphonates as models for interactions with DNA. These studies have led to the development of new vanadium phosphate and vanadium phosphonate clusters and other complexes that will cleave DNA in the absence of cooxidants or reductants.[28,29] Despite these recent advances, very little structural information is available on vanadium complexes formed from multidentate organic ligands containing the phosphonate group.

A range of different dinuclear V(IV), V(V), and mixed-valence complexes have been reported.[2,3,7−9,30−37] Although dinuclear vanadium complexes in general have been reported with a wide range of connectivities and geometries,[9,13,30,31,37−44] the dinuclear complexes generated from the simple and flexible polydentate ligands with O and N donor functionalites are surprisingly similar and only display a few selected types of geometries. The dinuclear V(IV) complexes reported include $[V_2O_2(\text{salahe})]$[13] and $[V_2O_2(\mu\text{-malonate})(Me_2pzH)\{HB(Me_2pz)_3\}_2]$,[38] in which the two vanadium atoms are linked by one or two bridging oxygen atoms. The dinuclear V(V) complexes reported include $[V_2O_3(\text{dihydroxyzobenzene})_2]$,[32] $[V_2O_3(\text{quinolinol})_4]$,[45] and $[V_2O_2(\text{salamhp})_2]$.[13] In the two former complexes the two vanadium atoms are connected by one linear mono(μ-oxo) unit. In $[V_2O_2(\text{salamhp})_2]$ the two vanadium atoms are connected by both a linear mono μ-oxo unit and another oxygen from the ligand. Many dinuclear mixed-valence V(IV) and V(V) complexes have been reported.[2,3,7−9,30−37] Complexes reported in this group contain the $[V_2O_3]^{3+}$ core, and perhaps surprisingly, the two vanadium atoms are connected through a linear mono(μ-oxo) unit. Typically, although exceptions have been reported,[13,38] the dinuclear complex forms if the V(V) precursor is in the presence of excess ligand or another reductant. Alternatively, the dinuclear complex forms if the V(IV) precursor is mixed with the ligand and reacted in the presence of oxygen. Thus, the oxidation state of the vanadium precursor does not always dictate the oxidation state of the vanadium in the product.

Two different crystals were isolated from an aqueous solution of V(IV)−pida from which X-ray crystallography revealed two different 2:2 vanadium−pida^{4-} complexes. These complexes were found to dissolve into a mononuclear 1:1 complex in aqueous solution; however upon addition of organic solvents or recrystallization from water, the dinuclear complex re-formed. These observations suggested that even aqueous solutions containing the well-known V(IV)−pida complex may contain dinuclear species. In view of the mechanistic proposals made for several systems involving oxidative chemistry[17] of synthetic relevance[46−48] in which the kinetics could only be explained by invoking the existence of dinuclear species, characterization

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of this unexpected dinuclear V(IV)−pida species is important for mechanistic considerations. Furthermore, the complexes described in this work are of interest because they document that even in a multidentate ligand system designed to favor mononuclear complexes in aqueous solution, the phosphonate group prefers coordination in a quadridentate binucleating manner and in organic solvents and the solid state will act on this tendency and dimerize.

Experimental Section

Materials and Methods. All manipulations were carried out under ambient conditions. Reagent grade sodium metavanadate, vanadium sulfate, $VO(acac)_2$, and *N*-(phosphonomethyl)iminodiacetic acid (H_4-pida) were purchased from Aldrich and used without further purification. Distilled and deionized water was used for the synthesis of the complexes. ^{51}V NMR spectra were recorded at 79 MHz on a Bruker ACP-300 NMR spectrometer, and chemical shifts were reported against the external reference neat $VOCl_3$ (0 ppm). ^1H NMR spectra were recorded at 300 MHz on a Varian JS300 NMR, employing routine parameters. EPR spectra were recorded on a Bruker ESP300 spectrometer and a Varian E9 spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 4B UV/vis spectrophotometer, and infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Desert Analytics Laboratory, Tucson, AZ, performed elemental analyses.

$Na_4[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]\cdot 10H_2O$, 1. Solid H_4pida (1.36 g, 6.00 mmol) was added to a solution of $NaVO_3$ (0.49 g, 4.0 mmol) in 50 mL of water at ambient temperature and stirred until dissolved. After adjustment of the solution pH to the decided pH value (from 2 to 6) using aqueous $NaHCO_3$ (1 M), the color changed from brown to dark green while stirring at ambient temperature for a few hours. The solution was then stirred for an additional 24 h during which time the reaction solution changed from green to blue. The reaction solution was then concentrated to 30 mL, and ethanol (95%, 20 mL) was added. The blue crystalline compound **1** formed after the solution was kept at 4 °C for 1 week. After removal of the crystals, the solution could yield additional crystalline material by further concentrating the solution and diffusing more ethanol. The material precipitated in this manner had the same properties as crystalline complex **1**. The crystalline product was filtered off, washed with ethanol (2 × 10 mL), and dried under vacuum, affording 1.24 g of **1** (73% with respect to V-atom, 49% based on H_4pida). Crystals of X-ray diffraction quality typically were obtained by allowing ethanol to diffuse into a concentrated aqueous solution of **1**. IR (KBr pellet cm^{-1}): 3445 (s, br), 2950 (m), 1636 (s), 1587 (s), 1431 (m), 1401 (s), 1378 (m), 1159 (m), 1113 (m), 1045 (s), 987 (m), 960 (s), 908 (w), 794 (w), 737 (w), 586 (m), 486 (w), 386 (w). Anal. Calcd for $C_{10}H_{32}N_2Na_4O_{26}P_2V_2$: C, 14.09; H, 3.78; N, 3.29; V, 11.96. Found: C, 14.36; H, 3.54; N, 3.55; V, 11.92.

Alternative Preparation of 1. Vanadium sulfate $VOSO_4$ (0.87 g, 4.0 mmol) or $VO(acac)_2$ (1.06 g, 4.00 mmol) and H_4pida (0.91 g, 4.0 mmol) were dissolved in 50 mL of distilled water. The solution was adjusted to pH 2 (or 4) with aqueous $NaHCO_3$ (1 M), and the mixture was stirred for 24 h at ambient temperature. Adding ethanol (20 mL) to the blue solution and storing the solution at 4 °C for 1 week generated blue crystals. The crystalline product was isolated by filtration, washed with ethanol (2 × 10 mL), and dried under vacuum. The 1.14 g of product (67% yield based on both V atom and H_4pida) had properties identical to those of crystalline **1** described above.

$Na_8[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]_2\cdot 16H_2O$, 2. $NaVO_3$ (0.49 g, 4.0 mmol) was dissolved in 80 mL of H_2O, and solid H_4pida (1.36 g, 6.00 mmol) was added. The pH of the reaction solution was adjusted to 8 with aqueous NaOH (2 M), generating a brown solution that was stirred for 24 h. The brown solution was then concentrated to 30 mL under vacuum. Green crystalline **2** was obtained by diffusing ethanol over the concentrated solution and storing the mixture for 2 days at ambient temperature, followed by cooling at 4 °C for 5 days. The best green crystals were collected, washed with ethanol (2 × 10 mL), and dried in vacuo. Compound **2** was obtained and afforded a total of 0.93 g (55%). IR (KBr pellet cm^{-1}): 3445 (s, br), 2935 (m), 1636 (s), 1595 (s), 1435 (m), 1402 (s), 1375 (m), 1160 (m), 1115 (m), 1044 (s), 985 (m), 962 (s), 950 (m), 908 (w), 793 (w), 670 (w). Solution characterization for this compound gave results identical to those described for compound **1** above. Anal. Calcd for $C_{20}H_{56}N_4Na_8O_{48}P_4V_4$: C, 14.51; H, 3.41; N, 3.38; Na, 11.11; V, 12.31. Found: C, 14.50; H, 3.54; N, 3.35; Na, 11.82; V, 12.59.

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
chem formula	$C_5H_{16}NNa_2O_{13}PV$	$C_{10}H_{28}N_2Na_4O_{24}P_2V_2$
fw	426.08	816.12
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	10.5632(1)	13.9822(2)
b (Å)	11.1868(1)	11.1888(2)
c (Å)	12.6921(1)	18.6519(3)
β (deg)	106.45	100.88
V (Å^3)	1438.44(2)	2865.51(8)
Z	4	4
T (K)	161	164
λ (Å)	0.710 73	0.710 73
D_{calc} (g cm^{-3})	1.97	1.89
F(000)	868	1656
reflcns collcd	9337	18164
indepdt reflcns	3436	6790
R	0.078	0.046
wR2	0.202	0.125
largest diff peak and hole (e Å^{-3})	1.41, −0.99	0.76, −0.53

X-ray Diffraction Studies of $Na_4[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]\cdot 10H_2O$ (1) and $Na_8[V_2O_2\{(O)_2P(O)CH_2N(CH_2COO)_2\}_2]_2\cdot 16H_2O$ (2). For both compounds **1** and **2**, X-ray diffraction data (crystal dimensions 0.58 × 0.26 × 0.26 mm^3 for **1**, 0.44 × 0.20 × 0.10 mm^3 for **2**) were recorded on a Bruker SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Crystallographic results and other details are listed for both compounds in Table 1. In both cases, intensities were integrated from a series of frames (ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS[49] (transmission factors 0.68−0.96 for **1**, 0.58−0.93 for **2**). The reflections thus obtained (9337 for **1**, 18 164 for **2**) were merged to provide the final data sets comprised of 3436 unique reflections ($R_{int} = 0.039$) for **1** and 6790 unique reflections ($R_{int} = 0.034$) for **2**. Both structures were solved by direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process ($R = 0.078$, w$R2 = 0.202$ for **1**; $R = 0.046$, w$R2 = 0.125$ for **2**). All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in idealized positions and refined by using a riding model; no attempt was made to assign hydrogen atoms to the water molecules (some with fractional site occupancy factors) found in the two structures. The final electron density maps showed features in the ranges −0.99 to +1.41 e Å^{-3} for **1** and −0.53 to +0.76 e Å^{-3} for **2**; the highest peaks in each case suggested the presence of additional water molecules with fractional site occupancy factors, but these were not pursued. In both cases, standard Bruker control (SMART) and integration (SAINT) software was employed, and Bruker SHELXTL[50] software was used for structure solution, refinement, and graphics. Further details of the data collections and structure determinations are listed in the Supporting Information.

UV−Visible Studies. Crystalline compound was dissolved directly into the solvent under examination. Dissolution of blue compound in aqueous solution resulted in a blue solution, whereas dissolution into organic solvent mixtures often was accompanied by a color change. Most of the work described in this paper was carried out in aqueous DMF mixtures; however, additional studies in aqueous CH_3CN, aqueous THF, and aqueous dioxane mixtures also were performed. Solvent ratio varied depending on the system under examination. The crystalline material was dissolved directly into the solvent mixture, and in cases of high organic solvent content (60−70% DMF or 50% dioxane), dissolution of 1.5 mM of **1** required sonication. Samples for analysis

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(49) Sheldrick, G. M. To be published, 1997.

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were prepared immediately before the absorption studies unless otherwise indicated. The extinction coefficients for the complexes were calculated from solution concentrations at the respective absorbance maxima.

EPR Spectroscopic Studies. The aqueous and DMF/H_2O samples examined by EPR spectroscopy were prepared as described above. A particularly important aspect of the studies with the V(IV) dinuclear species was that crystalline compound was used in all cases and was dissolved directly into the solvent mixture under examination. The EPR spectra were recorded using disposable glass flat-cells of 0.4 mm path length (room temperature) and 4-mm-o.d. quartz tubes (low temperature) on a Varian E-9 spectrometer. The spectrometer was operating at X-band (9.17 GHz) frequency with a microwave power of 50 μW (room temperature) and 0.2 μW (−146 °C). The EPR spectra were recorded using a modulation frequency of 100 kHz, a modulation amplitude of 5.0 G, a time constant of 128 ms, and a conversion time of 120 s (18 °C) and 240 s (−146 °C).

Magnetic Susceptibilities. Solutions of approximately 10 mM complex **1** and **2** in D_2O were subjected to ^1H NMR analysis on a Varian JS300 Spectrometer at 24 °C using 10% (v/v) acetonitrile as an internal reference. The experiments were performed in duplicates. The magnetic susceptibility was calculated using Evans method by comparing the chemical shifts of the acetonitrile in solution containing complex and the reference in the coaxial NMR tube.[51−53]

Results and Discussion

Synthesis and Isolation of Complexes 1 and 2. Addition of H_4pida to a solution of sodium metavanadate ($NaVO_3$) at ambient temperature immediately generates a brown solution that turns green upon stirring for a few hours. H_4pida was added to solutions of sodium metavanadate in a wide pH range, but we will specifically describe the experiments carried out at pH 4. After being stirred for 24 h at pH 4, the solution was clear blue and blue crystals could be obtained as described in the Experimental Section. The crystals of complex **1** were suitable for X-ray diffraction studies and proved to be dinuclear instead of the anticipated mononuclear molecule (see below). Although complex **1** was crystallized from an aqueous solution of V(V) precursor ($NaVO_3$), the X-ray structure for the dinuclear complex contained four sodium counterions. The crystal thus appeared to contain V(IV) and not V(V), which must have been reduced during the synthesis. The presence of V(IV) in this crystalline material was furthermore substantiated using EPR spectroscopy (see below) and the Evans method to determine whether the free electron was present. In addition, it was verified that the complex prepared by combining equimolar quantities of a V(IV) precursor ($VO(acac)_2$ or $VOSO_4$) and H_4pida had the same solid-state properties as **1**.

Reaction mixtures in a wide range of pH were prepared, and spectroscopic solution characterization (see below and ref 54) showed that different V(V)−pida complexes formed in these reaction mixtures. For example, a strong ^{51}V NMR signal at −527 ppm was observed for freshly prepared solutions at pH 6; however, the intensity of this signal decreased as function of time. Crystals were obtained by procedures similar to those described in the Experimental Section for solutions at pH 2 and 6. The solution at pH 2 was blue and very similar to the solution at pH 4; however, the solution at pH 6 was green. The blue crystal isolated from the pH 2 solution had exactly the same unit cell parameters as **1**, thus indicating this compound contained the same dinuclear core as complex **1**. Surprisingly, the crystal isolated from the green solution at pH 6 was blue and also had the same unit cell parameters as **1**. Furthermore, dissolution of this crystal and examination by ^{51}V NMR spectroscopy gave no observable signal, consistent with reduction of V(V) to V(IV). Our attempts to prepare crystalline V(V)−pida complexes at acidic pH values always led to reduction of the V(V) center to V(IV) and oxidation of the H_4-pida ligand as described previously under significantly different conditions. When crystalline materials were isolated in this entire pH range, they had the same unit cell parameters as complex **1**.

Attempts to isolate other crystalline materials, including perhaps the mononuclear V(IV) and V(V) complexes, also were carried out in the alkaline pH range. At high pH values the complexes will deprotonate, and in the case of a V(V)−pida complex, the charge will be −3 which may favor monomer formation and allow crystallization of the monomeric unit. Addition of white solid H_4pida to a colorless solution of sodium metavanadate at ambient temperature immediately generated a brown solution which remained brown after adjusting the pH to 8 and upon stirring for 1 day. The formation of a V(V) complex in the brown solution was verified by a ^{51}V NMR signal at −527 ppm that was observed in freshly prepared solutions. Diffusing ethanol into the concentrated brown solution over a period of a few days yielded blue-green crystals of complex **2** at the interphase of the bilayer. The unit cell parameters for this complex were different; however, X-ray diffraction studies on complex **2** again revealed a dinuclear complex. Although the major component in solution was the V(V) complex, the species we were able to crystallize from these solutions was the reduced V(IV)−pida complex (see below).

Addition of white crystalline H_4pida to a colorless solution of sodium metavanadate at ambient temperature generated a brown solution, which, upon the addition of NaOH to pH 10, immediately turned to a yellow solution (at pH 10) that remained yellow even upon stirring for 1 day. After incubation for 4−6 days yellow crystals of complex **3** had formed. Isolation and spectroscopic characterization by ^{51}V and ^1H NMR showed that complex **3** contained V(V) and no pida^{4-} ligand. Since the ^{51}V NMR signal in these solutions was consistent with the deprotonated vanadate monomer (−537 ppm, HVO_4^{2-}),[55−57] and X-ray structures of simple vanadate salts have been reported, further characterization of this product was not pursued.

Commonly, products are isolated in the oxidation state of the metal used for the starting material, although preparation of V(IV) complexes from V(V) precursors is not unprecedented.[2,30,43] Catalytic reduction of V(V) to V(IV) previously has been demonstrated by the H_4pida ligand, leading to $HOOCCH_2NHCH_2(O)P(OH)_2$ and other products.[17] Under our conditions, solutions of vanadate and H_4pida at pH below 3 generated cleanly $HOOCCH_2NHCH_2(O)P(OH)_2$ (as demonstrated by ^1H NMR spiking experiments). However, as pH increased to 5−6, $HOOCCH_2NHCH_2(O)P(OH)_2$ is oxidized and several ligand oxidation products are observed as evidenced by ^1H NMR. Interestingly, the only isolatable V−pida complexes (**1** and **2**) were the fully reduced dinuclear species, since relatively few V(IV) dinuclear species with O,N-containing ligands have been reported.[13,38] Complexes **1** and **2** are stable

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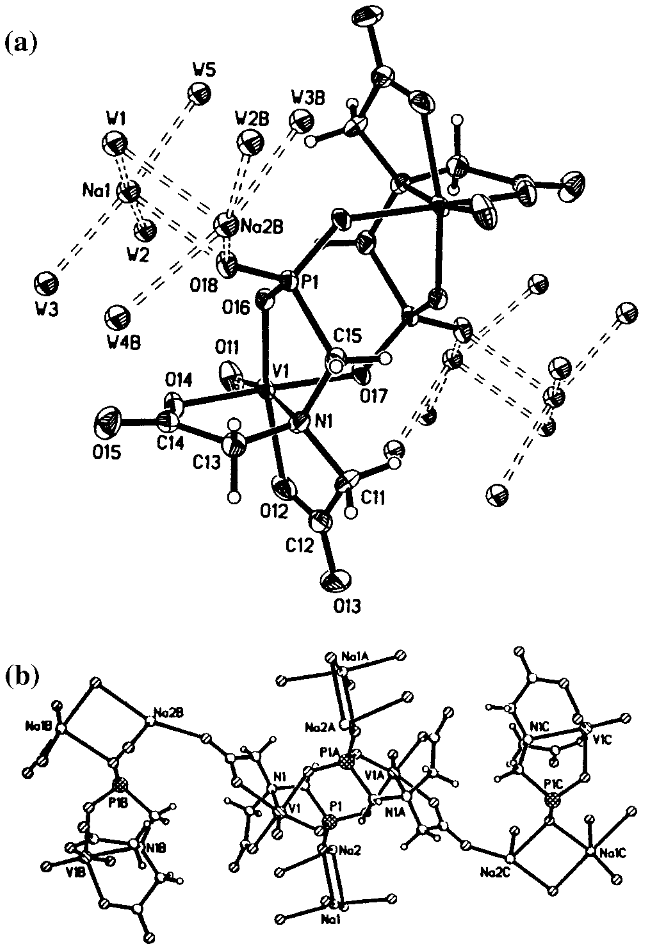

Figure 2. (a) Molecular geometry and atomic labeling scheme for complex **1**, with ellipsoids drawn at the 50% probability level. (b) View of an extended fraction of the crystal showing the packing of complex **1** in the unit cell.

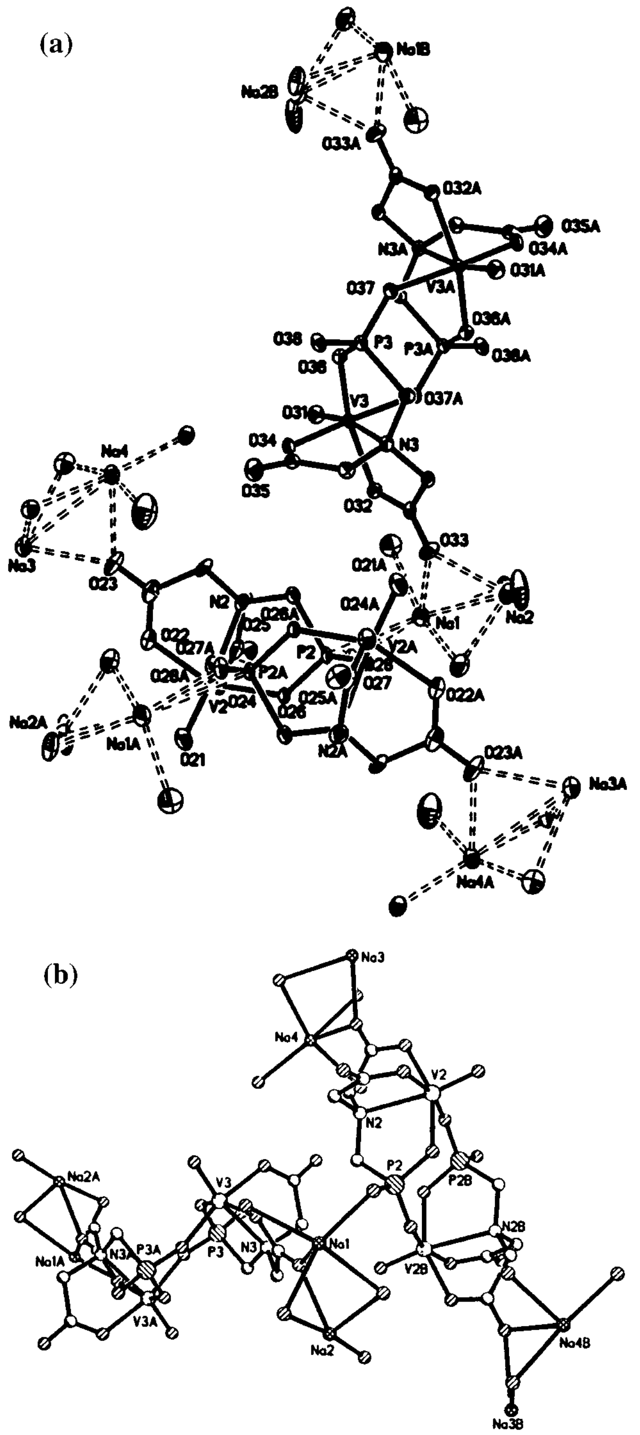

Figure 3. (a) Molecular structure of complex **2**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity. (b) Another view of an extended fraction of the crystal showing the packing of complex **2** in the unit cell.

as solids in air at ambient temperature and in solution at acidic pH. Both complexes **1** and **2** are soluble in water but are insoluble in a wide variety of organic solvents, including polar solvents such as DMF and DMSO. As a result, aqueous solvent mixtures were employed for solution studies of these complexes.

Crystallographic Studies of Compounds 1 and 2. The structures and numbering schemes for **1** and **2** are shown in Figures 2 and 3, respectively. The atomic coordinates and selected bond distances and angles are summarized in Tables 2−5. Other structural information has been supplied in the Supporting Information.

Description of the Structure of 1. Complex **1** contains an anionic V(IV)−pida fragment as a centrosymmetric dimer consisting of two vanadium atoms, two pida^{4-} ligands, and two oxo groups. The resulting dinuclear complex **1** is shown in Figure 2a, and the extended network that is linked by hydrated sodium ions is shown in Figure 2b. In addition to the oxo group, each vanadium atom is chelated by two carboxylate oxygen atoms (O12, O14), one amine nitrogen atom (N1), and one phosphonate oxygen atom (O16) from one pida^{4-} ligand. Each vanadium atom achieves a coordination number of 6 by also bridging to the phosphonate oxygen atom (O17A) from the pida^{4-} ligand in the other half of the dimer. Thus, the deprotonated phosphonate groups in the two pida^{4-} ligands form two bridges that give rise to the dimeric skeleton with the $V_2O_4P_2$ eight-membered ring, which possesses a crystallographic inversion center and the two phosphonate groups are chelated cis to the oxo groups. The X-ray structure of **1** reveals that the phosphonate group in the pida^{4-} ligand is coordinated to two vanadium atoms, thus supporting one more interaction (binucleating quadridentate) compared to the common quadridentate coordination mode reported for related ligands such as H_3nta, H_3hida, and H_3tea.[3,4,9] Despite the number of dimeric oxovanadium complexes reported with μ-O bridges and mixed N, O donor ligands,[2,3,7−9,30,32−35,45,58] the bridging phosphonate group found in **1** is a structural feature that represents a new type of coordination geometry. Furthermore, solution structures with a series of simple phosphonate ligands were interpreted as evidence for monochelation of phosphonates.[27]

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
V1	5754(1)	2781(1)	403(1)	17(1)
N1	6867(4)	3978(4)	1914(4)	20(1)
P1	4418(1)	4945(1)	1298(1)	16(1)
C11	8235(5)	4057(6)	1817(5)	32(1)
C12	8626(6)	2872(6)	1408(5)	33(1)
C13	6829(5)	3339(5)	2930(4)	25(1)
C14	5834(5)	2326(5)	2711(4)	23(1)
C15	6207(5)	5166(4)	1812(4)	21(1)
O11	5067(4)	1736(3)	−435(3)	32(1)
O12	7665(4)	2226(4)	823(4)	33(1)
O13	9788(4)	2587(5)	1600(5)	53(2)
O14	5434(4)	1908(3)	1739(3)	24(1)
O15	5481(4)	1900(4)	3506(3)	36(1)
O16	4301(3)	3853(3)	517(3)	18(1)
O17	6220(3)	3955(3)	−623(3)	20(1)
O18	3832(4)	4697(3)	2227(3)	24(1)
Na1	1772(3)	3803(2)	2109(3)	48(1)
Na2	3632(2)	5973(2)	3613(2)	34(1)
W1	1455(6)	5038(4)	3544(5)	58(2)
W2	2042(4)	2614(5)	573(4)	41(1)
W3	2693(5)	2131(4)	3104(4)	39(1)
W4	4317(8)	4132(8)	4758(7)	93(2)
W5	451(14)	4956(13)	458(12)	206(7)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Solution studies of the V(IV)−pida complex were consistent with the structural proposal of a mononuclear complex with tetradentate coordination mode (O_3N) of $pida^{4-}$ (vanadium chelates to an oxo, two carboxylates, one amine, one phosphonate, and one water molecule as shown in Figure 1).[17,18] Dimerization of this mononuclear V(IV)−pida complex by recrystallization thus involves the substitution of a water molecule coordinated to the vanadium atom by an oxygen atom of a coordinated phosphonate group. In the crystal, the $[V_2O_2(pida)_2]^{4-}$ dimers are loosely linked together by hydrated sodium ions through the third phosphonate oxygen atom, (Na1−O18, 2.360(4) Å; Na2−O18, 2.321(4) Å). Furthermore, a weak interaction is observed between the oxygen atom of one carboxylate group (O13) and additional sodium ions (Na1B−O13, 2.428(6) Å; Na2C−O13, 2.524(5) Å); together these Na−O interactions generate infinite chains. Sodium ions are also coordinated and bridged to additional water molecules with Na−O distances ranging 2.313(5)−2.580(5) Å. Although O13 and O18 are bound to sodium ions, such interactions have little effect on bond distances of O13−C12 (1.224(7) Å) and O18−P1 (1.505(3) Å), as compared with O15−C14 (1.264(6) Å) in **1** and P═O (1.497(4) Å) in other phosphonate complexes.[25]

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**[a]

	x	*y*	*z*	*U*(eq)[a]
V2	490(1)	12275(1)	140(1)	13(1)
V3	4377(1)	7213(1)	−195(1)	13(1)
P2	405(1)	10037(1)	−927(1)	13(1)
P3	4706(1)	5103(1)	959(1)	13(1)
N2	1870(2)	11145(2)	0(1)	14(1)
N3	3104(2)	6002(2)	67(1)	13(1)
C21	2477(2)	11146(3)	744(2)	19(1)
C22	2384(2)	12342(3)	1123(2)	19(1)
C23	2363(2)	11780(3)	−529(2)	18(1)
C24	1747(2)	12791(3)	−932(2)	16(1)
C25	1553(2)	9911(3)	−264(2)	15(1)
C31	2437(2)	5869(3)	−647(2)	17(1)
C32	2412(2)	7024(3)	−1081(2)	18(1)
C33	2626(2)	6651(3)	596(2)	18(1)
C34	3246(2)	7678(3)	965(2)	19(1)
C35	3522(2)	4831(3)	367(2)	16(1)
O21	−331(2)	13280(2)	166(1)	22(1)
O22	1590(2)	12945(2)	896(1)	19(1)
O23	3046(2)	12673(2)	1626(1)	26(1)
O24	1016(1)	13166(2)	−673(1)	18(1)
O25	2005(2)	13234(2)	−1484(1)	22(1)
O26	−103(1)	11128(2)	−632(1)	15(1)
O27	−223(1)	8899(2)	−893(1)	16(1)
O28	607(2)	10257(2)	−1679(1)	17(1)
O31	5122(2)	8266(2)	−319(1)	22(1)
O32	3164(1)	7727(2)	−918(1)	18(1)
O33	1704(2)	7232(2)	−1575(1)	27(1)
O34	3898(2)	8103(2)	641(1)	19(1)
O35	3069(2)	8093(2)	1548(1)	28(1)
O36	5116(1)	6189(2)	589(1)	15(1)
O37	5373(1)	3996(2)	932(1)	16(1)
O38	4566(2)	5381(2)	1721(1)	17(1)
Na1	1158(1)	8858(1)	−2439(1)	21(1)
Na2	384(1)	6160(1)	−2313(1)	25(1)
Na3	3921(1)	14123(1)	2506(1)	20(1)
Na4	4244(1)	11257(1)	2345(1)	22(1)
W1	1235(2)	7125(2)	−3161(1)	28(1)
W2	2942(2)	9129(2)	−2280(1)	29(1)
W3	−363(2)	4979(2)	−1497(1)	41(1)
W4	2796(2)	10157(3)	2516(2)	46(1)
W5	4871(2)	10035(2)	1481(1)	22(1)
W6	3783(2)	12546(2)	3273(1)	22(1)
W7	−435(2)	7949(2)	−2319(1)	27(1)
W8	5359(2)	12831(2)	2270(1)	25(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1**

V1−O11	1.608(4)	C14−O15	1.264(6)
V1−O12	2.033(4)	Na1−O13D	2.428(6)
V1−O14	2.065(3)	Na1−O18	2.360(4)
V1−O16	1.985(3)	Na1−W1	2.379(6)
V1−O17	2.006(3)	Na1−W2	2.442(6)
V1−N1	2.362(4)	Na1−W3	2.313(5)
P1−O16	1.556(3)	Na1−W5	2.519(10)
P1−O17A	1.541(3)	Na2−O18	2.321(4)
P1−O18	1.505(3)	Na2−W1	2.506(6)
C12−O13	1.224(7)	Na2−W4	2.506(8)
O11−V1−O12	100.4(2)	O12−V1−O16	153.6(2)
O11−V1−O14	93.0(2)	O12−V1−O17	87.8(2)
O11−V1−O16	105.9(2)	O12−V1−N1	74.4(2)
O11−V1−O17	101.2(2)	O14−V1−O16	85.22(14)
O11−V1−N1	167.6(2)	O14−V1−O17	165.8(2)
O12−V1−O14	91.2(2)		

The coordination geometry about the vanadium atom is distorted octahedral, with O−V−O angles varying from 74.4(2)° to 105.9(2)°. The short V−O(bridged phosphonate oxygen) distances are consistent with a deprotonated phosphonate group. Examining the V−O(phosphonate) bond lengths, it is clear that the internal V−O(phosphonate) bonds (V1−O16, 1.985(3) Å) are shorter than the V−O(phosphonate) bonds, where the oxygen atom bridges to a neighboring vanadium atom (V1A−O17, 2.006(3) Å). The latter bond is also longer than the corresponding bonds in other vanadium phosphonate complexes, such as $[(VO)_2Cl_4(t\text{-}C_4H_9PO_3H)_2]^{2-}$ (1.974(4) Å, 1.980(5) Å).[25] The amine nitrogen atom is coordinated trans to the V═O bond, and as expected from the oxo ligand's trans influence, a long V1−N1 bond length (2.362(4) Å) is obtained. The two V−O(carboxylate) bonds in **1** that are cis to each other (V−O12, 2.033(4) Å and V−O14, 2.065(3) Å) are longer than the corresponding bonds in other dimeric carboxylate complexes (1.977(5)−2.019(4) Å),[2,9,34,58] and the related monomeric vanadium(IV)−Hhida complex with trans carboxylates (1.969(3)−1.994(5) Å).[9] They are, however, similar to the bond length

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Table 5. Selected Bond Distances (Å) and Angles (deg) for **2**

V2−O21	1.615(2)	P3−O37	1.557(2)
V2−O22	2.024(2)	P3−O38	1.504(2)
V2−O24	2.063(2)	C22−O23	1.243(4)
V2−O26	1.990(2)	C24−O25	1.255(3)
V2−O27A	2.008(2)	C32−O33	1.240(4)
V2−N2	2.362(2)	C34−O35	1.250(4)
V3−O31	1.617(2)	Na1−O28	2.339(2)
V3−O32	2.041(2)	Na1−O33	2.455(3)
V3−O34	2.065(2)	Na1−W1	2.374(3)
V3−O36	1.987(2)	Na1−W2	2.474(3)
V3−O37	2.006(2)	Na2−O33	2.403(2)
V3−N3	2.361(2)	Na2−W1	2.408(3)
P2−O26	1.564(2)	Na3−O23	2.462(2)
P2−O27	1.554(2)	Na3−W6	2.303(2)
P2−O28	1.502(2)	Na4−O23	2.504(3)
P3−O36	1.559(2)	Na4−W6	2.431(3)
O21−V2−O22	99.93(10)	O31−V3−O32	100.18(10)
O21−V2−O24	92.25(10)	O31−V3−O34	93.84(10)
O21−V2−O26	105.60(10)	O31−V3−O36	105.45(10)
O21−V2−O27A	102.01(10)	O31−V3−O37	101.08(10)
O21−V2−N2	167.54(10)	O31−V3−N3	168.17(10)
O22−V2−O24	90.16(8)	O32−V3−O34	90.90(8)
O22−V2−O26	154.35(9)	O32−V3−O36	154.29(8)
O22−V2−O27A	88.46(8)	O32−V3−O37	88.12(8)
O22−V2−N2	75.27(8)	O32−V3−N3	74.54(8)
O24−V2−O26	86.38(8)	O34−V3−O36	85.43(8)
O24−V2−O27A	165.70(8)	O34−V3−O37B	164.99(9)
O24−V2−N2	76.43(8)	O34−V3−N3	75.88(8)
O26−V2−O27A	88.72(8)	O36−V3−O37	88.97(8)
O26−V2−N2	79.21(8)	O36−V3−N3	79.89(8)
O27−V2−N2	89.46(8)	O37−V3−N3	89.44(8)

Table 6. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[V_2O_2(pida)_2]^{4-}$ Units of **1** and **2**

	1	**2**	
V−O(oxo)	1.608(4)	1.615(2)	1.617(2)
V−O(carboxylate)	2.033(4)	2.024(2)	2.041(2)
V−O(carboxylate)	2.065(3)	2.063(2)	2.065(2)
P−O	1.541(3)	1.554(2)	1.557(2)
O(oxo)−V−O(carboxylate)	93.0(2)	92.25(10)	93.84(10)
O(carboxylate)−V−O(phosphonate)	85.22(4)	86.38(8)	85.43(8)
O(carboxylate)−V−O(carboxylate)	91.2(2)	90.16(8)	90.90(8)

observed for $[V_2O_3(nta)_2]^-$ (cis 2.041(5) Å, trans 1.970(6) and 1.982(5) Å).[3]

Description of the Structure of 2. The structure of **2** contains two distinct $[V_2O_2(pida)_2]^{4-}$ units, each of which is required to have crystallographic inversion symmetry (see Figure 3a). An extended network involving the hydrated sodium cations exists (see Figure 3b). The structures of these $[V_2O_2(pida)_2]^{4-}$ complexes are similar to that of **1** (see Table 6). However, subtle differences exist between the two independent $[V_2O_2(pida)_2]^{4-}$ complexes in **2**. Structural similarities include the fact that the vanadium atoms in the VO_6 units in **2** are in distorted octahedral geometry, and the positions cis to the V═O oxo groups are again occupied by phosphonate oxygen atoms instead of the H_2O molecules proposed for the mononuclear complex.[17,18] The trans influence of the V═O oxo group is again reflected in the long V−N bond lengths (V2−N2, 2.362(2) Å; V3−N3, 2.361(2) Å), which are similar to V1−N1 (2.362(4) Å) in **1**. These bonds, however, are longer than those found in other dinuclear complexes with trans amine nitrogen atoms, such as $[V_2O_3(Hhida)_2]^-$ (2.277(2) Å),[9] $[V_2O_3(S\text{-peida})]^-$ (2.278(4), 2.293(4) Å),[7,58] $[V_2O_3(nta)_2]^-$ (2.297(6) Å),[3] $[V_2O_3(quinolinol)_4]$ (2.310(6) Å).[35,45] A careful comparison of the structures of **1** and **2** reveals that one V−O(carboxylate) distance (V2−O22 =2.024(2) Å) in **2** is shorter than the corresponding distances in the other complexes in **2** and **1** (V3−O32 = 2.041(2) Å in **2**, V1−O12 = 2.033(4) Å in **1**), a difference which may be related to changes in the cation−anion network. The two vanadium atoms in **1** and **2** are bridged by the phosphonate groups with V···V distances averaging 5.230(3) Å in the two complexes.

The hydrated sodium cations are organized in a complex packing arrangement as shown in Figure 3b. In **2**, the cation−anion interactions mainly involve the carboxylate oxygen atoms that are not coordinated to the vanadium atoms. Despite the differences in the cation−anion networks in **1** and **2**, the structural changes in the basic V(IV)−pida anionic unit are minimal. Note that, in **2**, the phosphonate group is not involved in interactions with the sodium network in contrast to the case in **1**. The differences in the involvement of the hydrated cations between compounds **1** and **2** presumably reflects the differences in pH and crystallization conditions.

The V(IV)−pida complexes in **1** and **2** represent a new structural framework and coordination geometry involving mixed N, O donors in vanadium complexes. In these complexes, the two vanadium centers are not linked by oxo-bridged, μ-O or μ-OH groups, as previous observed in other V−N,O complexes[2,3,9,30,32−34,58] but by the bridging phosphonate oxygen from the $pida^{4-}$ ligand in a quadridentate binucleating coordination mode.

IR Spectroscopy. The IR spectroscopic data for complexes **1** and **2** were examined in KBr pellets. Complexes **1** and **2** showed strong V═O stretches at 960 cm^{-1} for **1**, as well as 960 and 962 cm^{-1} for **2**, respectively. The presence of one single band for **1** is consistent with a solid-state structure with symmetry (the two V═O groups are identical), and the two bands observed for **2** are consistent with two types of V═O groups in the compound. Complex **3** contained V(V) and gave an absorption band at 948 cm^{-1} very different from the bands observed for **1** and **2**. The bands at 1636 and 1595−1587 cm^{-1} in **1** and **2** are attributed to COO stretches and show metal coordination because the signal for the free ligand (1740 cm^{-1}) is shifted. The intense broad bands around 3440 cm^{-1} for the two compounds are attributed to −OH stretches of water groups.

Magnetic Moment of Complexes 1 and 2 in D_2O. The magnetic moment of dissolved **1** and **2** (1.75 and 1.68 μ_B) in D_2O were measured by the Evans method at room temperature using coaxial NMR tubes.[51−53] The values are similar to those found for other mononuclear V(IV) complexes (1.7−1.9 μ_B) and are consistent with complexes **1** and **2** containing d^1 metal ions.[34,39,40]

EPR Spectroscopy of Complexes 1 and 2. Despite the many solution studies of the mononuclear V(IV)−pida complex ($[VO(H_2O)(pida)]^{2+}$, Figure 1), no characterization by EPR spectroscopy has been reported.[17,18] Formation of mononuclear V(IV)−pida from dinuclear complexes **1** and **2** is chemically and structurally reasonable as seen by inspection of the molecular framework for both complexes: A simple substitution of the bridging phosphonate oxygen (O17 in **1**, O27 and O37 in **2**) from the neighboring $pida^{4-}$ ligand with a H_2O molecule will generate mononuclear V(IV)−pida. Mononuclear V(IV)−pida would be expected to show a simple eight-line EPR spectrum, whereas a dinuclear complex with paired electrons would be EPR silent.[13,42,59] Recording the ambient temperature EPR spectra of solutions of both **1** and **2** generated a symmetric eight-line hyperfine splitting pattern with a g_o value of 1.974 and an A_o of 110 G for **1** (Figure 4) and a g_o value of 1.973 and

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(59) Toftlund, H.; Larsen, S.; Murray, K. S. *Inorg. Chem.* **1991**, *30*, 3964−3967.

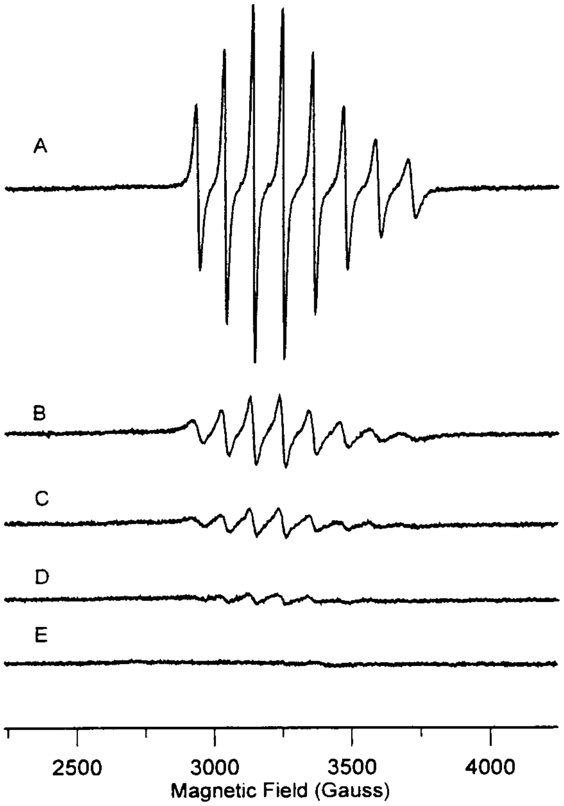

Figure 4. EPR spectrum of 1.5 mM complex **1** in (A) aqueous solution, (B) 50:50% DMF−water, (C) 60:40% DMF−water, (D) 62:38% DMF−water, and (E) 70:30% DMF−water.

an A_o of 109 G for **2**. These parameters are in the expected range of $g = 1.95-2.00$ for VO^{2+} groups surrounded by O- and N-donor ligands.[3,5,9,13,60] The differences in parameters between **1** and **2** are within experimental error as would be expected if compounds **1** and **2** generated the same mononuclear complex in aqueous solution. These spectra confirm that both complexes are typical mononuclear V(IV) species in aqueous solution and that a reduction of the V(V) starting material took place in generation of complexes **1** and **2**.

Additional structural characterization of the solution complex was desired, and low-temperature EPR spectra were recorded. The spectrum obtained by low-temperature (−147 °C) EPR spectroscopy of 1.5 mM **1** in a frozen aqueous solution is shown in Figure 5a. Complex **1** gave a broad symmetric line centered around a g_o of 1.970 with little structural information as characteristic of complex association and poor glass formation.[2] Recording the spectra at lower concentrations or in the presence of an additive should give spectra with more structural information.[61] However, most commonly used additives form complexes with vanadium. A spectrum of 1.5 mM of **1** was obtained in the presence of 127 mM NaCl[61b] that did provide more structural information (Figure 5b), and the parameters of $g_o = 1.969$ and $A_o = 116$ G could be obtained. These parameters are consistent with those expected for a complex with a quadridentate coordination mode of pida^{4-} and a water molecule coordinated to the vanadium atom in the equatorial plane, as in complex V(IV)−pida. However, until further information is available on the effectiveness of aqueous NaCl in forming gels, we caution the uncritical interpretation of parameters obtained under these conditions.

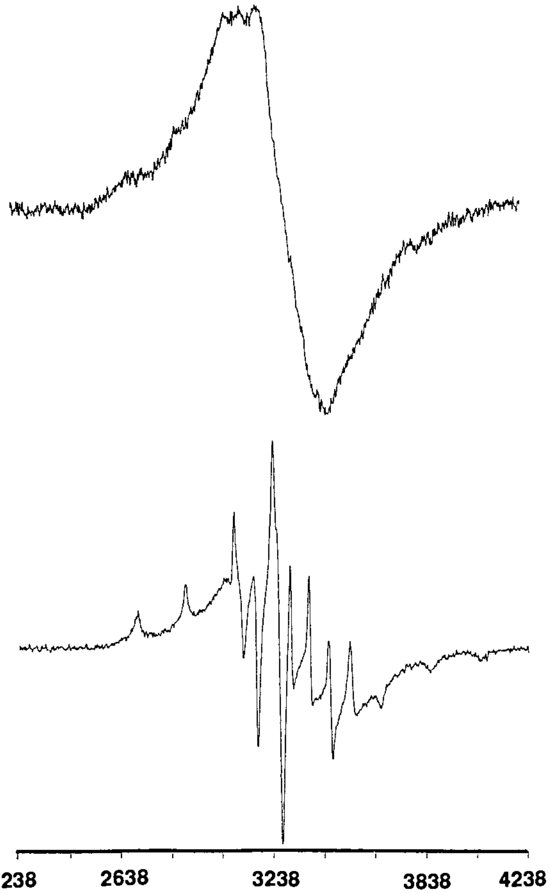

Figure 5. EPR spectra of 1.5 mM complex **1** (A) in frozen aqueous solution (−147 °C) and (B) in the presence of 127 mM NaCl (−147 °C).

Given the solid-state characterization of complex **1** and **2,** we were interested in examining the existence of dinuclear complexes in solution. Since the major species in aqueous solution was mononuclear, we considered modifying the solvent polarity by the addition of organic solvents. In Figure 4 the ambient EPR spectra of a solution of 1.5 mM **1** in water and with various ratios of mixed DMF−water solvent systems are shown. It was observed that the intensity of the EPR signal decreased as a function of time (data not shown; however, see visible studies below), and the data presented in this paper will describe the behavior of freshly made solutions. As indicated in Figure 4A−E, the EPR signal intensity gradually decreases from the solution containing 0% DMF to the 70% DMF solution where no signal was observed. These spectra show that solutions containing less than 70% DMF will contain some of the mononuclear complex (V(IV)−pida) whereas solutions containing 70% or more DMF no longer contain V(IV)−pida (Figure 4E). These changes in solvent systems are accompanied by distinct color changes. The solution in water and 50:50% DMF−water is clear blue. As the DMF content increases to 70% and more, the color of solutions of **1** changes to brown; at about 60:40% DMF−water, the color also has a brown component. Since the simple symmetric eight-line hyperfine pattern characteristic of a mononuclear V(IV) complex disappears, exchange of the water molecule coordinated to the V(IV) by a DMF molecule is not likely. The absence of EPR signals suggests either the complex is oxidizing and/or that some dimeric

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(60) Schulz, D.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chim. Acta* **1995**, *240*, 217−229.

(61) (a) Hanson, G. R.; Sun, Y.; Orvig, C. *Inorg. Chem.* **1996**, *35*, 6507−6512. (b) Crans, D. C. In *ACS Symposium Proceedings*; Tracey, A. S., Crans, D. C., Eds.; American Chemical Society: Washington, DC, 1998; Vol. 711, pp 82−103.

vanadium(IV) compound is present in solution. Further consideration of the properties of the species in these solutions is desirable. We conclude that formation of a dinuclear complex with antiferromagnetic pairing of the free electrons on the V(IV) atoms seems the most consistent interpretation of the EPR-silent spectra observed. Strong antiferromagnetic coupling has been observed among dinuclear vandium(IV,IV) complexes; however, in all these cases, the V···V distance is in the range of 3.6−3.7 Å.[59] Assuming that the structure for **1** observed in the solid state would exist in solution, the >5 Å distance between the V atoms would require that electrons were paired through-bond, in place of through-space, to form a diamagnetic complex. Although no solid-state structural information has been reported for a phosphoric acid cyclic trimer,[27,62] the structure of such material would also require long distances between vanadium atoms. However, the EPR spectrum for this trinuclear species in solution shows electron delocalization, giving precedence for this phenomena in these types of complexes with presumed long metal ion distances.[63] Furthermore, electron delocalization has been reported for a dinuclear vanadium(IV,IV) complex of hydridotris(pyrazolyl)borate, which was characterized in the solid state as having a V···V distance of 4.931(1) Å. Under some conditions this compound shows the typical 15-line spectrum expected for exchange-coupled divanadyl complex.[41] Assuming the complex in solution maintains a large distance between vanadyl cations, this compound provides further precedent for communication between two vanadium ions separated by approximate 5 Å.

A brown solution of 1.5 mM **1** in 70:30% DMF−water that is EPR silent does not yield any ^{51}V NMR signals suggesting the species in solution is not simply oxidized to vanadium(V). However, the conversion of dissolved dinuclear complex **1** to mononuclear V(IV)−pida was not successful under a variety of conditions. The problem with these types of experiments is 2-fold. First, the presence of air (oxygen) will oxidize the blue complex to a V(V)−pida complex that is also brown. Second, the conversions between the mononuclear and dinuclear complexes are slow. Accordingly, the solution must equilibrate, and during this time, the complexes are air oxidized. Thus, successful conversion of dissolved dinuclear complex to mononuclear complex is only observed when oxygen is excluded and the solution is equilibrated; after about 5−6 h the color of the solution had begun to change, and after 1 day it had turned blue. Alternatively, the brown solution of **1** could be evaporated to dryness (using a vacuum line) and immediately redissolved in water, generating a blue solution of mononuclear vanadium(V)−pida complex.

Further support for the existence of the dinuclear species was obtained by dissolution of crystalline **1** in dioxane−water and THF−water. The color changes of the solution were slower in these mixtures. For example, dissolution of 1.5 mM **1** in 70:30% dioxane−water or in 70:30% THF−water resulted in green-brown solutions that took about 5 h to convert to brown. Dissolution of compound **1** in 50:50% dioxane−water (blue solution) gave an EPR spectrum with the characteristic symmetric eight-line hyperfine splitting, whereas the 70:30% dioxane−water mixture (brown solution) produced no EPR signal. Thus, in general, these solvents systems show similar effects in color changes and EPR spectra as DMF, even though the rates of color changes and disappearance of EPR signals were different. On the basis of the observations by EPR spectroscopy, we were interested in substantiating the formation of a dinuclear complex, and given the color changes of the solutions, we felt that visible spectroscopy would be an excellent method for such studies.

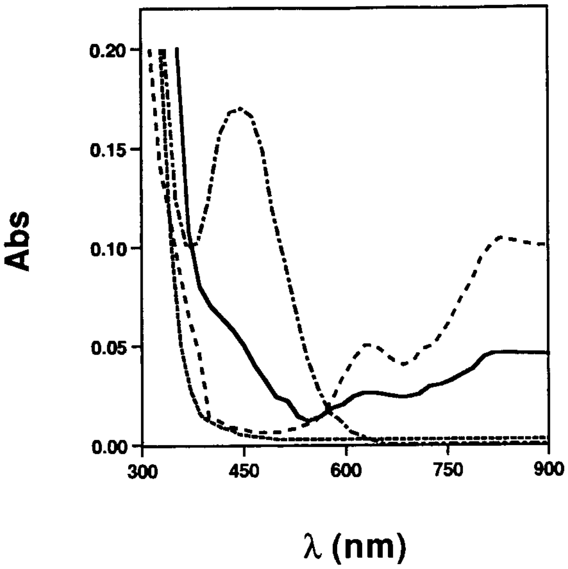

Figure 6. UV−vis spectra of solutions of 1.5 mM complex **1** in 70:30% DMF−water (- • -), 50:50% DMF−water (- - -), and 60:40% DMF−water (—). Also shown is 2 mM VO_2Pida^{3-} in H_2O (···).

Visible Spectroscopy of Complexes 1 and 2. In water solution, the visible spectrum of dissolved **1** (V(IV)−pida) contained two prominent absorption bands at 628 nm (16 M^{-1} cm^{-1}) and 865 nm (33 M^{-1} cm^{-1}) (Figure 6). These types of absorbances are also observed in other mononuclear V(IV) complexes, such as $[VO(pmida)(H_2O)]$,[2,6] $[VO(ada)(H_2O)]$ (H_2-ada = *N*-(carbamoylmethyl)iminodiacetic acid),[12] $[VO(Hheida)(H_2O)]$ (H_3heida = *N*-(2-hydroxylethyl)iminodiacetic acid),[12] [VOL(NCS)] (L = 1,4,7-triazacyclononane-*N*-acetate),[60] and $[VO(nta)(H_2O)]^-$,[2] and arise from d−d transitions. Thus both the absorption spectrum and the EPR spectrum are consistent with the formation of a mononuclear $[VO(pida)(H_2O)]^{2-}$ V(IV)−pida in water.

The optical spectrum of **1** in 70:30% DMF−water showed only one distinctive absorption band with a maximum near 431 nm (210 M^{-1} cm^{-1}) (Figure 6). This absorption band can be assigned to either d−d transitions or ligand-to-metal charge transfer (a transition from an occupied nonbonding orbital to a vacant antibonding orbital arising from $d\pi(V) - p\pi(O)$ interactions). A similar UV−vis spectrum (λ_{max} = 435−420 nm) eventually was observed when **1** was dissolved in 70:30% THF−water or 70:30% dioxane-water after 5 h at ambient temperature. Initially, these green-brown solutions only showed a shoulder around 430 nm; however as time passed, this absorption maximum increased in intensity. To rule out the possibility that the absorption at 430 nm was due to a V(V) complex, the absorption spectrum of a solution containing the V(V)−pida complex (verified by the −527 ppm signal in the ^{51}V NMR spectrum) was recorded and displayed no absorbance around 400 nm (data not shown). However, absorbance bands around 400 nm were reported for dinuclear oxovanadium complexes, $[V_2O_3(tpa)_2]^{2+}$ (tpa = tris(2-pyridylmethyl)amine),[59] $[V_2O_3L_2]^{2+}$ and $[V_2O_3L_2]^{+}$ (HL = *N*-(2-hydroxybenzyl)-1,4,7-triazacyclononane),[60] and $[V_2O_3(quinolinol)_4]^{-}$ [35] as well as $[V_2O_3(dihydroxyazobenzene)_2]$.[32] These observations support the interpretation that this absorption maximum at 430 nm is generated by a dinuclear species.

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(63) Micera, G.; Sanna, D. In *Vanadium in the Environment. Part 1: Chemistry and Biochemistry*; Nriagu, J. O., Ed.; John Wiley & Sons: New York, 1998; Vol. 30, pp 131−166.

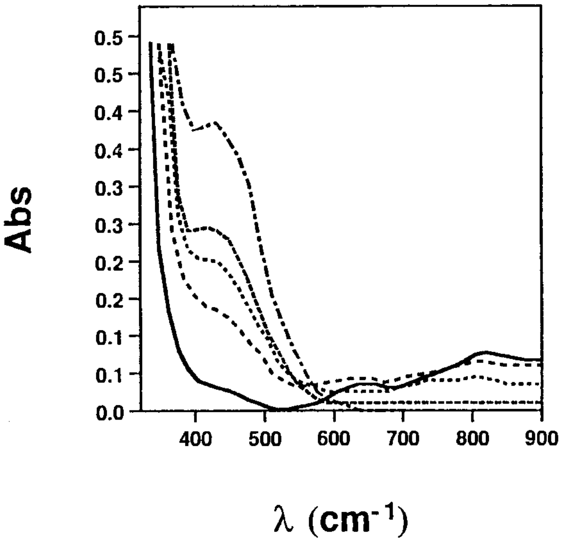


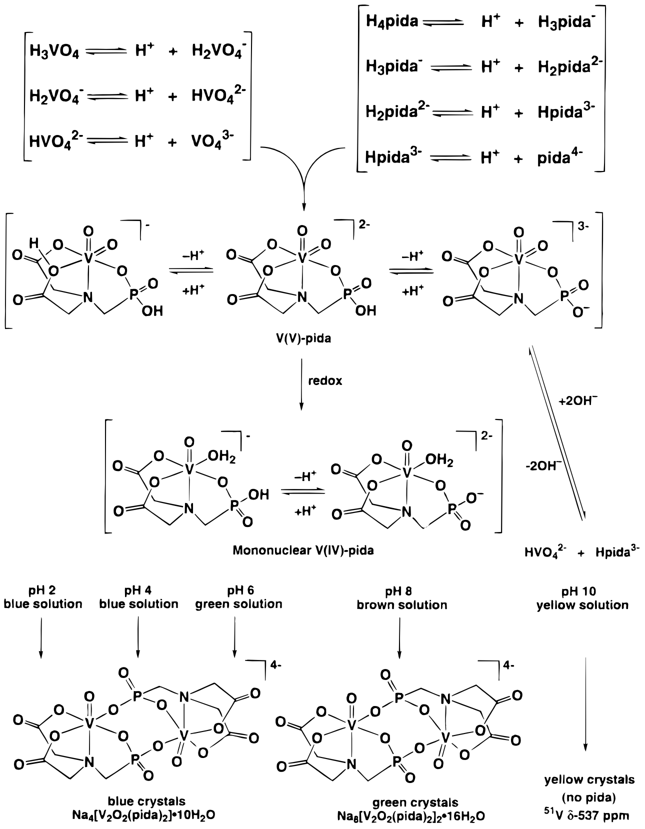
Figure 7. UV−vis spectra of a solution of 1.5 mM **1** in 50:50% dioxane−water after incubation at ambient temperature for (—) 0, 1, 2, 3, and (•—•) 7 days. No attempts were made to maintain constant pH, and the pH values of these solutions were 5.5, 4.6, 3.9, 3.7, and 3.5, respectively.

The changes in the absorption spectrum of a solution of 1.5 mM **1** in 50:50% dioxane−water at ambient temperature are illustrated as a function of time in Figure 7. Upon dissolution of **1**, the absorbances at 630 and 860 nm were highest in intensity, indicating the presence of the mononuclear V(IV)−pida. As time passed, V(IV)−pida was converted to a dinuclear species, consistent with the increase in the signals near 430 nm. In addition to the dimerization reaction, presumably the monomeric, and perhaps also the dimeric V(IV) complex, oxidize when exposed to atmospheric oxygen for extended periods of time. In this series of experiments, no attempts were made to characterize the pH dependence, time dependence, or oxidation of these complexes. This topic is complex and beyond the scope of the investigation reported here. However, dissolution of crystalline **1** in three different solvent systems shown in Figure 6 clearly showed the presence of the mononuclear complex (50:50% DMF−water), the dinuclear complex (70:30% DMF−water), and both mono- and dinuclear complexes (60:40% DMF−water, Figure 4). In this series of experiments recorded immediately after dissolution, the isosbestic point clearly illustrated that some conversion among these species occurred without significant oxidation or other alterations in the system. For future reference the spectrum of a solution of the V(V)−pida system is shown,[54] to document the difference between this spectrum and that of the solutions of **1**.

Conversion between Mononuclear and Dinuclear Complexes. In Scheme 1, the work described in this paper is summarized by an illustration of some of the species we envision forming in mixtures of V(V) precursor and H_4pida ligand. Although solid-state characterization plays a key role in this work, whether the solution species were the same as the solid state species was specifically addressed for each species and for various solvent systems. Accordingly, both EPR and visible spectroscopy were used to document when the dinuclear solid-state structure was likely to remain in observable concentrations in solution.

Since the V(V) precursor and the H_4pida ligand were combined, a V(V)−pida complex is first formed. This complex presumably exists in several protonation states as illustrated in Scheme 1; the speciation in this system will be examined in detail elsewhere.[54] As demonstrated by X-ray crystallography, two closely related dinuclear V(IV) complexes can be isolated in the acidic and neutral pH range from solutions with added vanadate and H_4pida. Although a number of dinuclear species with O- and N-containing donor ligands have been reported, most of these complexes contain mixed-valence V(IV) and V(V) with a linear V−O−V unit.[2,3,7−9,10,13,30−37] The isolated V−pida complex is the fully reduced V(IV) species which contains a dinuclear core, and when the vanadium precursor was in oxidation state V, the metal reduction occurred at the expense of oxidizing H_4pida to PMG. The isolation of a dinuclear vanadium(IV) complex is interesting given the synthetic conditions that were used to generate this complex; the V(V) precursor would not have been fully reduced in the presence of most other ligand systems (i.e., generated mixed valence dimers). Presumably the stability of the V(IV)−pida complexes at low pH was responsible for the outcome of this reaction; however, even at alkaline pH and in solutions containing mainly V(V)−pida, crystals of complex **2** were isolated. The phosphonic acid group, although considered an analogue of carboxylic acids, clearly has a much more profound effect on the vanadium complexes formed. Indeed, solution studies of various vanadium(IV)−phosphonate systems show that this functionality favors formation of dinuclear V(IV) systems.[27]

Scheme 1. The Wide Range of Chemical Processes That Occur in Solutions Containing Vanadium and the Pida Ligand



The dinuclear species exist in aqueous organic solvent mixtures in concentrations sufficient for characterization. In aqueous solution, the concentration of these species was too low to be measured, perhaps, in part, because the probes available to examine this species are not very sensitive. However, since the dinuclear species was observed in aqueous organic solvents and crystals were generated from aqueous solutions diffused with ethanol, low concentration of dinuclear species are likely to exist in aqueous solutions. Furthermore, because these studies were performed in solutions covering a wide pH range, the isolation of dinuclear species is not limited to a small pH range. Such speciation has not previously been considered in catalytic and solution studies with these complexes,[17,18] although dinuclear species are proposed as intermediates in other synthetic processes.[2,3,47,48,64]

Conclusion

The 1:1 complex formed between V(IV) and pida^{4-} has been of interest in view of its redox chemistry as well as the potential applications of this chemistry. Despite the interest in this complex, no structural information was available for this type of complex in the solid state nor had structural spectroscopic characterization been carried out in the solution state. We have obtained solid-state structural information of two different types of crystals and solution characterization of aqueous−organic mixtures containing these complexes. Surprisingly, it was found that both the structurally characterized complexes were dinuclear 2:2 species. This type of complex is particularly interesting because of its connectivity and illustration of the bridge-binding of two terminal oxygen atoms. Using EPR and visible spectroscopy, it furthermore was shown that the addition of organic solvents shifted the solution speciation from a monomeric 1:1 species to a dinuclear 2:2 species. Although the concentration of the dinuclear species may be low in aqueous solution, the existence of these types of complexes lends credibility to mechanistic proposals involving species with nuclearity greater than one in various applications of vanadium compounds as redox catalysts.

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Supporting Information Available: Tables listing crystal data, experimental parameters, bond lengths, bond angles, hydrogen coordinates, and anisotropic thermal parameters and an ORTEP diagram (12 pages). Ordering information is given on any current masthead page.

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