

Solution and Solid State Properties of $[N-(2\text{-Hydroxyethyl})\text{iminodiacetato}]\text{vanadium(IV)}$, $-(\text{V})$, and $-(\text{IV/V})$ Complexes¹

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A mononuclear vanadium(IV), a mononuclear vanadium(V), and a binuclear mixed valence vanadium(IV/V) complex with the ligand *N*-(2-hydroxyethyl)iminodiacetic acid (H₃hida) have been structurally characterized. Crystal data for [VO(Hhida)(H₂O)]·CH₃OH (**1**): orthorhombic; *P*₂₁2₁2₁; *a* = 6.940(2), *b* = 9.745(3), *c* = 18.539(4) Å; *Z* = 4. Crystal data for Na[V(O)₂(Hhida)₂]·4H₂O (**2**): monoclinic; *P*₂₁/*c*; *a* = 6.333(2), *b* = 18.796(2), *c* = 11.5040(10) Å; β = 102.53(2)°; *Z* = 4. Crystal data for (NH₄)₂[V₂(O)₂(μ-O)(Hhida)₂]·H₂O (**3**): monoclinic; *C*2/*c*; *a* = 18.880(2), *b* = 7.395(2), *c* = 16.010(2) Å; β = 106.33(2)°; *Z* = 4. The mononuclear vanadium(IV) and vanadium(V) complexes are formed from the monoprotonated Hhida²⁻ ligand, and their structural and magnetic characteristics are as expected for six-coordinate vanadium complexes. An interesting structural feature in these complexes is the fact that the two carboxylate moieties are coordinated trans to one another, whereas the carboxylate moieties are coordinated in a cis fashion in previously characterized complexes. The aqueous solution properties of the vanadium(IV) and -(V) complexes are consistent with their structures. The vanadium(V) complex was previously characterized; in the current study structural characterization in the solid state is provided. X-ray crystallography and magnetic methods show that the mixed valence complex contains two indistinguishable vanadium atoms; the thermal ellipsoid of the bridging oxygen atom suggests a type III complex in the solid state. Magnetic methods show that the mixed valence complex contains a free electron. Characterization of aqueous solutions of the mixed valence complex by UV/vis and EPR spectroscopies suggests that the complex may be described as a type II complex. The Hhida²⁻ complexes have some similarities, but also some significant differences, with complexes of related ligands, such as nitrilotriacetate (nta), *N*-(2-pyridylmethyl)iminodiacetate (pmida), and *N*-(*S*)-[1-(2-pyridyl)ethyl]iminodiacetate (*s*-peida). Perhaps most importantly, the mixed valence Hhida²⁻ complex is significantly less stable than the corresponding pmida and *s*-peida complexes of similar overall charge but very similar in stability to the nta and V₂O₃³⁺ complexes with higher charges. Thus, there is the potential for designing stable mixed valence dimers.

Introduction

The importance of understanding the coordination chemistry of vanadium in aqueous solution has increased since vanadate and vanadyl cations were tested as oral insulin substitutes in humans in 1994.^{2,3} Despite the current interest in these compounds, very little is known about the molecular mechanism by which orally administered vanadate, vanadyl cation, and other vanadium complexes exhibit the insulin-mimetic action.^{4–7} This lack of information is in part due to the complexity of signal

transduction in the insulin cascade, as well as the multitude of chemical reactions vanadium can undergo under physiological conditions.^{2,3} Vanadium can readily take on several coordination geometries. Furthermore, the lability and stability of the vanadium complexes and the nuclearity of its compounds affect their biological responses.^{8,9} It is generally assumed that vanadium(V) compounds are reduced in the reducing cellular environment;¹⁰ however, the possibility that cellular reduction can lead to a group of active mixed valence complexes has not previously been explored. In this paper we describe solid state and solution studies on a mononuclear vanadium(IV) complex and a dinuclear mixed valence vanadium(IV/V) complex with *N*-(2-hydroxyethyl)iminodiacetic acid (H₃hida) and compare the properties of these vanadium complexes with those known compounds containing O/N donor ligands.

A series of dinuclear mixed valence vanadium(IV/V) complexes have previously been described with ligands such as

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- (1) Abbreviations: DPPH, 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl; EPR, electron paramagnetic resonance; H₃hida, *N*-(2-hydroxyethyl)iminodiacetic acid; Hhida²⁻, *N*-(2-hydroxyethyl)iminodiacetic acid, monoanion; Hhida³⁻, *N*-(2-hydroxyethyl)iminodiacetate, dianion; Hhida³⁻, *N*-(2-hydroxyethyl)iminodiacetate, trianion; NMR, nuclear magnetic resonance; nta, nitrilotriacetate; pmida, *N*-(2-pyridylmethyl)aminodiacetate; *s*-peida, (*S*)-[1-(2-pyridyl)ethyl]iminodiacetate.
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nitrilotriacetate (nta),¹¹ *N*-(2-pyridylmethyl)iminodiacetate (pmida),¹² *N*-(*S*)-[1-(2-pyridyl)ethyl]iminodiacetate (s-peida),¹³ salicylideneserinate,¹⁴ azobenzene-2,2'-diolate,¹⁵ and 8-quinolinate.¹⁶ The solid state structures of several of these complexes have been characterized as type II^{12,14,15} and type III complexes¹¹ as well as complexes that do not fit either category.¹⁴ In this paper we use the definition for type II and III complexes described by Robin and Day.¹⁷ The complex is type III when the two metal ions are in exact equivalent sites and the free electron is shared equally between the two metal ions. In type II complexes the two metal ions are distinguishable; however, some delocalization of the free electron does take place. Both of these complexes are in contrast to type I complexes, which have the metals in different sites and/or coordination geometry and the free electron is not delocalized. It has been suggested that when the bridging oxide between the two vanadium units is at a basal site, delocalization is anticipated because of orbital overlap, whereas a bridging oxide at an apical site gives distinguished vanadium(IV) and (V) centers.^{18,19} A recent report of a thermally controlled delocalization phenomenon would perhaps indicate that geometry is not alone in determining when the free electron may delocalize in these systems.¹⁵

The mixed valence complexes from ligands structurally very similar to H₃hida that have been characterized in the solid state include the nta complex, which has two indistinguishable vanadium atoms,¹¹ and the complexes from pmida¹² and s-peida,¹³ which have two different vanadium atoms. The solution properties of these complexes have lead some workers to characterize the same complexes as both types II and III.¹³ The low stability of vanadium(IV,V) complexes from nta, pmida, and s-peida in aqueous solution decreases the likelihood that these types of complexes will play a role in biological systems, and although such compounds may exhibit biological activity, their activity is likely to remain unexplored until mixed valence complexes are identified that are stable in aqueous solution.

In this paper we describe the syntheses and solid state and aqueous solution properties of the vanadium complexes that form with the ligand H₃hida. The X-ray crystallography shows that the mixed valence binuclear complex with the Hhida ligand contains two indistinguishable vanadium atoms in a type III complex. The magnetic studies confirm that the mixed valence dimer contains a free electron with indistinguishable vanadium atoms. Multinuclear NMR spectroscopy is consistent with some electron delocalization over the two vanadium atoms. However, UV/vis, and EPR spectroscopic aqueous solution properties are consistent with a type II complex. The subtle effects of ligand on complex stability and structure in the solid state and aqueous solution, as well as a possible role of these types of mixed valence complexes in biological systems, are discussed.

Experimental Section

Materials. Reagent grade chemicals were obtained from Sigma or Aldrich and used without further purification. Tetrabutylammonium perchlorate was prepared as described previously²⁰ and recrystallized four times before use in order to obtain the desired purity. Distilled, deionized water was used for the synthesis of the complexes. Dimethylformamide (DMF) was dried over CaH₂ and distilled under reduced pressure.

Preparation of [V(O)(OH₂)(Hhida)]·CH₃OH, 1. A solid mixture of vanadyl acetylacetonate, VO(acac)₂, (0.50 g, 1.9 mmol) and H₃hida (*N*-(2-hydroxyethyl)iminodiacetic acid) (0.72 g, 4.1 mmol) was added to a 12 mL mixture of water and methanol (1:1). The reaction mixture was stirred for 50 h, and the resulting blue solution was filtered to remove undissolved solids. After acetone (15 mL) was added to the solution, needlelike blue crystals were formed in a period of 1 week at 4 °C. The solvent was decanted, and the crystals were dried in air, yielding 0.40 g (66% with respect to VO(acac)₂; 31% with respect to H₃hida). IR (Nujol, cm⁻¹): 3494 (v. br), 3176 (br), 1636 (br, s), 1588 (s), 1305 (w), 1212 (v. w), 1166 (sh), 1153 (m), 1112 (w), 1077 (w), 1046 (m), 978 (s), 930 (w), 887 (m), 847 (w), 769 (sh). Anal. Calcd: C, 28.77; H, 5.14; N, 4.79. Found: C, 29.18; H, 5.13; N, 4.63.

An alternative preparation for **1** is as follows. VO(acac)₂ (3.00 g, 11.3 mmol) and H₃hida (2.30 g, 12.9 mmol) were dissolved in 20 mL of distilled water. The solution was refluxed for 12 h. After adding acetone (20 mL) to the blue solution at room temperature, it was kept at -20 °C for 3 days. The blue precipitate was isolated by filtration, washed with acetone (2 × 20 mL), and dried under vacuum, yielding 2.0 g (65%). This material showed properties identical to those described above. Anal. Calcd: C, 25.91; H, 4.71; N, 5.04. Found: C, 25.96; H, 4.66; N, 4.96.

Preparation of Na[VO₂(Hhida)]·3H₂O, 2. Solid H₃hida (1.80 g, 10.2 mmol) was added to 25 mL of a solution of NaVO₃ (1.21 g, 9.92 mmol). The resulting mixture was stirred, and the pH was adjusted to pH 4–5 using NaOH until all of the ligand was dissolved. Ethanol (95%, 25 mL) was added to the yellow solution, and this solution was kept at -20 °C for 3 days. The yellow crystals were filtered, washed with ethanol (1 × 10 mL) and acetone (1 × 10 mL), and dried under vacuum, yielding 2.8 g (89%). Anal. Calcd: C, 21.50; H, 4.51; N, 4.18. Found: C, 21.54; H, 4.47; N, 4.13. IR (KBr, cm⁻¹): 3550 (s), 3376 (s,br), 2990 (m), 2995 (m), 1670 (s), 1637 (s), 1458 (w), 1438 (s), 1380 (s), 1344 (s), 1264 (w), 1147 (w), 1106 (w), 1071 (w), 1054 (w), 994 (w), 924 (s), 904 (s), 819 (m), 740 (w), 640 (m), 591 (w), 489 (w), 404 (m). ¹H NMR (300 MHz, D₂O, 24 °C): δ (4.25, d, 2H), (3.74, m, 4H), (3.10, t, 2H).

The vanadium(V) complex of Hhida was previously prepared in aqueous solution in the range pH 4–7.²¹ In addition to this complex, detailed ¹H, ¹³C, ⁵¹V and ¹⁷O NMR spectroscopic studies suggest two vanadium(V) complexes with Hhida form in aqueous solution, one at pH 7–10 (–499 ppm by ⁵¹V NMR) and another at pH 4–8 (–520 ppm by ⁵¹V NMR). We refer to the latter as **2** in this paper.

Preparation of NH₄[V₂(O)₂(μ-O)(Hhida)]·H₂O, 3. To a rapidly stirred suspension of the H₃hida ligand (3.54 g, 20.0 mmol) in water (10 mL) was added ammonium metavanadate, NH₄VO₃ (1.17 g, 10.0 mmol). The reaction mixture was stirred for 3 h at ambient temperature, and in this time the color of the reaction mixture changed from yellow to orange to yellowish green. After the solution was stirred for an additional 20 h, the final solution was pH 2.7. This solution was filtered to remove undissolved solids, and ethanol (20 mL) was added. Dark blue platelike crystals were obtained in a few days at 4 °C. After supernatant liquid was removed by filtration, the crystals were dried in air, yielding 1.89 g (70.4% with respect to V-atoms). A fluffy material can also be obtained by the addition of ethanol and precipitation of the product at -30 °C. This fluffy material has solid state properties similar to those observed for the crystalline complex. IR (Nujol, cm⁻¹): 3648 (m), 3495 (w), 3195 (w), 1631 (sh), 1595 (br), 1304 (w), 1209 (w), 1167 (sh), 1154 (m), 1112 (w), 1070 (m), 1048 (w), 1000(w), 953 (s), 921 (sh), 890 (w), 818 (w), 771 (w). ⁵¹V NMR (78.94 MHz, H₂O, 24 °C): δ -522.0 ppm. Anal. Calcd: C, 26.86; H, 4.48; N, 7.83. Found: C, 26.56; H, 4.89; N, 7.83.

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Table 1. Crystallographic Details for Complexes 1–3

	1	2	3
empirical formula	C ₇ H ₁₅ NO ₈ V	C ₆ H ₁₇ NNaO ₁₁ V	C ₁₂ H ₂₄ N ₃ O ₁₄ V ₂
fw	292.1	353.14	536.2
temp, K	173(2)	173(2)	173(2)
wavelength, Å	0.7107	0.7107	0.7107
cryst system	orthorhombic	monoclinic	monoclinic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	C2/c
a, Å	6.940 (2)	6.333 (2)	18.880 (2)
b, Å	9.745 (2)	18.796 (2)	7.395 (2)
c, Å	18.539 (4)	11.5040 (10)	16.010 (2)
β, deg		102.53 (2) ^a	106.33 (2)
vol, Å ³	1253.8 (5)	1336.8 (5)	2145.1 (7)
Z	4	4	4
ρ _{calcd} , Mg/m ³	1.55	1.76	1.66
absorpn coeff, mm ⁻¹	0.82	0.830	0.94
R, R _w ^a	0.069, 0.1876	0.0745, 0.2257	0.0456, 0.0623

^a For complexes 1 and 2 refinement was on F², using the program SHELXL-93 and the full data set. For complex 3 refinement was on F for the observed data.

X-ray Structure Determinations for Compounds 1–3. Intensity data were collected on a Siemens P4 diffractometer. The unit cell constants in Table 1 were determined by a least-squares fit of the setting angles of 25 high-angle reflections. Data were collected to (sin θ)/λ = 0.595 Å⁻¹ by using θ/2θ scans. The intensities of three standard reflections were monitored every 97 reflections; no significant changes were noted in any of the cases. Lorentz and polarization corrections were applied for all three compounds, but no absorption corrections were applied for 1 or 2. For 3, an empirical absorption correction was applied on the basis of ψ-scan data (T_{max} = 0.67, T_{min} = 0.57).

The structures were solved by using the direct methods routine TREF in the Siemens SHELXTL program library.²² Full-matrix, weighted least-squares refinement was employed (on F² for 1 and 3; on F for 2), with anisotropic displacement parameters generally employed for non-hydrogen atoms. Hydrogen atoms were generally included in idealized positions. Neutral atom scattering factors and anomalous dispersion correction terms were used.²³ Residual indices at convergence may be found in Table 1 for each of compounds 1–3.

Magnetic Susceptibility and Molar Magnetization Measurements. Magnetic measurements were made using a commercial magnetometer based on a superconducting quantum interference device (SQUID). The sample for measurements consisted of randomly oriented crystals in a size-4 gelatin capsule (approximately 0.1 g of compound). The diamagnetic moment of an empty capsule was subtracted from the measured paramagnetic moment of the sample.

Molar susceptibilities were on the order of 10⁻⁶ m³·mol⁻¹ (0.08 emu·mol⁻¹), about 2–3 orders of magnitude larger than any diamagnetic corrections that might be achieved using Pascal's constants or other inorganic systems.^{24–26}

UV/Vis Spectroscopic Studies. The UV/vis spectra were recorded on a Lambda 4B Perkin-Elmer spectrometer. The extinction coefficients for 1 and 2 were calculated from solutions containing varying concentrations of compounds 1 and 2 at the respective absorbance maxima. The measurements of extinction coefficients for compound 3 were complicated by the hydrolytic chemistry of this compound (see eq 1) and the associated changes in the absorbance maxima of various



equilibrium mixtures of compounds 1–3. It was therefore necessary to estimate the extinction coefficients for compound 3 from solutions

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- (25) To convert susceptibility from SI (rationalized MKS) units of m³·mol⁻¹ to CGS units of cm³·mol⁻¹ (or emu·mol⁻¹), divide by 4π × 10⁻⁶.
- (26) To convert magnetization from SI units of A·m²·mol⁻¹ to CGS units of erg·G⁻¹·mol⁻¹ (or emu·mol⁻¹), multiply by 1000.

of compound 3 with added large excesses of compound 2. Spectra were recorded at increasing concentrations of compound 2 until the absorbance maxima for compound 3 were reached asymptotically.

The concentrations of compounds 1–3 in solution can then be obtained from eqs 2–4. Here, ε1–ε3 are the extinction coefficients

$$\epsilon 1 [1] + \epsilon 3 [3] = \text{Abs}_{824} \quad (2)$$

$$[1] + [2] + 2 [3] = [V]_{\text{tot}} \quad (3)$$

$$[1] + [3] = [3]_{\text{tot}} \quad (4)$$

for compounds 1–3; [1]–[3] are the concentrations of compounds 1–3 in solution, Abs₈₂₄ is the absorbance for the equilibrium mixture of the compounds at the wavelength 824 nm, [V]_{tot} is the concentration of all vanadium atoms added to the solution, and [3]_{tot} is the concentration of compound 3 added to the solution. Equation 4 only applies in the presence of a large excess (saturating concentrations) of compound 2. Once the concentrations of compounds 1–3 are obtained, the equilibrium constant for reaction 1 can be calculated (K_{eq} = [3]/[1][2]). Measurements were made in triplicates at five different wavelengths (824, 680, 640, 609, and 570 nm) for a minimum of six different concentrations covering three different ranges. The pH of the solutions were 4.2, and the solutions were incubated in a thermostat at 25 °C. K_{eq} was calculated for all of these measurements; the reported K_{eq} represent the average value, and the indicated error is the largest deviation from this average.

Other Spectroscopic Studies and Electrochemical Methods. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR both in KBr disks and in Nujol on AgBr plates. The aqueous solution IR spectra were also recorded between AgBr plates. Electrochemical measurements were performed on a Princeton Applied Research (PAR) Model 173 potentiostat in a 1 mL cell with fitted reference and auxiliary compartments using a calomel electrode in DMF (saturated with tetrabutylammonium perchlorate) as a reference electrode and a platinum wire as the auxiliary electrode. The electrochemistry was recorded in DMF under N₂, and the supporting electrolyte was tetrabutylammonium perchlorate (0.10 M). Platinum disk electrodes were used as working electrode for the cyclic voltammetry. The number of electrons involved were measured with coulometry. The spectra were acquired at several scan rates (from 2 to 200 mV/s). Each peak was observed separately and as part of a scan. In this way we were assured that the observed signals were not artifacts of other redox processes during the scan. All potentials throughout this paper are relative to the normal hydrogen electrode (NHE)²⁷ using ferrocene (+0.400 V NHE).²⁸

The EPR spectra were recorded using 4 mm o.d. quartz tubes on a Bruker ESP 300 spectrometer. The spectrometer was operating at X-band (9.465 GHz) with a microwave power of 200 μW and calibrated using a powder sample of 2,2-bis(4-tert-octylphenyl)-1-picrylhydrazyl (DPPH, g = 2.0037). The EPR spectra were recorded at -133 °C using a modulation frequency of 100 kHz, a modulation amplitude of 7.95 G, a time constant of 20.48 ms, and a conversion time of 81.92 ms. The X-band spectrum was analyzed to second order using the perturbation equations of Bleaney.²⁹ NMR spectra were recorded on a Bruker ACP-300 spectrometer operating at 79 MHz for ⁵¹V and 300 MHz for ¹H in external lock mode. ⁵¹V NMR spectra were recorded in nondeuterated solvents, and the chemical shifts were reported against VOCl₃ (0 ppm). Parameters were those reported previously.³⁰ Microanalyses were performed by Desert Analytics, Tucson, AZ.

Results

Synthesis of [V(O)(OH)₂(Hhida)]·CH₃OH, 1, Na[V(O)₂(Hhida)]·4H₂O, 2, and NH₄[V₂(O)₂(μ-O)(Hhida)₂]·H₂O, 3. Complex 1 was synthesized by the addition of a solid mixture of vanadyl acetylacetonate and H₃hida to a mixture of water and methanol (1:1). This material was isolated as a blue

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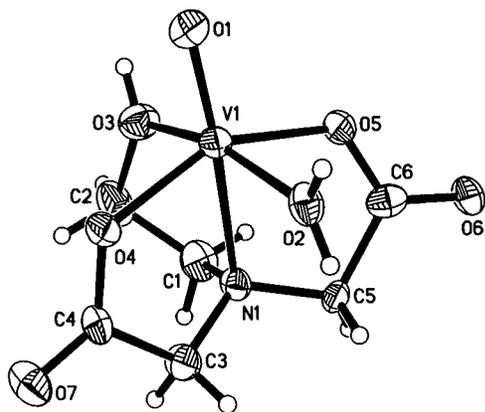


Figure 1. Structure and atom-numbering scheme of complex **1**, $[V(O)(OH_2)(Hhida)] \cdot CH_3OH$ as determined by X-ray crystallography.

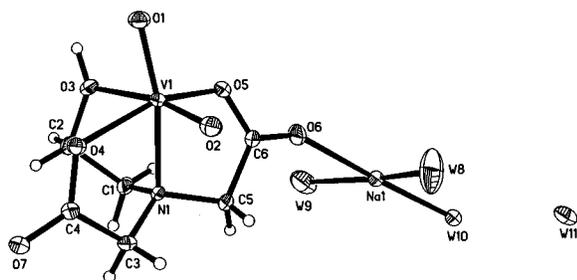


Figure 2. Structure and atom-numbering scheme of complex **2**, $Na[V(O)_2(Hhida)] \cdot 4H_2O$ as determined by X-ray crystallography.

crystalline material by the addition of acetone at 4 °C. The X-ray structure of this material was solved (see below), and complex **1** contained one molecule of methanol in the crystal. In an alternative synthesis in water, the cocrystallized molecule of methanol was substituted with a molecule of water. Complex **2** had been characterized previously in aqueous solution;²¹ however, these studies were carried out on solutions containing variable ligand and vanadate, and no attempt was made to isolate **2**. In this work we were able to isolate the sodium salt of the vanadate–Hhida complex at pH 4–5 as a yellow crystalline solid and characterize the solid state of this compound. Complex **3** was obtained by reacting a suspension of excess H_3hida with NH_4VO_3 (or $NaVO_3$) at acidic pH. At lower concentrations gentle heating is needed to generate this product, which was isolated as the NH_4^+ or Na^+ salt as a grayish blue crystalline material by the addition of ethanol. Alternatively, compound **3** can be prepared by mixing **1** and **2** in a 1:1 ratio. The stoichiometry as established by elemental analysis and mass and charge balance as $[V(O)(OH_2)(Hhida)] \cdot MeOH$ for **1**, $Na[V(O)_2(Hhida)] \cdot 3H_2O$ for **2**, and $(NH_4)[V_2(O)_2(\mu-O)(Hhida)_2] \cdot H_2O$ for **3**. The blue crystalline compound **1**, yellow compound **2**, and the grayish blue compound **3** are very soluble in water, soluble in DMF and dimethyl sulfoxide (DMSO), and insoluble in other organic solvents. Both complexes are stable for over 6 months in solid state at room temperature. In solution these complexes are stable for at least 24 h.

X-ray Crystallography of Complexes 1–3. The numbering systems and the structures of complexes **1–3** are shown in Figures 1–3. Table 2 contains the atomic coordinates and equivalent isotropic displacement parameters for **1–3**. Table 3 contains a listing of selected bond lengths and bond angles.

Structural Description of 1. In the mononuclear complex **1** (Figure 1), the vanadium atom is coordinated to a tetradentate Hhida²⁻ ligand. A terminal oxo ligand and a water molecule complete the distorted octahedral coordination sphere. The amine nitrogen atom (N1) and terminal oxo ligand (O1) occupy the trans positions that may arbitrarily be assigned as axial

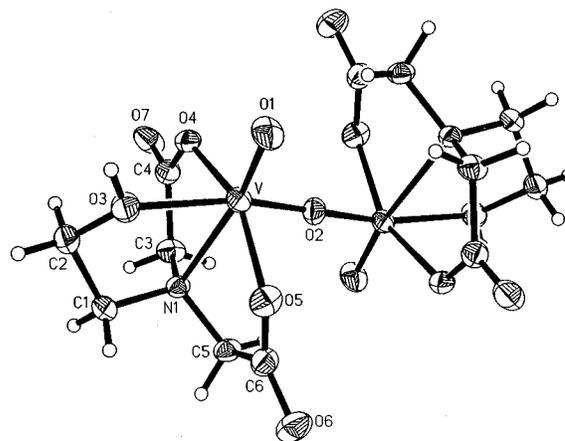


Figure 3. Structure and numbering scheme of complex **3**, $(NH_4)[V_2(O)_2(\mu-O)(Hhida)_2] \cdot H_2O$ as determined by X-ray crystallography.

positions; the two carboxylate oxygen atoms (O4 and O5), the hydroxyl oxygen atom (O3) of Hhida, and the water molecule (O2) then define the equatorial plane. The two carboxylate oxygen atoms are bound to the metal in trans positions.

The short V–O(oxo) bond length (1.596(5) Å) indicates considerable π -bond character, as in other monomeric V(IV) complexes with similar coordination geometries.^{13,31–33} However, the other axial bond, V1–N1 is slightly longer (2.307(6) Å) than V–N(amine) bonds (around 2.1–2.3 Å) in other vanadium(IV) and vanadium(V) complexes.^{11–13,34,35} The V1–O2(H_2O) bond length in **1** (2.021(6) Å) compares well with corresponding bond lengths for other V(IV) complexes.^{31,33} The V–O(carboxylate) bond lengths are also within the previously reported range.³¹ The considerable distortion from an idealized octahedral structure in complex **1** results from the restricted “bite” of the Hhida²⁻ ligand; as a result the vanadium atom is displaced significantly (0.37 Å) from the least-squares plane through atoms O2–O5 toward the oxo ligand. In related five- and six-coordinate oxovanadium(IV) complexes, the vanadium atom is also out of the corresponding plane by a similar distance.^{13,31}

Structural Description of 2. The molecular structure of complex **2** consists of a polymeric lattice of mononuclear complexes connected through Na–O interactions. In the mononuclear complex **2** (Figure 2) the vanadium atom is coordinated by a tetradentate Hhida²⁻ ligand. Two terminal oxo ligands exist in the distorted octahedral coordination sphere. The amine nitrogen atom (N1) and one terminal oxo ligand (O1) occupy the trans positions that may arbitrarily be assigned as axial positions; the two carboxylate oxygen atoms (O4 and O5), the hydroxyl oxygen atom (O3) of Hhida²⁻, and the oxo ligand (O2) then make up the equatorial plane. The two carboxylate oxygen atoms are bound to the metal in trans positions.

The two short V–O(oxo) bond lengths (1.623(3) and 1.663(3) Å) indicate considerable π -bond character, as in other monomeric V(V) complexes with similar coordination geometries.^{13,31,32,35–37} The other axial bond, V1–N1, is

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for 1–3^a

	x	y	z	U(eq)
For 1 ^b				
V1	0.9781(2)	0.62689(11)	0.86905(6)	0.0231(4)
N1	1.2634(9)	0.7228(6)	0.8298(3)	0.0232(13)
O1	0.8021(8)	0.5591(6)	0.9115(3)	0.0384(14)
O2	0.8660(9)	0.6659(7)	0.7705(3)	0.0291(13)
O3	1.1614(8)	0.6099(6)	0.9566(3)	0.0332(13)
O4	1.1109(7)	0.4698(5)	0.8227(3)	0.0245(11)
O5	0.9482(8)	0.8282(5)	0.8844(3)	0.0263(12)
O6	1.0031(9)	1.0383(5)	0.8435(3)	0.0311(12)
O7	1.3416(8)	0.3872(5)	0.7524(3)	0.0336(13)
C1	1.3869(13)	0.7406(8)	0.8940(4)	0.035(2)
C2	1.3646(12)	0.6183(11)	0.9439(4)	0.040(2)
C3	1.3459(11)	0.6289(7)	0.7768(4)	0.029(2)
C4	1.2642(11)	0.4817(7)	0.7846(4)	0.024(2)
C5	1.2090(11)	0.8571(7)	0.8032(4)	0.026(2)
C6	1.0422(11)	0.9124(7)	0.8464(4)	0.026(2)
O8	1.3542(14)	0.5523(10)	0.5688(5)	0.081(3)
C7	1.0998(37)	0.2992(24)	1.0600(12)	0.061(6)
For 2 ^c				
V1	0.0186(1)	0.3490(1)	0.1262(1)	0.012(1)
N1	0.1326(6)	0.3137(2)	-0.0396(3)	0.013(1)
O1	0.0039(5)	0.3943(2)	0.2483(2)	0.018(1)
O2	-0.1743(5)	0.2905(2)	0.1092(3)	0.020(1)
O3	0.2973(5)	0.4233(2)	0.1111(2)	0.017(1)
O4	-0.1249(5)	0.4155(2)	0.0028(2)	0.015(1)
O5	0.2567(5)	0.2806(2)	0.1865(2)	0.018(1)
O6	0.3934(7)	0.1761(2)	0.1528(3)	0.029(1)
O7	-0.2578(5)	0.4390(2)	-0.1889(2)	0.020(1)
C1	0.3376(8)	0.3485(2)	-0.0475(4)	0.018(1)
C2	0.3442(7)	0.4244(2)	-0.0066(4)	0.017(1)
C3	-0.0473(7)	0.3315(2)	-0.1373(3)	0.017(1)
C4	-0.1536(6)	0.4007(2)	-0.1090(3)	0.014(1)
C5	0.1726(7)	0.2370(2)	-0.0143(3)	0.017(1)
C6	0.2831(7)	0.2284(2)	0.1166(3)	0.017(1)
Na1	0.5001(3)	0.0616(1)	0.1211(1)	0.018(1)
W8	0.1659(9)	0.0264(2)	0.1640(5)	0.056(1)
W9	0.8030(7)	0.1288(2)	0.0686(3)	0.038(1)
W10	0.6161(5)	-0.0572(2)	0.0964(3)	0.021(1)
W11	0.3535(6)	-0.1628(2)	0.1696(3)	0.026(1)
For 3 ^d				
V	0.19087(2)	0.20647(4)	0.56874(2)	0.02083(11)
O1	0.18598(9)	-0.0101(2)	0.57354(10)	0.0325(3)
O2	0.2500	0.2500	0.5000	0.0240(4)
O3	0.12601(9)	0.2398(2)	0.65567(10)	0.0281(3)
O4	0.27467(8)	0.2617(2)	0.67222(9)	0.0249(3)
O5	0.10253(8)	0.2728(2)	0.47332(9)	0.0280(3)
O6	0.05220(9)	0.4772(3)	0.37193(10)	0.0374(4)
O7	0.35773(8)	0.4613(2)	0.74143(10)	0.0368(4)
N1	0.18049(8)	0.5111(2)	0.58216(9)	0.0191(3)
N2	0.0000	0.1990(5)	0.2500	0.0403(7)
C1	0.12582(11)	0.5523(3)	0.63026(12)	0.0252(4)
C2	0.13094(13)	0.4115(3)	0.70013(13)	0.0289(4)
C3	0.25591(11)	0.5724(2)	0.62809(13)	0.0248(4)
C4	0.29947(10)	0.4232(3)	0.68560(12)	0.0235(4)
C5	0.15252(11)	0.5734(2)	0.49141(12)	0.0235(4)
C6	0.09764(11)	0.4342(3)	0.44081(12)	0.0257(4)
O11	0.0416(5)	0.1371(14)	0.8483(7)	0.080(4)
O12	0.0147(7)	0.0486(19)	0.0329(8)	0.137(6)
O13	-0.0278(9)	-0.0703(26)	0.1055(13)	0.115(8)
O14	0.0000	0.1967(38)	0.7500	0.101(12)

^a U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b Symmetry transformations used to generate equivalent atoms: $x - 1, -y + 1/2, z - 1/2$. ^c Symmetry transformations used to generate equivalent atoms: $x + 1, -y + 1/2, z + 1/2$. ^d Symmetry transformations used to generate equivalent atoms: $x + 1, -y, -z$.

somewhat shorter (2.251(3) Å) than V–N(amine) bonds (~2.29 Å) in other vanadium(IV) and vanadium(V) complexes.^{11–13,34,35,37} The V–O(carboxylate) bond lengths are also within the previously reported range.³¹ The considerable distortion from

an idealized octahedral structure in complex **2** is due to the restricted bite of the Hhida²⁻ ligand, and as a result the vanadium atom is displaced significantly (0.317(3) Å) from the least-squares plane through atoms O2–O5 toward the oxo atom O1. In related five- and six-coordinate oxovanadium(V) complexes, the vanadium atom is also out of the corresponding plane by a similar distance.^{13,31}

Structural Description of 3. Crystals of complex **3** contain binuclear [V₂(O)₂(μ-O)(Hhida)₂]⁻ units interacting with NH₄⁺ counterions through Coulombic forces and hydrogen bonds. The bridging oxygen atom in the binuclear anion is part of a linear V–O–V system as a result of occupying the crystallographic inversion center that relates the two halves of the complex anion. The asymmetric unit also contains a total of approximately one molecule of water, which is disordered over several sites. In each half of the binuclear complex Hhida²⁻ acts as a tetradentate ligand, with a terminal and a bridging oxo ligand completing the distorted octahedral coordination sphere. The axial positions may be defined as those occupied by the amine nitrogen atom (N1) and the terminal oxo ligand (O1). The equatorial plane is then defined by the two carboxylate oxygen atoms (O4 and O5), the bridging oxo ligand (O2), and the hydroxyl oxygen atom (O3). The hydroxyethyl group of the Hhida²⁻ ligand is protonated and is weakly coordinated to the vanadium center trans to the bridging oxygen atom; thus, the two carboxylate groups coordinate trans to each other, in analogy with the situation in **1** and **2**.

The V=O (terminal) distance (1.607(1) Å) compares well to those observed in other mixed valence vanadium(IV/V) complexes;^{11,12–16,38} its shortness indicates considerable π-bond character.^{11,15} The amine nitrogen atom is coordinated trans to the terminal oxo group at a distance (2.277(2) Å) that is in the range observed for related complexes.^{11–13,34,35,38} The V–O(μ-O) bond distance of 1.8033(4) Å in **3** is in the range found for other oxo-bridged mixed valence binuclear vanadium(IV/V) complexes (1.776–1.822 Å).^{11,12,38–41} The V–O(carboxylate) bond lengths, 1.9851(15) and 1.9807(15) Å, are also similar to those reported previously. The bond between the vanadium atom and the hydroxyethyl oxygen atom is longer (at 2.1109(15) Å) than the other V–O bond lengths as a result of the protonation of the oxygen atom.

The octahedral coordination arrays are again distorted from ideality as a result of the constrained bite of the Hhida²⁻ ligand. Concomitantly, the vanadium atom is displaced from the least-squares plane through the four equatorial ligand atoms by 0.37 Å in the direction of the apical bridging oxo ligand. Related compounds show similar distortions.^{11,13}

Weak hydrogen bonding interactions are observed between the ammonium ion and carboxylate oxygen atoms in complex **3** (N2...O6 = 2.817(3) Å, N2...O7 = 2.904(3) Å).

The X-ray structure of **3** contains indistinguishable vanadium atoms suggesting a type III or a disordered type I compound. These possibilities can be distinguished by examining the thermal ellipsoid of the bridging oxygen atom, O2; since it is fairly regular, the X-ray study support a type III type compound.

Structural Comparison of Complexes 1–3 with Related Complexes. Complexes **1–3** have several structural similarities. All of three complexes involve six-coordinate ligand arrays in which an oxo ligand is trans to an amine nitrogen atom. In

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Table 3. Bond Lengths (Å) and Angles (deg) for Complexes **1–3**

			For 1		
V1–O1	1.596(5)	N1–C1	1.477(10)	O6–C6	1.258(9)
V1–O2	2.021(6)	N1–C3	1.460(9)	O7–C4	1.221(9)
V1–O3	2.070(5)	N1–C5	1.449(9)	C1–C2	1.517(12)
V1–O4	1.983(5)	O3–C2	1.432(10)	C3–C4	1.549(10)
V1–O5	1.994(5)	O4–C4	1.284(9)	C5–C6	1.506(10)
V1–N1	2.307(6)	O5–C6	1.264(9)		
O1–V1–O2	103.2(3)	O3–V1–N1	75.7(2)	N1–C1–C2	109.9(7)
O4–V1–O2	86.2(2)	O4–V1–N1	77.1(2)	O3–C2–C1	104.2(7)
O5–V1–O2	84.5(2)	O5–V1–N1	74.7(2)	N1–C3–C4	112.0(6)
O1–V1–O3	92.9(3)	C3–N1–C1	112.8(6)	O7–C4–O4	124.4(7)
O2–V1–O3	163.9(2)	C5–N1–C1	108.6(6)	O4–C4–C3	116.0(6)
O4–V1–O3	89.5(2)	C5–N1–C3	116.1(6)	O7–C4–C3	119.5(6)
O5–V1–O3	91.8(2)	C1–N1–V1	106.9(5)	N1–C5–C6	110.0(6)
O1–V1–O4	104.4(3)	C3–N1–V1	107.2(4)	O6–C6–O5	123.0(7)
O1–V1–O5	104.9(3)	C5–N1–V1	104.5(4)	O5–C6–C5	117.5(6)
O4–V1–O5	150.5(2)	C2–O3–V1	118.1(5)	O6–C6–C5	119.5(7)
O1–V1–N1	168.5(3)	C4–O4–V1	123.7(5)		
O2–V1–N1	88.2(2)	C6–O5–V1	120.3(5)		
			For 2		
V1–O1	1.663(3)	N1–C1	1.482(5)	C3–C4	1.531(5)
V1–O2	1.624(3)	N1–C3	1.474(5)	C4–O7	1.239(5)
V1–O3	2.287(3)	N1–C5	1.477(5)	C4–O4	1.293(5)
V1–O4	1.969(3)	C1–C2	1.500(5)	C5–C6	1.524(5)
V1–O5	1.988(3)	C2–O3	1.448(5)	C6–O5	1.302(5)
V1–N1	2.251(3)			C6–O6	1.225(5)
O2–V1–O1	105.7(2)	O4–V1–O3	79.24(12)	O4–C4–C3	115.6(3)
O1–V1–O4	100.25(13)	O5–V1–O3	83.20(12)	O7–C4–C3	121.5(3)
O2–V1–O4	96.54(14)	N1–V1–O3	74.01(11)	O7–C4–O4	122.8(4)
O1–V1–O5	102.33(13)	C3–N1–C1	112.2(3)	N1–C5–C6	107.5(3)
O2–V1–O5	95.7(2)	C5–N1–C1	109.0(3)	O6–C6–O5	122.3(4)
O4–V1–O5	150.30(12)	C3–N1–C5	115.7(3)	O5–C6–C5	115.9(3)
O1–V1–N1	160.35(14)	C1–N1–V1	112.5(2)	O6–C6–C5	121.7(4)
O2–V1–N1	93.96(13)	C3–N1–V1	104.6(2)	C2–O3–V1	113.5(2)
O4–V1–N1	77.05(12)	C5–N1–V1	102.4(2)	C4–O4–V1	121.0(2)
O5–V1–N1	75.18(12)	N1–C1–C2	111.1(3)	C6–O5–V1	117.4(3)
O1–V1–O3	86.35(13)	O3–C2–C1	106.4(3)		
O2–V1–O3	167.83(13)	N1–C3–C4	109.1(3)		
			For 3		
V–O1	1.6071(15)	O3–C	–1.446(2)	N1–C3	1.478(2)
V–O2	1.8033(4)	O4–C4	1.279(2)	N1–C5	1.473(2)
V–O3	2.1109(15)	O5–C6	1.295(3)	C1–C2	1.512(3)
V–O4	1.9851(15)	O6–C6	1.233(2)	C3–C4	1.521(3)
V–O5	1.9807(15)	O7–C4	1.239(2)	C5–C6	1.522(3)
V–N1	2.277(2)	N1–C1	1.483(2)		
O1–V–O2	105.11(6)	O3–V–N1	74.99(6)	C5–N1–V	103.45(10)
O1–V–O3	91.89(7)	O4–V–N1	77.72(5)	N1–C1–C2	109.49(15)
O2–V–O3	162.75(5)	O5–V–N1	75.61(6)	O3–C2–C1	105.0(2)
O4–V–O3	84.25(6)	V–O2–V	180.0	N1–C3–C4	111.11(15)
O5–V–O3	87.76(6)	C2–O3–V	117.26(12)	O7–C4–O4	122.8(2)
O1–V–O4	102.00(7)	C4–O4–V	120.01(12)	O4–C4–C3	117.7(2)
O2–V–O4	89.29(4)	C6–O5–V	119.20(12)	O7–C4–C3	119.4(2)
O5–V–O4	153.31(6)	C5–N1–C1	109.82(14)	N1–C5–C6	108.37(15)
O1–V–O5	103.68(7)	C3–N1–C1	113.12(15)	O6–C6–O5	123.4(2)
O2–V–O5	90.95(5)	C5–N1–C3	115.03(15)	O5–C6–C5	116.6(2)
O1–V–N1	166.87(7)	C1–N1–V	110.08(11)	O6–C6–C5	120.0(2)
O2–V–N1	88.02(4)	C3–N1–V	104.70(10)		

addition, the Hhida²⁻ ligand is tetradentate, the monoprotonated hydroxyl group is coordinated to the vanadium atom, and the vanadium atom is displaced by a similar amount toward one of the oxygen atoms in the ligand. Furthermore, the two carboxylate ligands coordinate trans to each other in all three complexes. Most of the bond lengths and bond angles are similar, including all of the bond angles and bond lengths within the Hhida²⁻ ligands.

Several structural differences are expected and observed for complexes **1–3**. The water molecule in complex **1** is replaced by an oxo ligand in complex **2** and by a bridging oxo group in complex **3**. The V=O(terminal) distance is 0.011 Å shorter in complex **1** than in the mixed valence complex **3** and 0.055 Å shorter than the corresponding bond in **2**. Furthermore, the

V1–N1 bond length in complex **1** is longer than the corresponding bond in complex **3** by 0.030 Å and in complex **2** by 0.026 Å.

The ligands pmida and s-peida both contain two carboxylate groups, as does the Hhida²⁻ ligand. Since both the pyridine and the hydroxyl moieties are neutral, the mononuclear complexes formed by using these ligands will have the same overall charge as **1** and **2**. The most striking difference between these mononuclear vanadium(IV) and -(V) complexes^{13,35} and that of **1** and **2** is the fact that the carboxylate groups are cis in the former complexes and trans in **1** and **2**.

Several complexes containing V₂O₃³⁺ units exhibit structural similarities with **3**. Complex **3** resembles most the mixed valence complex formed from nta and vanadate^{11,38} in which

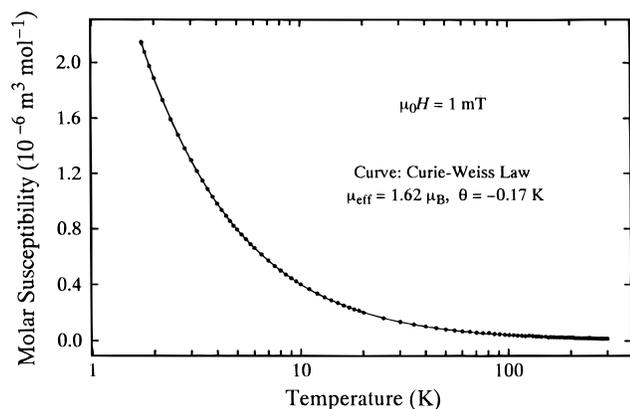


Figure 4. Molar susceptibility for compound **1** as a function of temperature (log scale) for compound **1**.

X-ray crystallography also revealed two indistinguishable vanadium atoms. In addition, most of the bond lengths and bond angles in the binuclear nta complex were similar to those observed for **3**. However, the charge difference resulting from the substitution of one carboxylate group by a hydroxyl group could explain the differences in the properties of these complexes despite their similar structures.

The mixed valence complexes formed by pmida and s-peida will have the same overall charge as the complex anion in **3**. Accordingly, many similarities are anticipated and observed in bond lengths and bond angles, including the almost 180° V—O—V angles (175.3(7) and 179.5(3)° compared to 180.0° in **3**).^{12,13} However, the mixed valence complexes formed from pmida¹² and s-peida¹³ contain vanadium atoms that are different from each other as determined by X-ray crystallography, although in the case of the pmida complex this difference appears to be induced by crystal packing forces.

Additional mixed valence vanadium(IV) and -(V) complexes have been characterized involving ligands such as salicylidene-serinate,¹⁴ azobenzene-2,2'-diolate,¹⁵ and 8-quinolinolate.¹⁶ Most of these complexes exhibit structural parameters similar to those for **3**. However, these complexes contain distinguishable vanadium atoms that have been assigned as the vanadium(IV) and -(V) in the binuclear complex. Comparison of complex **3** with binuclear vanadium(V) complexes shows that the structural parameters observed are within the expected range.³² Although there is no doubt that some changes in bond lengths are observed for different oxidation states of the metal ion, other factors such as increased orbital overlap, hydrogen bonding, and crystal packing can modify these changes so that further information on the properties of complexes **1–3** in the solid state is desirable.

Magnetic Susceptibility. Compound 1. Compound **1** is a vanadium(IV) complex with $S = 1/2$. The molar susceptibility χ_{mol} follows a Curie–Weiss law, eq 5, with a Curie constant

$$\chi_{\text{mol}} = \frac{C}{T - \theta} \quad (5)$$

per mole C of $4.10 \times 10^{-6} \text{ m}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and a Weiss constant θ of -0.172 K (almost zero) (Figure 4). The strength of antiferromagnetic coupling for **1** is thus minimal, as suggested by a Weiss constant of about zero. The effective moment μ_{eff} of $1.62 \mu_{\text{B}}$, where μ_{B} is the Bohr magneton, is obtained from C .

Magnetic Susceptibility and Molar Magnetization Measurements. Compound 3. Molar susceptibility of compound **3** was measured as a function of temperature T from 1.75 to 300 K in a measuring field $\mu_0 H$ of 1 mT, as shown in Figure 5.²⁵ The molar susceptibility χ_{mol} precisely follows a Curie law, eq 6, where C is the molar Curie constant, a fitting parameter

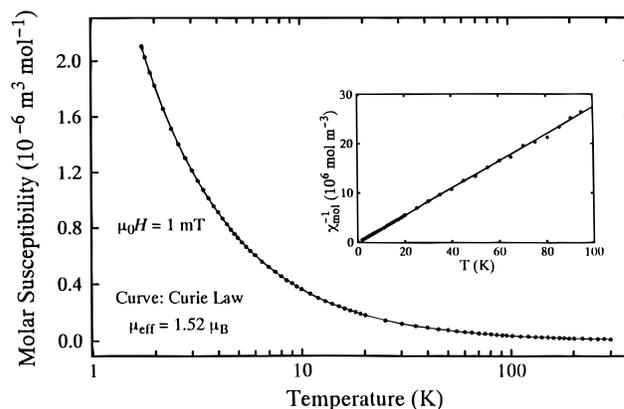


Figure 5. Molar susceptibility of compound **3** as a function of temperature (log scale) for compound **3** (inset: reciprocal susceptibility vs. temperature).

$$\chi_{\text{mol}} = C/T \quad (6)$$

equal to $3.64 \times 10^{-6} \text{ m}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. As in **1**, compound **3** does not demonstrate any antiferromagnetic coupling, as evidenced by the pure Curie dependence. The inset in Figure 5 shows the linear dependence of reciprocal molar susceptibility on temperature. An effective moment μ_{eff} of $1.52 \mu_{\text{B}}$ can be deduced from eq 7 where N is the Avogadro number, k is the Boltzmann constant, and μ_0 is the permeability of vacuum.

$$C = N\mu_0\mu_{\text{eff}}^2/3k \quad (7)$$

If we assume that the effective moment arises only from spin angular momentum (quantum number S) and that the orbital angular momentum (quantum number L) is quenched by the crystalline field, then the total angular momentum quantum number J equals S , and the Landé factor g equals 2. Using eq 8 and the above value of μ_{eff} , we get $J = S = 0.411$, closest to

$$\mu_{\text{eff}} = g[J(J + 1)]^{1/2}\mu_{\text{B}} \quad (8)$$

the allowed value $1/2$. If we consider that there are two vanadium ions per molecule, the most likely oxidation states are vanadium(IV), with $S = 1/2$, and vanadium(V), with $S = 0$. As an isolated ion, vanadium(IV) has $S = 1/2$, $L = 2$, $J = 3/2$, $g = 0.8$, μ_{eff} (theoretical) = $1.55 \mu_{\text{B}}$, μ_{eff} (spin only) = $1.73 \mu_{\text{B}}$, and μ_{eff} (exptl) = $1.75 \mu_{\text{B}}$; vanadium(V) has $S = 0$ and $\mu_{\text{eff}} = 0$.⁴²

As shown in Figure 5, measurements of molar magnetization M as a function of the ratio of field to temperature support these conclusions.²⁶ The low-temperature data follow the Brillouin function (eqs 9–11). Since the magnetization is expressed as

$$M = M_s \left[\frac{2J + 1}{2J} \coth \left(\frac{2J + 1}{2J} a \right) - \frac{1}{2J} \coth \frac{a}{2J} \right] \quad (9)$$

$$a = gJ\mu_{\text{B}}\mu_0 H/kT \quad (10)$$

$$M_s = NgJ\mu_{\text{B}} \quad (11)$$

(42) Van Vleck, J. H., *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: Oxford, U.K., 1932.

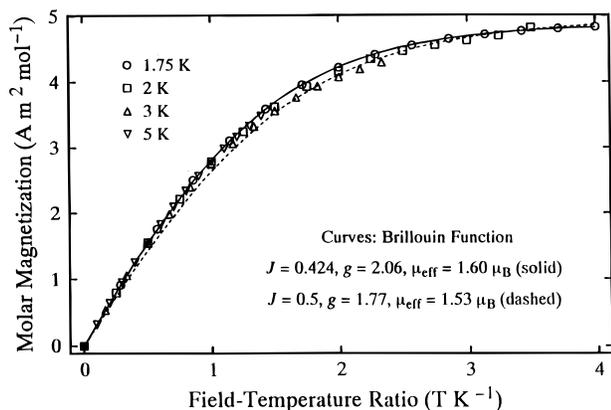


Figure 6. Molar magnetization as a function of field/temperature ratio for complex **3**.

magnetic moment per mole, the number of molecules in the definition of saturation magnetization M_s is the Avogadro number N .

The best fitting parameters for the 1.75 K data are $J = 0.424$ and $g = 2.06$. These parameters are used to obtain $\mu_{\text{eff}} = 1.60 \mu_B$, close to the $1.52 \mu_B$ obtained from the susceptibility data, and $M_s = 4.87 \text{ A}\cdot\text{m}^2\cdot\text{mol}^{-1}$ (Figure 6, solid curve). If we assume $J = 1/2$, relax the associated requirement $g = 2$, and use g as an adjustable parameter, we get a good fit with $g = 1.77$ and $\mu_{\text{eff}} = 1.53 \mu_B$ (Figure 6, dashed curve). The magnetic susceptibility is linear in field except at low temperature, where the usual Brillouin dependence of magnetization (Figure 6) gives a decreasing susceptibility with field. Thus, we conclude that the most likely oxidation states of the two vanadium atoms in the dimer are vanadium(IV) and vanadium(V). Although magnetic susceptibility shows **3** contains one unpaired electron, this method does not provide information on where it resides whether or not the electron is delocalized. However, these studies do show that the two vanadium atoms are indistinguishable.

A series of vanadium(IV) dimers, including complexes prepared from tetrakis(2-pyridylmethyl)ethylenediamine⁴³ and *N*-(hydroxyalkyl)salicylideneamines,³² have been structurally and magnetically characterized. Since the spin-orbit coupling in nearly all vanadium(IV) complexes is efficiently quenched, a significant reduction of the magnetic moment from $1.73 \mu_B$ in these complexes usually indicates antiferromagnetic coupling between vanadium centers.⁴⁴ Indeed, significant coupling has been observed in dimeric complexes with a variety of structural frameworks (see ref 32), demonstrating the various possibilities for orbital overlap in vanadium dimers.

Magnetic properties have been previously examined for several vanadium mixed valence dimers.^{12,15} The magnetic behavior of the mixed valence dimers of pmida¹² and azobenzene-2,2'-diolate¹⁵ give effective magnetic moments in the range 1.75 – $1.80 \mu_B$, corresponding to one free electron. The difference between the pmida and Hhida²⁻ complexes is particularly striking, since these two complexes have many structural similarities and identical overall charges. One major structural difference is the trans chelation of the carboxylate groups in complexes **1** and **3** which is not observed in other monomeric complexes or the mixed valence pmida and s-peida complexes that give magnetic moments in the vicinity of $1.73 \mu_B$. The trans chelation of the carboxylate groups are observed for the nta complex, and, although no magnetic studies have been carried out on this complex, EPR spectroscopic studies are

consistent with the observation of a magnetic moment less than $1.73 \mu_B$ for this complex.¹¹ These results suggest that, although many geometries of dimeric complexes may support orbital overlap and electron delocalization, few of these complexes will show electron delocalization in the mixed valence complexes.

These differences in magnetic properties in the solid state, even among structurally similar mixed valence dimers, are interesting because properties of $[\text{V}_2\text{O}_3(\text{pmida})]^-$, $\text{H}[\text{V}_2\text{O}_3(\text{pmida})]$, and $[\text{V}_2\text{O}_3(\text{s-peida})]^-$ in solution are similar to those of $[\text{V}_2\text{O}_3(\text{nta})]^{3-}$ ^{13,14} and justify further exploration of the solution properties of complex **3**.

Solution State Studies of Hhida²⁻ Complexes. The study of $[\text{V}_2\text{O}_3(\text{pmida})]^-$, $\text{H}[\text{V}_2\text{O}_3(\text{pmida})]$, $[\text{V}_2\text{O}_3(\text{s-peida})]^-$, and $[\text{V}_2\text{O}_3(\text{nta})]^{3-}$ has been complicated by the hydrolysis of the dimers into monomeric units.^{11–13} Organic solvents have been used to increase the concentration of dimer in solution in order to better characterize the mixed valence dimer.¹³ However, information on the stability of such compounds in an aqueous environment is also of interest in interpretation of the biological responses induced by these types of mixed valence complexes (Crans et al., unpublished). Accordingly, a series of questions need to be addressed concerning the solution properties of complex **3**. First, will a significant amount of the dimer remain intact in aqueous solution? To appropriately address this question, the properties of complex **3** will be compared to the properties of the monomeric units (compounds **1** and **2**). Second, is the free electron delocalized in this system? Spectroscopic properties of the complex in solution will be used to probe this and the following questions. Third, what is the lability of the complex? Fourth, how does complex **3** compare to the mixed valence systems previously characterized? The results obtained in the solid state studies described above and the solution studies described below are summarized in Table 4.

UV/Vis Spectroscopy of Complexes 1–3. The UV/vis spectra of the aqueous solutions of complexes **1** and **2** were recorded in the region 190–900 nm in water and DMF. Absorbances were observed with λ_{max} at 194 nm ($\epsilon = 7000 \text{ cm}^2\cdot\text{mol}^{-1}$), 240 nm ($\epsilon = 1300 \text{ cm}^2\cdot\text{mol}^{-1}$), 609 nm ($\epsilon = 9.1 \text{ cm}^2\cdot\text{mol}^{-1}$), 824 nm ($\epsilon = 23.4 \text{ cm}^2\cdot\text{mol}^{-1}$) for **1** and at 192 nm ($\epsilon = 13\,300 \text{ cm}^2\cdot\text{mol}^{-1}$) for **2** in water (Table 5). The UV spectra consist of absorbances attributed to ligand to metal charge transfer transitions. The third expected d–d transition for compound **1** is probably covered by the lower energy charge transfer absorbance. Since compound **3** is not stable in water (see below), the UV/vis spectrum changed as a function of time until the equilibrium mixture of complexes **1–3** was obtained. Thus, it was necessary to measure the UV/vis spectrum of compound **3** after addition of excess **2** (60–300-fold excess in water and 5–20-fold excess in DMF). All UV/vis spectroscopy studies were carried out at 25 °C; the possibility of major changes in the formation constant for **3** has been discussed under EPR spectroscopic studies. The spectrum for **3** was obtained by subtracting the spectrum for compound **2**. Identical absorbance spectra for compound **3** were obtained in solutions at pH 4.2 from mixtures containing a minimum of six different concentrations of crystalline compounds **1** and **2**, **1** and **3**, or **2** and **3**.

The absorbance spectrum for **3** in water consists of two strong peaks at 569 and 681 nm and a shoulder at 745 nm (Table 5). The absorbance peaks for compound **3** are significantly shifted from the peaks for corresponding monomers in contrast to the corresponding pmida and nta complexes. Furthermore, the spectrum for complex **3** is different from the spectra for the pmida and nta mixed valence vanadium(IV,V) complexes which have two peaks. The absorbance spectrum for complex **3** is

(43) Neves, A.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1988**, *150*, 183–187.

(44) Syamal, A. *Coord. Chem. Rev.* **1975**, *16*, 309–339.

Table 4. Summary of Data Provided for Characterization of Mixed Valence Dimer [V^{IV}.V^V(O)₂(μ-O)(Hhida)₂]⁻ (Complex **3**)

exptl method	state of compd	dimer intact	dimer categorized as		comments
			type II	type III	
X-ray crystallography	solid	yes		X	the two vanadium atoms are indistinguishable; thermal ellipsoid of bridging oxygen atom is fairly regular
magnetic susceptibility	solid	yes		X	the complex contains one unpaired electron; the two vanadium atoms are indistinguishable
magnetization	solid	yes		X	the two vanadium atoms are indistinguishable
UV/VIS spectroscopy	solution	some ^a	X		
EPR spectroscopy	solution and frozen solution	some ^a	X		the parameters and splitting patterns in the EPR spectra of complexes 1 and 3 suggest that the free electron is partly delocalized
NMR spectroscopy	solution		X	X	no new signals are observed in solutions containing complex 3 ; this is consistent with a complex with delocalized electrons since such a complex should not give any NMR signals
electrochemistry	solution	some ^a	inconclusive	inclusive	
IR spectroscopy	solid	yes		X	
	solution	no ^a			

^a The dimer (**3**) is in equilibrium with the two mononuclear complexes (**1** and **2**), and only low concentrations of **3** remain upon dissolution in water at pH 4.2 and ambient temperature. Excess mononuclear compounds (**1** and **2**) have been added for studies of the dimer. The dimer could not be identified by IR spectroscopy.

Table 5. UV/Vis Absorption Data for **1–3** in H₂O and DMF Solutions^a

complexes/ solvent	wavelength, nm (extincn coeff, cm ² ·M ⁻¹)
1 /H ₂ O	824 (23.4), 609 (9.1), 240 sh (1300), 194 (7000)
1 /DMF	880 (30), 640 (15)
2 /H ₂ O	192 (13300)
3 /H ₂ O	745 sh (280), 681 (310), 569 (380)
3 /DMF	744 sh (300), 664 (305), 568 (315)

^a The H₂O solutions were characterized at pH 4.2. All UV/vis studies were done at 25 °C.

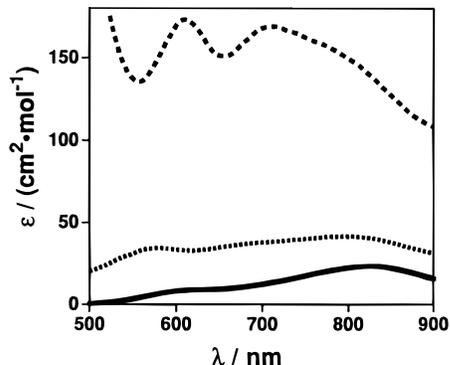


Figure 7. UV/vis spectra of 36.0 mM **1** (solid line), 15.5 mM complex **3** (dashed line), and 200 mM **2** and 36.0 mM **3** in water (dotted line). The spectra were recorded in H₂O at pH 4.2 and at 25 °C.

similar to the spectrum of hydrated V₂O₃³⁺, in which the third peak was attributed to a low-symmetry vanadium(IV) site which caused a splitting of the *e* level.⁴⁵ However, a symmetrical structure with indistinguishable vanadium atoms would not result in a splitting of the *e* level and thus is inconsistent with a symmetrical solution structure of complex **3** in water (or DMF). That is, UV/vis spectroscopy supports the interpretation that complex **3** is a low-symmetry complex and is inconsistent with a type III complex in solution.

The spectra of complexes **1** and **3** both show features that are characteristic for oxovanadium(IV) complexes with various polyfunctional aminocarboxylate ligands. This observation supports the argument that complex **3** in solution contains a vanadium(IV)-like center; that is, complex **3** is of type II (or perhaps type I) rather than type III complex.¹² However, as

previously shown for the mixed valence complex with s-peida, its absorption spectrum in solution⁴⁶ resembles the reflectance spectrum in the solid state, suggesting that the electronic structure is identical in solution and the solid state.¹³ Since these authors also showed that the reflectance spectrum of the nta mixed valence dimer resembled that of the s-peida dimer, they concluded that the two compounds have similar electronic structure. The latter is particularly interesting since the s-peida dimer has been categorized as a type II complex,⁴⁷ on the basis of X-ray crystallography,¹³ whereas the nta dimer has been categorized as a type III dimer on the basis of X-ray crystallography and EPR spectroscopy.¹¹

The formation constant for compound **3** from compounds **1** and **2** can be calculated from the visible absorption spectra of equilibrium mixtures of compounds **1–3**. We recorded spectra of solutions containing from 1 to 200 mM of **1** and **2** and measured the absorbances at 824, 640, 609, and 570 nm. Using the extinction coefficients listed in Table 5, *K*_{eq} was determined to be 3 ± 1 M⁻¹ in water and 200 ± 15 M⁻¹ in DMF.

The [V₂O₃(pmida)₂]⁻ complex is significantly more stable than [V₂O₃(nta)₂]³⁻ in aqueous solution. The stability has been attributed to the lower charge on the former complex.¹³ The spectra suggest that the [V₂O₃(Hhida)₂]⁻ complex has stability similar to that of the [V₂O₃(nta)₂]³⁻ complex and the hydrated V₂O₃³⁺ complex⁴⁵ even though compound **3** has a significantly lower numerical charge. Since the Hhida²⁻ complex has obvious structural differences from the pmida and the hydrated V₂O₃³⁺ complexes, it is likely that the stability can be attributed to the ligand. That is, the stronger the bonds generated to the ligands trans to the V–O–V unit, the more stable the complex. This projection is particularly interesting in light of the fact that preliminary results suggest mixed valence complexes induce some biological responses (Crans, D. C., unpublished results).

EPR Spectroscopy of Complexes 1 and 3. The EPR spectrum of 20 mM **1** at ambient temperature (Figure 8A) exhibits an eight-line spectrum with a *g*₀ = 1.916 ± 0.001 cm⁻¹ and *A*₀ = (-114.6 ± 0.5) × 10⁻⁴ cm⁻¹ characteristic of monomeric V(IV). The EPR spectrum of 12.5 mM **3** (Figure 8B) shows evidence that compound **3** has decomposed and that one of the resulting species has a spectrum identical to that of compound **1**. An indistinguishable spectrum is obtained upon dissolution of a 1:1 mixture of 12.5 mM compounds **1** and **2**

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(46) Okazaki, K.; Saito, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 785–791.

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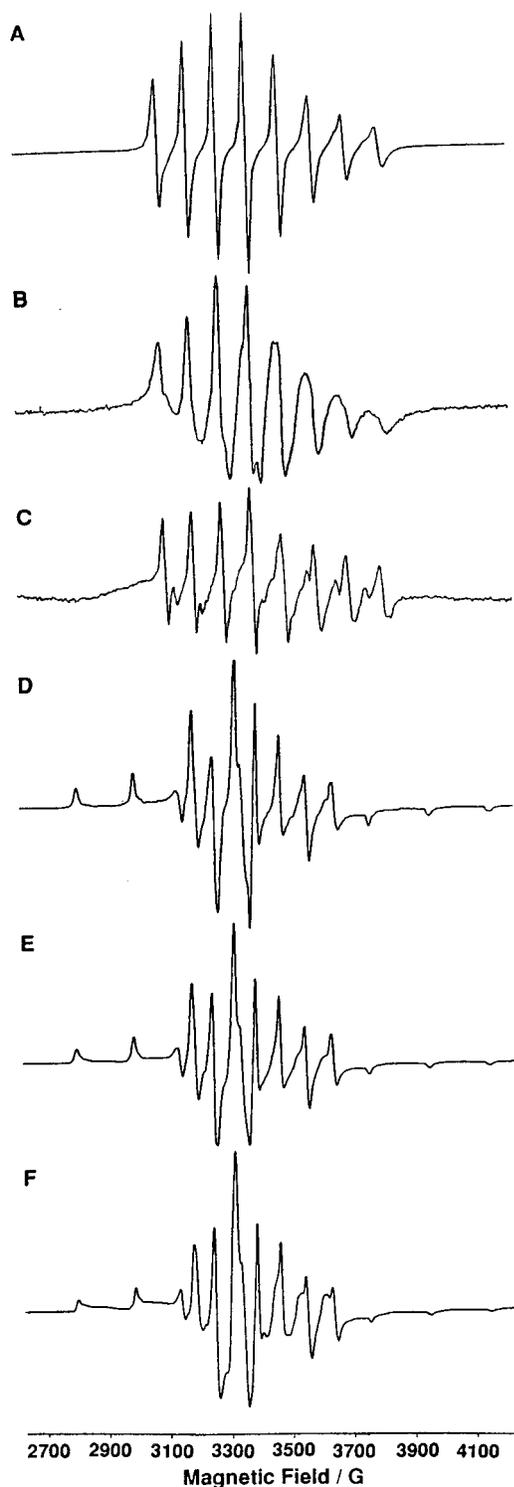


Figure 8. EPR spectra at ambient temperature (A–C) and at -133 °C (D–F) of solutions prepared from dissolution of 20 mM **1** in DMF (A), 12.5 mM **3** in DMF (B), a saturated solution of **3** (<1.0 mM) in CH_3CN (C), 5.00 mM **1** in DMF (D), 5.00 mM **3** in DMF (E), and 5.00 mM **3** and 110 mM **2** in DMF (F).

(data not shown). The equilibrium constant for formation of the mixed valence dimer in DMF was determined by UV/vis spectroscopy at ambient temperature and found to be 200 M^{-1} (see above); on the basis of the UV/vis studies, the concentration of 12.5 mM generates a mixture of complexes **1**, **2**, and **3** in DMF solution. Since **2** is diamagnetic, it does not contribute to the EPR spectrum, so that the spectrum shown in Figure 8B indicates a mixture of **1** and a second species, presumably the binuclear complex **3**. The spectrum of **3** is not the 15-line spectrum that would be observed if the unpaired electron were uniformly delocalized over the two vanadium nuclei. Precedents

for such 15-line spectra were reported for $[\text{V}_2\text{O}_3(\text{pmida})_2]^{-13}$ and $[\text{V}_2\text{O}_3(\text{nta})_2]^{3-}$.¹¹ The EPR spectrum for **3** shows only evidence for weak interaction with the second vanadium nuclear spin, which indicates that the unpaired electron is largely localized on the V(IV) center in the mixed valence complex. The lines in the spectrum of **3** are broader than those in the spectrum of **1**. Weak coupling to the second vanadium nucleus may contribute to the broader lines for **3** than for **1**. The higher molecular weight of **3** than of **1** causes slower molecular tumbling, which also contributes to the broadening of the lines for **3**. The EPR spectra for compound **3** were also examined in DMSO and CH_3CN and various mixtures of these and other solvents. In Figure 8C the EPR spectrum of a saturated solution of **3** in CH_3CN (<1 mM) is shown documenting that **3** also dissociates in this solvent albeit reflecting a different formation constant.

EPR spectra of 5.0 mM **1** (Figure 8D) and 5.0 mM **3** in the presence of excess **2** (Figure 8F) in frozen solution (-133 °C) are consistent with the assignments of the ambient-temperature spectra. The frozen DMF solution containing complex **1** (Figure 8D) gave 16 lines with $g_{\parallel} = 1.936 \pm 0.001$ cm⁻¹, $A_{\parallel} = (-176.7 \pm 0.5) \times 10^{-4}$ cm⁻¹, $g_{\perp} = 1.973 \pm 0.001$, and $A_{\perp} = (-67.1 \pm 0.5) \times 10^{-4}$ cm⁻¹. Solution of 5.0 mM **3** at -133 °C in DMF resulted in a spectrum indistinguishable from that obtained from compound **1** (Figure 8E). Addition of excess **2** will stabilize a higher concentration of complex **3** at -133 °C, and indeed a second species is observed in these solutions (Figure 8E). In summary, both the ambient- and low-temperature EPR studies described here are consistent with the possibility that the electron is partly localized on one of the two vanadium atoms and thus characterizes complex **3** as a type II complex on the EPR time scale.

NMR Spectroscopic Studies of Complexes 1–3. As anticipated, because of the paramagnetic nature of complex **1**, no signal is observed by ⁵¹V or ¹H NMR spectroscopy for this compound. A solution of vanadate and Hhida^{2-} , on the other hand, shows two chemical shifts at -499 and -520 ppm.²¹ As described previously, the resonance at -499 ppm represents the V(V)– Hhida complex that forms in the range pH 7–10. The resonance at -520 ppm represents complex **2**.

Complex **3** gives an ¹H NMR spectrum which, with respect to chemical shifts, resembles the ¹H NMR spectrum for complex **2**, albeit with significantly broader lines. In light of the fact that complex **3** forms in significant quantities only in the presence of large excesses of complex **2**, such a spectrum was expected. However, since the examined concentration ranges of complexes should allow observation of a new complex, it is significant that no new signals were observed in solutions containing complex **3**. These results are consistent with the expectation that no NMR spectra will be observed in compounds containing delocalized electrons, or the spectra for complexes **2** and **3** will be identical. Given the structural differences between the two complexes, the former explanation is more likely. To summarize, the ⁵¹V and ¹H NMR spectroscopic studies are consistent with the interpretation that complex **3** contains a partly or fully delocalized electron.

Cyclic Voltammetry of Complexes 1–3. The redox behavior of complexes **1–3** was examined by cyclic voltammogram in DMF (see Figure 9). Each peak was observed separately and as part of a scan. In this way we were assured that the observed signals were not artifacts of other processes. The cyclic voltammogram of **1** shows the presence of two one-electron irreversible waves (Figure 9A). The first irreversible peak is the oxidation of **1** (anodic peak, $+0.78$ V). After the oxidation, a new peak appears during the reverse scan (-0.08 V). The intensity of this peak depends on the scan rate; at scan

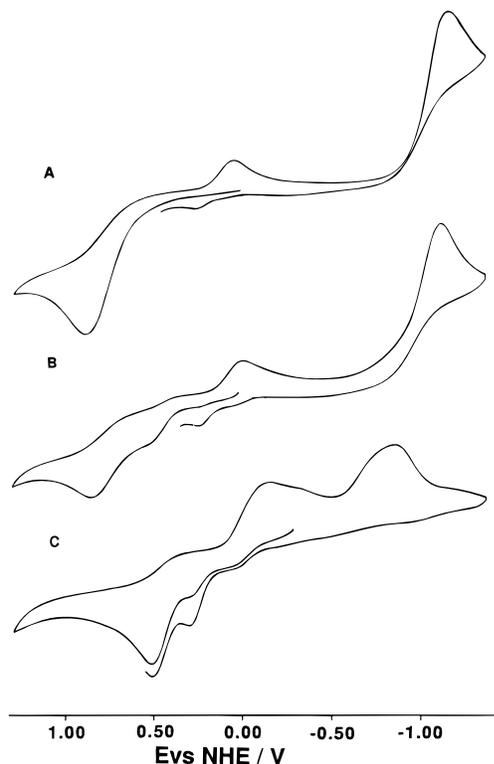


Figure 9. Cyclic voltammograms of DMF solutions prepared from dissolution of 10 mM **1** (A), 10 mM **3** (B), and 10 mM **3** and 50 mM **2**. The dc cyclic voltammograms were recorded at 24 °C at a platinum electrode with the supporting electrolyte tetrabutylammonium perchlorate (0.10 M).

rates less than 20 mV·s⁻¹ no peak was observed. Since compound **2** or the free ligand does not have any redox chemistry in this range (data not shown), compound **1** is oxidized to a vanadium(V) compound different from compound **2**, and this compound is rapidly decomposed. The second irreversible peak is the reduction of **1** (cathodic peak, -1.33 V) to a vanadium(III) compound.

The cyclic voltammogram of a solution prepared by dissolving complex **3** in DMF is shown in Figure 9B. This spectrum contains the peaks observed for **1** and some additional peaks. The cyclic voltammogram of a solution prepared by dissolving complex **3** and adding 5-fold excess **2** is shown in Figure 9C. In this spectrum the peaks for complex **1** have disappeared. Characterization of these solutions by other means (UV/vis, NMR, and EPR spectroscopy) confirm that solutions prepared in this manner contain complexes **2** and **3**. The remaining peaks in Figure 9C are also observed in Figure 9B, in accord with the interpretation that these peaks are caused by a mixed valence complex, complex **3**.

The cyclic voltammogram of **3** shows the presence of two one-electron irreversible waves (Figure 9A). The first irreversible peak is the oxidation of **3** (anodic peak, +0.50 V), perhaps to form the vanadium(V) dimer. The hydrolytic instability of this compound can explain the irreversibility observed in the cyclic voltammogram of **3**. After the oxidation, a new peak appears during the reverse scan (-0.13 V). The intensity of this peak is also dependent on the scan rate. The second irreversible peak is the reduction of **3** (cathodic peak, -0.92 V). However, the broadness of this peak suggests that this process is not a simple reduction of **3** to the vanadium(IV) compound. In the reverse scan, a second scan-rate dependent peak appears at +0.255 V. This spectrum is complex, and detailed understanding of these reactions requires exhaustive electrolysis and characterization of stable species formed during the reaction. However, some information can be obtained from

this spectrum. The redox potential of complex **3** is very similar to that of the pmida mixed valence compound: the $E_{1/2}$ for oxidation of the mixed valence dimer of pmida occurs at +0.52 V and the $E_{1/2}$ for reduction of this species occurs at -0.92 V.¹²

The electrochemistry of complex **3** described here varies from that of other mixed valence vanadium(IV/V) complexes of N/O containing ligands. The mixed valence complex of azobenzene-2,2'-diolate has an $E_{1/2}$ of 0.056 V, and the two homodimers can be generated by exhaustive electrolysis.¹⁵ The electrochemistry of the mixed valence dimer of 8-quinolinate shows oxidation at -0.22 V in acetonitrile, DMSO, and DMF. The vanadium(V) monomer and dimer are both reduced at the same potential (-0.27 V), implying that these species are in equilibrium with each other.¹⁶ In contrast, the electrochemistry of vanadium(IV) and -(V) homodimers of *N*-(hydroxylalkyl)salicylideneamines show no evidence for formation of the mixed valence dimer in appreciable concentrations.³² The vanadium(IV) homodimer is oxidized at +0.50 V, whereas the reverse scan shows reduction at +0.35 V. The vanadium(V) homodimer is reduced at -0.36 V and oxidized at 0.35 V. Both processes are reversible, showing that these homodimers are stable, in contrast to the mixed valence dimer of Hhida²⁻ and related ligands. In the present characterization of complex **3**, the most significant information may be that some ligands of this type will yield both homodimers and mixed valence dimers, whereas others will form one or the other. In the case of Hhida²⁻, it appears that the vanadium(V) homodimer formed from compound **3** is not a stable species.

IR Spectroscopic Characterization of Complexes 1–3. IR spectral data for complexes **1–3** in water, in Nujol suspension, and in KBr plates were obtained.

The IR spectra of the solid state show the V=O stretches at 978 cm⁻¹ for **1**, 924 and 904 cm⁻¹ for **2**, and 956 cm⁻¹ for **3**. This is consistent with the X-ray crystallographic information in which the V=O bond for **1** is shorter than the V=O bonds for **2** and **3**. Furthermore, the fact that only one signal was observed for **3** suggests that the two V=O groups are indistinguishable. The V=O signals observed in the spectra recorded in Nujol suspension confirm this interpretation. The V=O signals in 0.20 M aqueous solutions are 970 cm⁻¹ for **1** and a broad peak at 920 cm⁻¹ for **2**. The spectrum recorded from dissolved complex **3** shows two V=O peaks, one at 970 cm⁻¹ and one at 920 cm⁻¹, consistent with the expectation that complex **3** hydrolyzed in this solution.

The $\nu(\text{COO})$ bands appear at 1616 for complex **1**, in the solid state at 1637 and 1670 cm⁻¹ for **2**, and at 1642 cm⁻¹ for **3**. The fact that compound **3** generates only one signal which is different from the signals for compounds **1** and **2** is in accord with a symmetric structure for compound **3**. Compounds **1–3** contain water and/or methanol and prevent unambiguous assignment and observation of the -OH stretches. Suffice to say that this signal at 3250 cm⁻¹ in the free ligand is sufficiently shifted in the complexes as expected for coordinated residues.

Exploration of the Question, Is Complex 3 a Type II or III Complex? As summarized in Table 4 most of the experimental methods employed in this work generate results consistent with complex **3** containing delocalized electrons. The X-ray studies show the vanadium atoms are indistinguishable and furthermore that the bridging oxygen atom had a fairly regular thermal ellipsoid strongly supporting a type III compound. Magnetic methods confirm the free electron in **3** but provide no further information regarding possible delocalization of the electron. The irreversibility of the redox processes in the cyclic voltammogram preclude conclusions concerning a type II or type III complex without more detailed electrochemi-

cal studies. No new NMR signals are observed in the solution containing **3** consistent with a complex containing some delocalized electrons. However, the results obtained by UV/vis and EPR spectroscopy do not support the above observations. The EPR studies were carried out both at low temperature in frozen solution and at ambient temperature, so it is not possible that subtle changes in the aqueous or DMF media can account for the observations. The UV/vis studies were also carried out at ambient temperatures in both water and DMF without altering the spectroscopic characterization of **3**. It is possible that the type II/type III interchange rate is on the time scale of these experiments, or that the dynamic equilibrium between compounds **1–3** are affecting the results obtained with these methods. In view of the fact that we were interested in the properties of these complexes in aqueous solution, suffice it to say that detailed understanding of these types of complexes is exceedingly difficult, even with careful experimental analysis of the properties of the complex using a variety of methods.

Mixed Valence Dimers: Role in Biological Systems?

Vanadium oligomers bind to proteins and result in inhibition or activation of enzymes.^{4,9,48} Accordingly, it would be surprising if mixed valence dimers did not exert some effect on enzymes. The characterized mixed valence vanadium(IV,V) dimers so far all showed limited stability in aqueous solutions. Regardless of their stability, and even with limited lifetimes, mixed valence dimers could act in biological systems if formed. Since vanadium complexes are receiving increasing interest as potential antidiabetic agents,⁸ it is of interest to address the possibility that such mixed valence complexes could form under physiological conditions.

Mixed valence complexes can form if both vanadium(IV) and -(V) complexes are present at the same time. It is reasonable to expect that most vanadium(V) complexes, at least in part, reduce after entering a cell since vanadate reduces upon entering cells.¹⁰ Presumably these compounds enter through a phosphate transport system or a nonspecific ion transport system and the reduction is proposed to occur once the compound is inside the cell. Many alternative possible pathways to formation of mixed valence dimers exists. One route is the possibility that the monomeric vanadium(IV) complex after reduction rapidly combines with a monomeric vanadium(V) compound (that has not yet reduced) to form a mixed valence complex. The fact the pmida complexes are significantly more stable than the nta and Hhida²⁻ complexes suggests that it may be possible to generate mixed valence complexes of greater stability, which would make their biological properties of greater interest.

Since no information is available on how any mixed valence species interacts in biological systems, the known mechanisms by which other vanadium clusters or compounds act may provide some information. The mixed valence compound could be a vehicle for accumulation of vanadium compounds in various compartments, either as a detoxification mechanism, or by enhancement of the effects of the vanadium compound through temporary storage and/or conversion to more active vanadium compounds. However, before such studies can be undertaken, the chemistry of such species must be understood.

In the present study we have characterized the properties of the Hhida mixed valence dimer and compared it to other known mixed valence compounds. Since the Hhida²⁻ and pmida complexes have the same charges and both have two chelated carboxylate groups, the differences in the stabilities of these complexes attest to the possibility that mixed valence complexes of greater stability can be prepared. Further studies with related

ligands may provide information if the origin of these differences are mainly a result of the structural differences in these complexes (carboxylate cis vs trans) or ligand orbital–metal orbital interactions.

Conclusions

A mononuclear vanadium(IV) complex and a binuclear mixed valence vanadium complex with the ligand *N*-(2-hydroxyethyl)-iminodiacetic acid (H₃hida) have been characterized. The vanadium(IV) complex is formed from the monoprotinated Hhida²⁻ ligand, and its structural and magnetic characteristics are as expected for a six-coordinate vanadium(IV) complex. The solution properties of this complex are consistent with this structure. The vanadium(V) complex was previously characterized in aqueous solution; however, in the current study we crystallized this material and also provide structural characterization in the solid state. Solid state and solution characterization of the two monomeric units thus provide a solid foundation for characterization of the mixed valence complex both in solution and in the solid state. X-ray crystallography, magnetic methods, and IR spectroscopy show that the mixed valence complex contains two indistinguishable vanadium atoms; the thermal ellipsoid of the bridging oxygen atom furthermore strongly points to a type III complex in the solid state. In contrast, characterization of aqueous solutions of this complex by UV/vis and EPR spectroscopies do not provide a consistent description of the complex; these methods suggest the complex is best described as a type II complex. Perhaps the observations with UV/vis and EPR spectroscopy reflect the interchange rate of the type II and type III complexes of **3** versus the time scale of each measurement.

The Hhida²⁻ complexes have some significantly different properties compared to complexes of related ligands: nta, pmida, and s-peida. The overall charge of the mixed valence complex is -1 , as observed for the pmida and s-peida complexes; however, structurally and magnetically the solid state properties of the Hhida²⁻ complex are more similar to the nta complex. In solution, the Hhida²⁻ complex deviates from the known complexes with respect to UV/vis, EPR, and NMR characterization. Furthermore, the mixed valence Hhida²⁻ complex is significantly less stable than the corresponding pmida and s-peida complexes but very similar in stability to the nta and V₂O₃³⁺ complexes. The two latter complexes have significantly higher charges ($3-$ and $3+$). The studies presented in this work suggest that mixed valence dimers can be designed with significantly greater stability: overall low charge and a strongly bonding ligand trans to the V–O–V moiety in the mixed valence dimer.

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Supporting Information Available: Table S3 listing, bond lengths and angles, Table S4, giving anisotropic displacement coefficients, and Table S5, listing hydrogen atom coordinates and isotropic displacement coefficients for complexes **1–3** (9 pages). Ordering information is given on any current masthead page.