N,N′-Bis(2-hydroxyethyl)-1,10-diaza-18-crown-6-KI (5-KI). Recrystallization (THF) gave pure 5-KI (56%) as a white crystalline solid (mp 187–188° C). Anal. Calcd for $C_{18}H_{38}N_2O_6KI$: C, 37.20; H, 6.65; N, 5.42. Found: C, 37.58; H, 6.68; N, 5.42.

N,N′-Bis(2-hydroxyethyl)-1,10-diaza-18-crown-6-NaI (5-NaI). This complex was prepared as previously described.[6]

N-(3-Oxabutyl)monoaza-18-crown-6-KI (6-KI). Recrystallization (THF) gave pure 6-KI (94%) as a white crystalline solid (mp 125–126.5 °C). Anal. Calcd for $C_{15}H_{27}NO_6KI$: C, 36.96; H, 6.42; N, 2.87. Found: C, 37.00; H, 6.55; N, 2.79.

N-(Ethoxycarbonylmethyl)monoaza-15-crown-5-NaBr (7-NaBr). Recrystallization (acetone) gave pure 7-NaBr (53%) as a white crystalline solid (mp 125–126.5 °C). Anal. Calcd for $C_{14}H_{27}NO_6NaBr$: C, 41.19; H, 6.84; N, 3.22; Br, 21.10. Found: C, 41.02; H, 6.84; N, 3.22; Br, 21.10.

X-ray Experimental. Intensity data were collected by ω–2θ scans of variable rate designed to yield measurements of equal relative precision for all significant reflections, using an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. A maximum was placed on the scan time spent on any reflection. One quadrant of data was collected for each crystal within the specified angular limits, one octant for the orthorhombic $K^+ \subset 5\text{-}1$ I^-. Crystal data and specifics of data collection are given in Tables VIII and IX. Data reduction included corrections for background, Lorentz, po-

larization, absorption, and in two cases decay. The absorption corrections were based on ψ scans of reflections near $\chi = 90°$. Equivalent data were merged, and all reflections having $I > 3\sigma(I)$ were used in the refinements. All structures were solved by the heavy atom method and refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_0)$, using the Enraf-Nonius SDP programs. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in difference maps but placed in calculated positions where possible. In the case of $K^+ \subset 1\text{-}22\text{-}1$ I^-, refinement of H atoms was possible.

R factors and residuals in final difference maps are given in the tables.

Vanadium Phenolates as Models for Vanadium in Biological Systems. 1. Synthesis, Spectroscopy, and Electrochemistry of Vanadium Complexes of Ethylenebis[(*o*-hydroxyphenyl)glycine] and Its Derivatives

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Abstract: The ligand ethylenebis[(*o*-hydroxyphenyl)glycine] (EHPG) and its derivatives have been studied as models for vanadium binding sites in biomolecules. A series of vanadium complexes are presented which elucidate the behavior of oxovanadium–phenolate coordination. Vanadium–phenolate chemistry is shown to be quite diverse with stable complexes involving the VO^{2+}, VO^{3+}, $VOOH^{2+}$, and VO_2^+ moieties being isolated and characterized by NMR, UV–visible, EPR, and infrared spectroscopy. Several of these forms of vanadium are seldom observed in chelate chemistry. The electrochemical behavior of these species is also described. In the pentavalent state, vanadium is seen to promote an unusual, stepwise, metal-assisted, oxidative decarboxylation of the EHPG ligand to yield oxovanadium(IV) complexes of *N*-[2-(*o*-salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine (EHGS) and *N,N′*-disalicylideneethylenediamine (SALEN). This reaction has been investigated and a mechanism is proposed. The results of this work should be of value in elucidating the coordination chemistry of vanadium in a variety of biological systems.

In contrast to many other of the biologically important transition metals (Fe, Cu, Mo, etc.), the biochemistry of vanadium has remained for the most part obscure. Vanadium is normally found only in trace amounts in living systems, but certain organisms have been found which concentrate this element, for unknown purposes, to an extraordinary degree.[1,2]

In order to better understand the biological role of vanadium, the coordination chemistry of this element in its three accessible oxidation states (+III, +IV, and +V) with relevant ligands needs to be explored. In light of the reported binding of vanadium to the metal–tyrosinate protein transferrin[3] and its interaction with the recently characterized polyphenol, tunichrome, in the vanadocytes of the tunicates,[4] vanadium–phenolate chemistry seemed an appropriate starting point. To this end we report here the extensive coordination and redox chemistry of vanadium with the ligand, *N,N′*-ethylenebis[(o-hydroxyphenyl)glycine] (EHPG) (Table I) and its derivatives. This ligand has already proved useful

in providing insights into the structure and chemistry of a number of iron–phenolate proteins.[5,6] Some of the data reported here have already appeared in communication form.[7]

Experimental Section

Materials. EHPG was purchased from Sigma and purified by extensive soxhlet extraction with acetone. As obtained commercially, EHPG consists of a 50:50 mixture of two isomers, the racemic *R,R/S,S* pair and a meso *R,S* form. No attempt was made to separate these isomers. Sodium vanadate and 8-hydroxyquinoline purchased from Fisher Scientific and vanadyl sulfate from Aldrich were used without

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Table I

compd	oxidation state[a]	ligand[b]	color
1	IV	*rac*-HEHPG	pale blue
2	IV	*meso*-H₂EHPG	violet
3	IV	EHGS	orange
4	V (dioxo)	*rac*-EHPG	yellow
5	V	*meso*-HEHPG	dark blue
6	V	EHGS	dark blue
7	IV	SALEN	green

a All are monooxovanadium complexes except where noted.
b Ligands used in this study: EHPG = N,N'-ethylenebis[(*o*-hydroxy-phenyl)glycine], EHGS = N-[2-(*o*-salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine, SALEN = N,N'-disalicylideneethylenediamine.

further purification. Acetonitrile and dimethylformamide were obtained from Burdick and Jackson Laboratories and kept stored under nitrogen. Methanol was dried over magnesium methoxide and distilled as needed. N,N'-Disalicylideneethylenediamine (SALEN) was prepared by standard literature methods.

Synthesis. To prevent oxidation of basic solutions of uncomplexed EHPG, all operations were performed via Schlenk line techniques under a nitrogen atmosphere unless otherwise specified.

Ammonium *rac*-[N,N'-Ethylenebis[(*o*-hydroxyphenyl)glycine]]oxovanadium(IV) (1). To 6 mmol of EHPG (0.57 g) was added 18 mmol of aqueous ammonium hydroxide. Following the addition of 6 mmol of vanadyl sulfate (1.3 g) in water, the solution was stirred for 12–16 h during which time the solution turned a blue color. The solution was flash evaporated to dryness and the residue repeatedly recrystallized from 95% ethanol. Slow evaporation of an ethanol solution in the cold afforded large light blue crystals. The crystal structure indicated that the solid product contained only the racemic form of the ligand.[8] Anal. Calcd for NH₄[VO(EHPG)]·H₂O·EtOH: C, 47.4; H, 5.8; N, 8.3. Found: C, 47.1; H, 5.9; N, 8.2.

meso-[N,N'-Ethylenebis[(*o*-hydroxyphenyl)glycine]]oxovanadium (IV) (2). Sodium hydroxide, 40 mmol (1.6 g), and EHPG, (7.2 g), 20 mmol were dissolved in 250 mL of degassed water. To this was added 20 mmol of vanadyl sulfate (4.34 g) and the solution was allowed to stir for 1 day. The flask was left sealed for several weeks, during which time fine purple crystals were deposited. Anal. Calcd for [VO(EHPG)]·3.5H₂O: C, 44.4; H, 4.9; N, 5.7; V, 10.5. Found: C, 44.3; H, 4.9; N, 5.8; V, 10.5.

Sodium [N-[2-(*o*-Salicylideneamino)ethyl](*o*-hydroxyphenyl)-glycine]oxovanadium(IV) (3).[9] To a Schlenk tube containing 250 mL of degassed water was added 44 mmol of sodium hydroxide (1.76 g) and 20 mmol of EHPG (7.2 g) followed by the addition of 20 mmol of sodium vanadate (3.0 g). The resulting mixture was then allowed to stir for 24 h. The red solution was flash evaporated to dryness and the residue was taken up in methanol and filtered 3 times to remove inorganic salts. Slow evaporation of the solution produces crude product as an orange solid. The product can be further recrystallized from methanol. Anal. Calcd for Na[VO(EHGS)]·1.5H₂O·1MeOH: C, 46.9; H, 6.1; N, 4.8. Found: C, 46.8; H, 6.6; N, 5.0.

Trisodium *rac*-[N,N'-Ethylenebis[(*o*-hydroxyphenyl)glycine]]dioxo-vanadium(V) (4). This compound was isolated as a minor product in later collections of 3 from the mother liquor. The small yellow beads

were washed with cold methanol to remove the last traces of 3. Anal. Calcd for Na₃[VO₂(EHPG)]·3H₂O: C, 38.4; H, 3.9; N, 5.0. Found: C, 38.7; H, 4.1; N, 5.0.

meso-[N,N'-Ethylenebis[(*o*-hydroxyphenyl)glycine]]oxovanadium(V) (5). If the synthesis mixture for 2 was opened after a day of stirring and diluted with a 3-fold excess of methanol or ethanol, the vanadyl complex oxidized and within 24 h the solution changed to an intense blue color. Slow evaporation of this solution produced crystals of the desired complex. An alternative route to 5 involved the use of ethanol rather than water as a solvent in the synthesis of 2. However, the product is very difficult to isolate in clean form by this route. Anal. Calcd for [VO-(EHPG)]·1H₂O: C, 48.9; H, 4.3; N, 6.3. Found: C, 49.5; H, 4.5; N, 6.3.

[N-[2-(*o*-Salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine]oxo-vanadium(V) (6). To a solution of pure 3 in methanol was added an equivalent amount of anhydrous ferric chloride. The solution was allowed to stir for 12 h and turned from pale orange to deep blue. This solution was flash evaporated and the residue taken up in a minimum of methanol and chromatographed on a column of neutral alumina with methanol as an eluant. The first band off the column was the dark blue product. A second deep red band, eluted later, is the iron analogue of 6 and is the subject of a separate report.[6] The dark blue product must be evaporated quickly and without heat as it is very unstable toward oxidative decarboxylation. Anal. Calcd for [VO(EHGS)]·1H₂O: C, 51.5; H, 4.3; N, 7.1. Found: C, 51.5; H, 4.4; N, 7.0.

[N,N'-Disalicylideneethylenediamine)oxovanadium(IV) (7). This complex was synthesized for use as a standard by mixing equimolar amounts of vanadium(III) acetylacetonate and SALEN as methanol solutions. After overnight stirring in an open vessel the vanadium(IV) complex 7 precipitates out as green crystals. Thorough washing of the crystals with methanol gives pure product in greater than 95% yield.

Vanadium(III) EHPG Complexes. Equimolar amounts of vanadium-(III) chloride and EHPG were mixed with 3 equiv of base, producing a yellow precipitate from aqueous solution. The resulting solid was schlenk-filtered and dried under vacuum. The air-sensitive product was not characterized further.

Physical Measurements. UV–visible spectra were recorded on a Perkin-Elmer 553 spectrophotometer and near-IR spectra on a Cary 14 spectrophotometer. Infrared spectra were obtained on a Nicolet 6000 FT-IR as KBr pellets. Both ¹³C and ¹H NMR were recorded on a Bruker 250-MHz instrument with Me₄Si as an internal standard for nonaqueous systems. NMR spectra run in deuterium oxide were internally referenced to 1,4-dioxane, dimethyl sulfoxide, or methanol and reported relative to Me₄Si. Spectral simulations of the NMR spectrum of 5 were produced as previously described.[10] Chemical analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY.

Cyclic voltammetry and bulk electrolysis studies at a platinum working electrode utilized a Bioanalytical Systems CV-1B-120 or PAR 174A polarographic analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as the supporting electrolyte and all potentials are reported vs. the saturated calomel electrode, SCE. Electron paramagnetic resonance spectra were obtained on a Varian E-4 spectrometer operating at 9.2 GHz, using quartz flat cells for high dielectric solvents or cylindrical quartz tubes for low dielectric ones. Mass spectrometry was carried out on a Finnegan MAT 4500 instrument by using direct exposure techniques. Thermogravimetric analyses utilized a Perkin-Elmer TGS-2 system. Conductivity measurements were made on ~10⁻³ M solutions using a Model RC 16B2 conductivity bridge from Industrial Measurements Inc.

Values for the pK_as of the complexes were determined either from Schwartzenbach plots of spectrophotometric titrations[11] or via nonlinear least-square refinement of potentiometric data using the program OR-GELS.[6]

The identity of the ligand isomer (racemic or meso) in the metal complexes was determined either by NMR methods[12] or by the TLC

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(9) Alternate neomenclature for the ligand EHGS previously reported include N,N'-ethylene((*o*-hydroxyphenyl)glycine)salicylidenimine and N-[2-((*o*-hydroxyphenyl)glycino)ethyl]]salicylidenimine.

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(12) The isomer form of the ligand can be ascertained by NMR analysis of the free ligand obtained by 8-hydroxyquinoline demetalation of the vanadium complexes. At "pDs" below 13.5 the α-proton on the chiral carbons has a distinct chemical shifts for each of the two forms and can be identified by this method. The chemical shifts of these peaks are seen to vary as a function of pH and above pH 13.5 coalesce into a single peak at 4.25 ppm. These changes are caused by sequential deprotonation of the two phenol groups. A complete NMR titration of the α-protons as a function of pH for the two isomers from the solubility threshold (~pH 9) to its fully deprotonated form (pH 14) is given in the supplementary material.

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behavior of the iron complexes prepared by a transmetalation reaction [R_f 0.38 (meso), R_f 0.58 (rac); silica gel, 5:3:2 ethanol/toluene/methanol as eluting solvent].

Results

Synthesis and Characterization. A listing, summarizing the compounds prepared in this study, is shown in Table I.

Vanadium(III) Complexes. A vanadium(III) complex of EHPG was isolated but not well characterized. The isolated yellow compound was very air-sensitive in solution and moderately so as a dry solid, making most studies very difficult. Exposure of solutions of the vanadium(III) species to air resulted in rapid formation of a deep blue color characteristic of vanadium(V) complexes (vide infra). Further work on this species will be reported at a later time.

Vanadium(IV) Complexes. Since EHPG has four acidic protons the resultant charge of a metal complex and the nature of the donor atoms which will coordinate to the metal will depend upon pH. We have noted the formation of several colored species with the vanadyl ion and EHPG.

Ammonium *rac*-[*N,N*-Ethylenebis[(o-hydroxyphenyl)-glycine]]oxovanadium(IV) (1). The addition of 3 equivalents of base to a solution of VO^{2+} and EHPG yields a blue solution of **1**. This complex has been characterized by X-ray structural analysis[8] to be six coordinate with the two nitrogens, two carboxylates, and one phenolate group bound to the vanadyl ion. The other phenolate group is protonated and uncoordinated. The structure is unusual in that one of the ethylenediamine nitrogens is trans to the vanadyl oxygen rather than cis, as is almost always observed in these types of complexes.

Protonation of **1** leads to the formation of a green solution below pH 4. Further addition of acid (ca. pH 2.5) leads to precipitation of a white solid which has been identified as free *rac*-EHPG by NMR.[12] Addition of base to **1** results in formation of a red solution. The apparent pK_a of this process was 8.1 as determined by optical titration. The titration curve displays considerable hysteresis upon reacidification of the red solution. We interpret these results as indicating that as the pH of a solution of **1** is lowered, the lone coordinated phenol is protonated and released giving the green, five-coordinate, square-pyramidal complex with only carboxylate and nitrogen donors. Further protonation leads to complete ligand dissociation. If the pH of a solution of **1** is raised, the previously uncoordinated phenol is deprotonated with a pK_a = 8.1. As it is a better base than carboxylate, the deprotonated phenol replaces a carboxyl group in the coordination sphere to produce the red complex. Maintenance of octahedral geometry in the red complex is supported by infrared analysis (vida infra). The hysteresis in the titration curve suggests that **1** is in a metastable geometry and that, upon coordination of the second phenol, probably returns to the more stable geometry with the two ethylenediamine nitrogens in the equatorial plane. This would also place the two phenolates into the equatorial plane, and the lone carboxylate group trans to the vanadyl oxygen in the axial position (as is seen for all other *rac*-EHPG metal complexes studied so far).[13]

***meso*-[*N,N'*-Ethylenebis[(o-hydroxyphenyl)glycine]]oxovanadium(IV) (2).** Reaction of vanadyl ion and EHPG with 2 equiv of sodium hydroxide yields a violet solution from which **2** can be isolated as fine purple crystals. Compound **2** is a nonelectrolyte in methanol and has been determined by pH titration to have an equivalent weight of 465 g/mol. The potentiometric titration of **2** (Figure 1) reveals two break points at 1 and 2 mol of base/mol of complex with pK_a's of approximately 3.5 and 8.0. These represent the titration of unbound carboxyl and phenol groups, respectively. The presence of a free, protonated carboxyl group in **2** is also indicated by the presence of a 1700-cm^{-1} band in the infrared spectrum. The IR also reveals a V=O stretch at 979 cm^{-1}, indicative of five-coordinate square-pyramidal geometry (vide infra). The coordination environment therefore consists of two ethylenediamine nitrogens, a carboxylate, and a phenolate
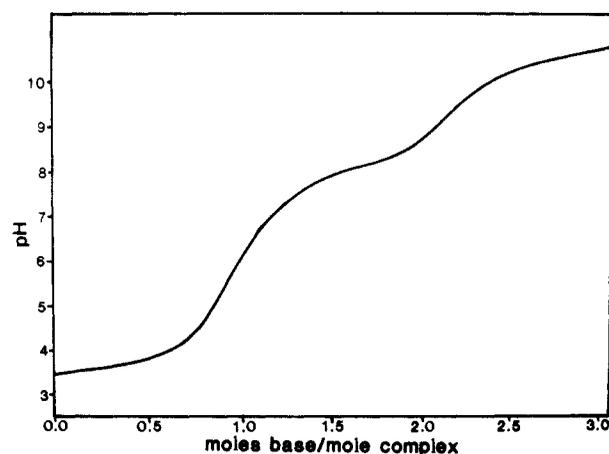

Figure 1. Potentiometric titration of **2** in water.

Table II. EPR Data for Vanadium(IV) Complexes

compound	g_0	$g_\perp$	$g_\parallel$	$A_0{}^a$	$A_\perp{}^a$	$A_\parallel{}^a$
1 (H_2O)	1.968	1.975	1.954	91.8	54.0	165.3
2 (pH 10.5)	1.978			87.3		
2 (MeOH)	1.984			85.8		
3 (H_2O)	2.000	2.019	1.961	87.7	50.0	163.0
7 (DMF)	1.974	1.985	1.951	92.6	59.2	159.3

$^a \times 10^{-4}$ cm^{-1}.

oxygen, with the vanadyl oxygen completing the coordination sphere. The remaining carboxyl and phenolate groups of the potentially hexadentate EHPG ligand are protonated and uncoordinated. Although **2** is stable in aqueous solution it is rapidly oxidized to deep blue **5** in undegassed alcohol containing solvents.

Sodium [*N*-[2-(o-Salicylideneamino)ethyl](o-hydroxyphenyl)-glycine]oxovanadium(IV) (3). Attempts to prepare vanadium(V) complexes of EHPG by reaction with vanadate ion resulted, upon introduction of alcohol solvents, in the surprising isolation of **3** in good yield. Compound **3** was shown to be a vanadyl complex by the characteristic eight-line EPR signal (Table II) and a solution magnetic moment, as measured by the Evans method,[14] of 1.65 μ_B, near the spin only value expected for a d^1 vanadium(IV) species. The complex was found to be 1:1 electrolyte by conductivity measurements and ion exchange chromatography indicated that it was an anion. Elemental analysis indicated the loss of the elements of CO_2 from a vanadium(IV) EHPG complex, and a new IR band at 1615 cm^{-1} suggested the formation of an imine bond. Thus it appears that in the presence of vanadium(V) the EHPG ligand has undergone an oxidative decarboxylation with the formation of a complex with a reduced metal center and a new pentadentate ligand, *N*-[2-(o-salicylideneamino)ethyl](o-hydroxyphenyl)glycine (EHGS) (see Table I). This has subsequently been borne out by a single-crystal X-ray diffraction analysis of **3**, which shows the two phenolate oxygens, the saturated amine nitrogen, and the imino nitrogen all in the equatorial plane, with the lone remaining carboxylate group occupying an axial position trans to the vanadyl oxygen.[8] This remarkable oxidative decarboxylation of EHPG by vanadium(V) appears to be a characteristic feature of these systems (vide infra).

Vanadium(V) Complexes: Trisodium *rac*-[*N,N'*-Ethylenebis-[(o-hydroxyphenyl)glycine]]dioxovanadium(V) (4). When we began this work we expected to be able to form complexes of vanadium(V) with EHPG similar to those formed by other multidentate chelates such as EDTA.[15] Almost all the previously reported complexes involve the dioxovanadium(V) moiety, VO_2^+, as the coordinating center. We have found to our surprise that such compounds are extremely difficult to prepare by direct reaction of vanadate with deprotonated EHPG due to the unexpected decarboxylation of the ligand in the presence of the pentavalent

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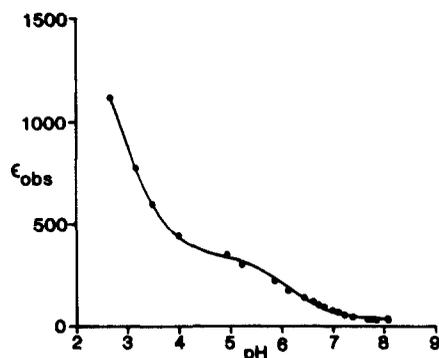(15) Amos, L. W.; Sawyer, D. T. *Inorg. Chem.* **1972**, *11*, 2692.

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Figure 2. Spectrophotometric titration of **4** in 25% methanol/water. The solid line is the nonlinear-least-squares fit and circles the experimental data.

metal. A small quantity of a yellow crystalline material, **4**, was isolated, however, from the same reaction mixture which produced **3**. This new material was diamagnetic and appeared to be a 3:1 electrolyte in water as determined by its conductivity. Ion exchange chromatography indicated that it was an anion. Elemental analysis was consistent with the formulation $Na_3[VO_2$-$(EHPG)] \cdot 3H_2O$. There are two V=O stretching bands at 926 and 981 cm^{-1} in the IR spectrum, indicating a cis dioxo arrangement as is seen in all other VO_2^+ complexes.[16]

Titration of **4** with acid showed a sharp break at 1 equiv of acid which gave an equivalent weight of 545, compared to a theoretical value of 558 based on analysis. Addition of further equivalents of acid led to a second low pH buffer region below pH 4, which resulted in a change in color from pale yellow to deep blue.[3] Below pH 2 a white solid was observed to precipitate which proved to be the free, protonated, racemic isomer of EHPG, as determined by NMR.[12] The first buffer region was fit for a single ionization with a pK_a of 6.3. The second buffer region, which occurred over the addition of 4 equiv of acid, was not fit since it clearly involved a number of overlapping protonations with similar pK_a's in the 3.0 range.

Absorbance spectra were also recorded over the same pH range as above. The initial protonation increases the molar absorbtivity slightly (λ_{max} = 580 nm). The second protonation causes a much larger increase in the absorbance, such that by pH ~2.5 there is an intense band at 595 nm with an extinction coefficient of approximately 1200 M^{-1} cm^{-1}. The spectral data were fit to two successive ionizations by using a nonlinear least-squares refinement to give pK_a's of 6.1(1) and 3.1(1) in agreement with the pH titrations. Several sets of data were fit, Figure 2 being representative.

All these results taken together indicate that the initial complex has the VO_2^+ moiety coordinated to the EHPG through the two ethylenediamine nitrogens and the two phenolate oxygens. The two remaining carboxylate groups are uncoordinated but ionized. The pK_a of the first protonation [6.1(1)] is not in the range expected for either carboxyl or phenol groups on EHPG and has little effect on the optical spectrum of **4**. This protonation has been assigned as the reaction

$$VO_2(L) + H^+ \rightarrow VOOH(L) \qquad L = EHPG$$

Here the VO_2^+ group is being protonated to yield the $VOOH^{2+}$ moiety. The second protonation is seen to have a substantial effect on the optical spectrum, the intense band of which must (in this d^0 system) arise from a phenolate to metal charge-transfer transition. There are several possible means by which this optical change could occur. First, coordination of an additional phenolate group would be expected to increase the intensity of a phenolate to metal charge-transfer transition. However, it is unreasonable to suppose that lowering the pH would cause a phenolate group, that was free, to coordinate to the metal center. Protonation of the dangling carboxyl groups would not be expected to have any

Table III. $E°$ Values of the Vanadium IV/V Couples for the Complexes in This Study[a]

compd	solvents			
	H_2O	MeOH	AN	DMF
2	+0.460	+0.310	+0.208	+0.176
3/6	+0.285	+0.134	+0.065	+0.020
4a	+0.455	+0.280	+0.220	+0.140
5	NS	−0.003	−0.050	−0.104
7	NS	+0.300	+0.460	+0.375

[a] NS = not soluble; all potentials reported vs. SCE (**4a** is the blue, protonated form of **4**).
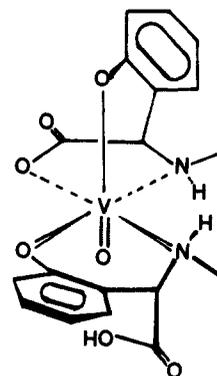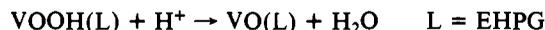

Figure 3. Proposed configuration of EHPG about monooxovanadium(V) in complex **5**.

significant effect on the phenolate oxygen to metal charge-transfer transition. The final possibility, which we feel is correct, is protonation of the $VOOH^{2+}$ center:

$$VOOH(L) + H^+ \rightarrow VO(L) + H_2O \qquad L = EHPG$$

This would be expected to result in the formation of an intense LMCT band (vide infra) if the phenolates were already coordinated.

The dark blue product of the protonation of **4** appears to be the *rac*-EHPG analogue of **5**, although we have been unable to isolate and purify it. Work on this material is hampered by the decarboxylation of vanadium(V) EHPG complexes to form **3**[17] and by our failure to crystallize it, as was possible with the meso form, **5**. Nevertheless, optical and electrochemical measurements are consistent with the interpretation that it is the racemic isomer analogue of **5**, i.e., a vanadium(V) monooxo complex.

Although dioxovanadium(V) complexes of EHPG are difficult to prepare, a series of monooxovanadium(V) complexes could be isolated by the oxidation of the parent vanadyl species. The oxidations proved to be very solvent dependent. In alcohol-containing solvents the vanadium(IV) species were generally spontaneously oxidized by molecular oxygen to yield the monooxovanadium(V) species. However, in aqueous solvents the complexes were inert to oxygen and could only be oxidized with more vigorous oxidants. These observations are consistent with the measured redox potentials in these solvents (Table III).

***meso*-[*N*,*N'*-Ethylenebis[(*o*-hydroxyphenyl)glycine]]oxovanadium(V) (5).** Deep blue compound **5** was a neutral, diamagnetic complex of vanadium(V). Mass spectrometry (direct exposure probe) revealed a molecular ion at 424 amu which corresponds to [VO(EHPG)]. We believe that a VO^{3+} moiety is bound to the potentially hexadentate EHPG through the two ethylenediamine nitrogens, two phenolates, and a carboxylate group (Figure 3). The remaining carboxylate group is protonated

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(16) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 400.

(17) The meso form of the ligand is much labile toward decarboxylation to produce **3** than the racemic form. Periodic checking of the reaction mixture that precipitates **3** reveals that all the *meso*-EHPG has been consumed in 2–3 days. This apparently explains the ability to crystallize only the dioxo-vanadium(V) complex of the racemic isomer, as the meso complex is consumed too rapidly to be isolated. The complex **4** does decarboxylate in methanol to produce **3** but at a much slower rate. The decarboxylation of **4** also occurs in water to produce a mixture of **3**, **6**, and **7**.

Table IV. NMR Chemical Shift Data (ppm vs. Me$_4$Si)
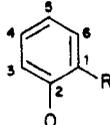
carbon	EHPG	5	SALEN
		^{13}C	
carboxyl	180	171, 169	–
imine	–	–	166
2-ring carbons	163	162, 161	161
1,3–6-ring carbons	130–115	133–113	132–117
methylene	63	67, 65	60
α	47	52, 46	–

proton	EHPG	5	6	SALEN
		^{1}H		
amine	NA	6.38 [A]*, 5.02 [C]	8.45 (s)*	–
imine	–	–	9.04 (s)	8.6 (s)
α	~4.5 (s)	5.27 [B], 4.28 [D]	4.55 (s)	–
methylene	2.63 (s)	3.05 [E], 3.04 [F], 2.62 [G], 2.27 [H]	4.47 (s), 4.08 (s), 3.60 (s), 3.20 (s)	3.95 (s)
phenol	6.5 (m), 7.0 (m)	6.9 (m), 7.0 (m), 7.1 (m), 7.2 (m)	7.0 (m), 7.3 (m), 7.8 (m)	6.9 (m), 7.4 (m)

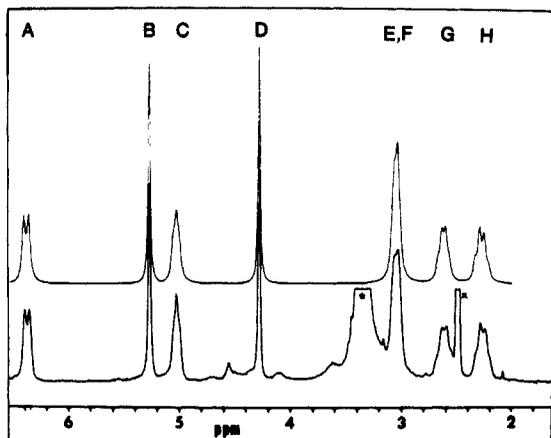*^{a}– = does not apply; * = exchanges with deuterium oxide; NA = not available; [] = peak designations in Figure 5.*

Figure 4. ^{1}H NMR spectra of 5 in Me$_2$SO-d_6 (bottom) and spectral simulation (top) (* is due to H$_2$O and X is due to undeuterated impurities in the Me$_2$SO).

and uncoordinated as is indicated by a broad NMR peak, integrating to one proton at 13.6 ppm and a characteristic infra red band at 1704 cm^{-1}. The overall structure is supported by ^{13}C and ^{1}H NMR data, summarized in Table IV. Computer simulation of the ^{1}H spectra in Me$_2$SO-d_6 gave a satisfactory fit (Figure 4), but required a line width of 9 Hz (probably due to traces of paramagnetic vanadium(IV)). The magnitude of this line width made a Karplus analysis of the ethylenediamine region of the complex impossible. The absolute value of the coupling constants for the entire spectra, as generated by the simulation of each proton's decoupled spectra, are J_{AH} = 11, J_{EG} = 8, J_{CF} = 6, J_{FH} = 10, J_{CG} = 8, and J_{GH} = 10 Hz. A change in the sign of these values produced no significant effects due to the magnitude of the line widths employed. The remaining coupling constants were assumed to be zero. It should be noted, however, that some of the couplings could be as high as 3 Hz before any change in the simulation would be observed. Assignments of the peaks in Figure 4 are based on off resonance decoupling and are given in Table IV. The ABMX pattern observed for the methylene protons, rather than the A$_2$B$_2$ pattern seen in simplier complexes of this ligand,[16] is believed to be caused by the anisotropic shielding of the axial phenyl ring, causing protons G and H to be shifted upfield to different degrees. The downfield portion of the spectrum (not shown) contains an AA'BB' pattern in the region near 7 ppm, integrating to eight protons and assigned to the phenol ring protons.

Table V. UV–Visible Spectral Parameters

compd	λ_{max}, nm	ϵ, M/cm	10Dq, cm^{-1}
	Vanadium(IV) Complexes		
1 (H$_2$O)	570, 820	45, 25	17 500
2 (MeOH)	540	160	18 500
3 (H$_2$O)	520, 800	110, 23	19 200
7 (CHCl$_3$)	592	180	16 900
7 (Me$_2$SO)	576		17 400
	Vanadium(V) Complexes		
4a^a	595	1200	LMCT
5 (MeOH)	570	3013	LMCT
6 (MeOH)	580	1992	LMCT

^{a}25% MeOH/H$_2$O.

Experiments done in both DMF and Me$_2$SO show that the downfield amine proton (A) exchanges on addition of small quantities of deuterium oxide. However, the upfield amine proton (C) is shielded from exchange, probably due to strong hydrogen bonding with the free carboxyl group. The presence of two distinct sets of peaks in the ^{13}C spectrum of 5 demonstrates the asymmetry in the coordination of the EHPG ligand to VO^{3+}. NMR studies of the demetalated ligand show it to be exclusively the meso form of EHPG.[12]

Although we have been unable to obtain an X-ray structure for 5, a geometry such as that shown in Figure 3 can be inferred.[18] The presence of the axial phenol is based on our detailed electrochemical analysis of this complex.[19]

[*N*-[2-(*o*-Salicylideneamino)ethyl](*o*-hydroxyphenyl)glycine]-oxovanadium(IV) (6). A final vanadium(V) complex was prepared by oxidation of 3 either electrochemically or by FeCl$_3$ in methanol. This dark blue, diamagnetic, neutral solid, 6, is V^{V}O(EHGS). Compound 6 was sufficiently stable in dimethylsulfoxide to allow NMR studies (Table IV). The observation of an imine proton, at 9.04 ppm, and a shift in the lone chiral center's proton to 4.55 ppm show the effects of ligand oxidation. The amine proton was also observed (8.45 ppm) and was identified by its ability to exchange on addition of deuterium oxide. Infrared spectral data also support the presence of the imine group. Since the completely reversible electrochemical transformation of 3 to 6 (vide infra) suggests no significant structural changes to 3 upon oxidation, we can safely assign the structure of 6 as simply the oxo-vanadium(V) analogue of 3, whose structure is already well established by X-ray crystallography.[8]

Discussion

Optical Spectroscopy. The optical spectra of all of the vanadium(IV) species are outlined in Table V. Oxovanadium(IV) compounds generally display three d–d bands in the regions 900–625, 690–520, and 470–330 nm, with extinction coefficients in the 5–100 M^{-1} cm^{-1} range. The highest energy band is frequently obscured by the tail of strong transitions in the ultraviolet. In the Ballhausen–Grey ligand field scheme these are assigned as b$_2$ → e, b$_2$ → b$_1$, and b$_2$ → a$_1$ transitions, with the second transition maximum yielding the value of 10Dq directly. However, it should be noted that there is still no real agreement on the ordering of the levels.[20] Most of the EHPG-like complexes reported here show only two bands in the 330–900-nm range. We assign the higher energy band as the b$_2$ → b$_1$ transition with the b$_2$ → a$_1$ transition obscured by the tails of intense intraligand transitions in the UV. The low energy, b$_2$ → e transition is observed in 1 and 3 at 820 and 800 nm, respectively.

Vanadium(V) is a d^0 species and as such no d–d bands are expected or observed. Indeed all complexes containing the common VO$_2$$^+$ cation are pale yellow, including 4. However, complexes with the VO^{3+} or bare V^{5+} bound to phenolic or catecholate groups all display intense absorbance bands in the visible region

(18) The structure of a related monooxovanadium(V) complex will be reported separately.

(19) Bonadies, J. A.; Carrano, C. J., submitted for publication in *Inorg. Chem.*

(20) Selbin, J. *Coord. Chem. Rev.* **1966**, *1*, 293.

Vanadium Phenolates as Models for Vanadium

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Table VI. V=O Stretching Frequencies for Vanadium EHPG Complexes

complex	ν (V=O), cm^{-1}	medium	coordination geometry[a]
Vanadium(IV) Complexes			
1	948	KBr	octahedral
1 (pH 9)	955	D$_2$O	(octahedral)
2	979	KBr	(sq pyramidal)
3	952	KBr	octahedral
7	981	KBr	sq pyramidal
7	953	DMSO	(octahedral)
Vanadium(V) Complexes			
4	926, 981	KBr	ND
5	973	KBr	ND
6	950	KBr	ND

[a]Geometry in parentheses is that suggested from IR data; others were determined crystallographicly. ND = not determined from IR data.

from about 550 to 800 nm (Table V). These must be assigned as ligand to metal charge transfer (LMCT) transitions from the phenolate oxygens to empty d orbitals on the vanadium. Such transitions are characteristic of phenolate or catecholate coordination to all easily reducible metal ions.[21,22] The lack of visible charge transfer bands when VO$_2{}^+$ is coordinated to phenolate groups, and the very weak band seen for VOOH^{2+}, are consistent with a raising of the d orbital energy due to a decreasing net positive charge at the metal center. This has the effect of raising the LMCT energy into the UV region of the spectrum. There also appears to be a correlation between the intensity of the charge-transfer band and the formal charge on the coordination center, with the highest intensity seen for the highest charge.

Infrared. The stretching frequencies for all the vanadium(IV) EHPG and related complexes are shown in Table VI. Crystal structure data are available now for three of the species[8] and their coordination geometries are well established. Although it is dangerous to indiscriminently use the V=O stretching frequency as a probe of complex coordination geometry, it does appear safe to conclude (within this set of very similar complexes) that values ~950 cm^{-1} are indicative of octahedral geometry and values of ~980 cm^{-1} of square pyramidal. The reduction in V=O stretching frequency from 980 cm^{-1} in square-pyramidal complexes to 950 cm^{-1} in octahedral is due to the expected weakening of the V=O bond by the trans effect of the added ligand.

The V=O stretching frequencies for the pentavalent vanadium complexes, 4–6, are also given in Table VI. Since we have less of a basis to apply the above criteria on the vanadium(V) members of this series, no attempt has been made to correlate V=O stretching frequencies and structure. The significance of the pair of peaks for 4 with respect to a cis dioxo geometry about vanadium(V) has already been discussed.

Electrochemistry. The electrochemical behavior of both 2 and 5 is quite complex and has been extensively studied (the two are opposite corners in an ECEC square mechanism) and is the subject of a forthcoming paper.[19] However, under certain conditions (see Table III) the chemical reactions that follow electron transfer can be supressed and electrochemical data restricted to the electron transfer steps can be collected. Under these conditions 2 and 5 undergo reversible one-electron oxidation and reduction, respectively. The E° values of the vanadium +4/+5 couple of 2 and the vanadium +5/+4 couple of 5 are given in Table III.

Compound 3 was found to undergo a completely reversible one-electron oxidation as evidenced by cyclic voltammetry in a variety of solvents (Table III, Figure 5). The one-electron nature of this process was confirmed by exhaustive electrolysis which consumed the expected number of Coulombs. Upon oxidation, the pale orange 3 turned an intense blue (Figure 6). The blue oxidized species proved to be compound 6, as determined by cyclic voltammetry, optical spectroscopy, and thin-layer chromatography.

(21) Gaber, B. P.; Miskowski, V.; Spiro, T. G. *J. Am. Chem. Soc.* **1974**, *96*, 6868.

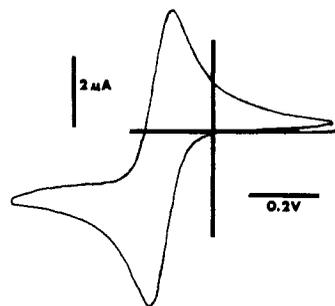(22) Patch, M. G.; Carrano, C. J. *Inorg. Chim. Acta* **1981**, *56*, L71.

Figure 5. Cyclic voltammogram of 3 in methanol (0.1M TBAPF$_6$) at 0.1 V/s on a spherical platinum electrode.
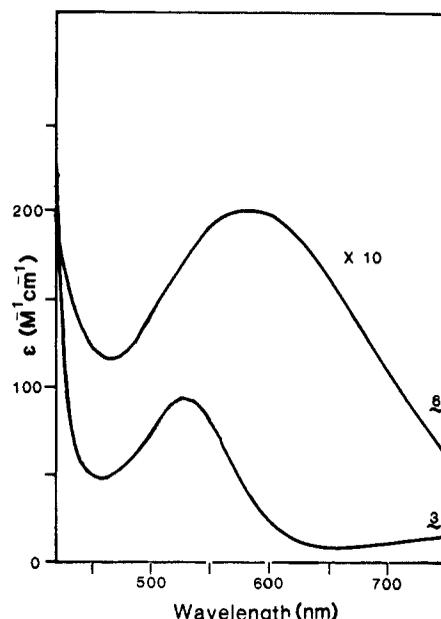

Figure 6. Visible spectra of 3 and 6 in methanol. Compound 6 is shown at one-tenth intensity. Spectra interchange on bulk electrolysis across the vanadium +4/+5 couple.

Rereduction yielded 3 unchanged. The process could be repeated many times without any evident chemical degradation. Oxidation of 3 either chemically or electrochemically proved to be a useful means for the synthesis of 6. As would be expected with all potential donor groups of the ligand coordinated, the electrochemistry of the 3–6 redox couple is pH-independent. Cyclic voltammograms of pure compound 6 were identical with those for 3 with the exception that the initial process was a reduction rather than an oxidation. Bulk electrolysis of 6 gave 3, as expected.

The highly charged nature of 4 (a trianion) makes its study in nonaqueous solvents difficult due to its low solubility. The addition of small amounts of acid, however, generates the dark blue species (designated 4a) seen previously in the potentiometric and optical titrations. Cyclic voltammetry on 4a reveals a one-electron reduction with an E° value in the range expected for a five-coordinate monooxovanadium species on the basis of other members in this series. The fact that the reduction is completely reversible indicates that the five-coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. In contrast, our other five-coordinate complex 2 (a vanadium(IV) compound) is unstable upon oxidation and undergoes a followup chemical reaction to add a ligand donor group, stabilizing the now more electron-deficient vanadium(V) center.[19] That 4a does not add an additional ligand donor to become six-coordinate despite the presence of two additional potential donor groups is probably due to the fact that initially the EHPG utilizes only four donor groups (two amines, two phenols) on the dioxovanadium(V) center of 4. With the loss of an oxo group (by protonation) the stereochemistry of the ligand precludes coordination of either of the dangling donors without dissociation of a previously bound group.

Thus the metal is unable to adopt the more favorable six-coordinate geometry and remains five-coordinate in both oxidation states.

The $E°$ values for compounds 2-6, including 4a, all show a similar solvent dependence, H_2O < MeOH < AN < DMF, with respect to potential (see Table III). These shifts are consistent with those seen in previous electrochemical solvent studies,[23] with respect to the polarity of the solvent.

Oxidative Decarboxylation Reaction. Although the oxidative decarboxylation of the EHPG ligand was first observed in the synthetic reaction that produced 3, this reaction proved difficult to study. However, the instability of 5 toward decarboxylation provided a convenient system. In air, solid 5 is stable indefinitely at room temperature, but in solution it was found to decompose more or less rapidly, depending upon solvent. Allowing a solution of dark blue 5 to stand in warm acetone for several days yielded large green crystals of a decomposition product. These crystals have been identified by X-ray crystallography as the previously reported vanadyl (SALEN) 7.[24] This remarkable transformation of the EHPG complex to the SALEN complex requires the loss of two CO_2 molecules, two protons,[25] and two electrons per EHPG ligand with the concomitant oxidation of the two amino nitrogens to imino nitrogens. Although there are a number of reported metal-assisted ligand oxidation reactions which convert coordinated amines to imines,[26-28] most notably involving Fe^{3+} or Ru^{2+}, to our knowledge this is one of the few examples of this type of reaction involving an oxidative decarboxylation[29] and the first with vanadium(V). The reaction can be readily followed by the loss of the charge-transfer band at 590 nm in the optical spectrum of 5 upon heating to 50 °C in DMF. The reaction occurs rapidly in this solvent but the kinetics of the process are extremely complex and we have been unable to analyze them quantitatively. The reaction also occurs rapidly in other high donor number solvents including dimethyl sulfoxide, formamide, or pyridine. In alcohol the same reaction occurs only extremely slowly; however, the formation of a transient dark blue species is observed by TLC. Its isolation and characterization demonstrate it to be the monodecarboxylated, monoimine complex 6. Thus the expected intermediate in the transformation of 5 to 7 can be isolated in hydroxylic solvents. Electrochemistry in methanol (0.1 M TEACl) was also capable of following the transformation of 5 through the intermediate to 7. The initial cyclic voltammograms showed only the couples expected for 5. Over time, however, a new couple developed at the expense of 5 which corresponded to the monodecarboxylated vanadium complex 6. Still later this new couple disappeared and a third couple grew in corresponding to 7. The time frame involved is approximately 16 days to a predominantly 6 stage and 6 weeks to predominantly 7.

Evidence for several intermediates can also be seen in DMF by optical spectroscopy. Rather than the single isosbestic point expected if 5 were converted directly into 7, several sequential sets of isosbestic points were observed in the UV–visible spectra during the breakdown of 5. This is indicative of the multistep nature of the reaction. The monodecarboxylated intermediate complex could also be detected upon reaction in the solid state. Thermogravimetric analysis of the decomposition of 5 displayed two thermal processes. The first transition occurred at ∼190 °C and resulted in a 10% weight loss, corresponding to the loss of a single CO_2. The second transition occurred at ∼330 °C and involved a 9% weight loss, corresponding to loss of a second CO_2.
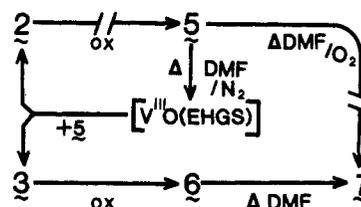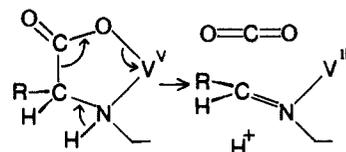

Figure 7. Decarboxylation scheme summarizing the processes occurring for EHPG conversion to SALEN through the various intermediates.

Thus the sequential loss of CO_2 is seen in the solid-state decomposition of 5 as well as that in solution.

While the mechanism of this decarboxylation reaction is still not clear, a number of additional observations suggest a reasonable possibility. When dark blue 5 is heated in DMF in the *absence* of oxygen no production of 6 or 7 is observed, rather a pale yellow solution is formed. If air is allowed into the hot solution, 7 is rapidly generated. If, however, the solution is first cooled and then oxygen admitted, the pale yellow solution gradually turns a dark blue again.

EPR and solution magnetic measurements by the Evans method[14] on the pale yellow solution indicated that reduction of the previously diamagnetic 5 has occurred. Vanadium(IV) is indicated by the presence of the characteristic eight-line EPR spectrum and the solution moment of ∼1.9 μ_B.[30] If the DMF is removed prior to oxygen exposure and the residue dissolved in MeOH, two major products can be identified by electrochemical analysis. These are $V^{IV}O(EHGS)$ (3) and $V^{IV}O(EHPG)$ (2). When the cooled yellow DMF solution is exposed to air for several hours it regains a deep blue color. Removal of DMF and redissolving the residue in methanol also reveals two products (as determined by TLC) in ∼1:1 ratio. These products are $V^VO(EHGS)$ (6) and V^VO-(EHPG) (5).[31] A mechanism which is consistent with all the data presented can easily be envisioned.

Upon heating 5 in the absence of oxygen the ligand is oxidatively decarboxylated with the concomitant reduction of vanadium(V) to vanadium(III). This is consistent with two-electron stoichiometry.[32] The $V^{III}O(EHGS)$ thus generated can then be

oxidized by the unreacted $V^VO(EHPG)$ (5) by the following route to generate $V^{IV}O(EHGS)$ (3) and $V^{IV}O(EHPG)$ (2).[33]

$$V^{III}O(EHGS) + V^VO(EHPG) \rightarrow$$
$$V^{IV}O(EHGS) + V^{IV}O(EHPG)$$
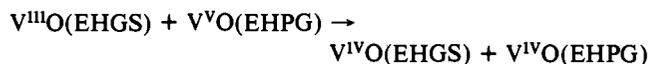
Upon addition of O_2 to the cooled solution (in DMF) both $V^{IV}O(EHGS)$ (3) and $V^{IV}O(EHPG)$ (2) should be oxidized to their respective vanadium(V) states, as is indeed observed. Evans measurements on the regenerated blue solution also indicate a return to diamagnetism as expected for vanadium(V) species. The

(23) Gutmann, V.; Gritzner, G.; Danksagmuller, K. *Inorg. Chim. Acta* **1976**, *17*, 81.

(24) Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198.

(25) A third proton is ultimately lost from the dangling protonated carboxyl in 5 when it coordinates to the open site.

(26) Meyer, T. J.; Brown, G. M.; Weaver, T. R.; Keene, F. R. *Inorg. Chem.* **1976**, *15*, 190.

(27) Diamond, S. E.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884.

(28) Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1972**, 207.

(29) Sayre, L. M.; Jin, S. J.; Urbach, C. L. *Abstr. Pap.—Am. Chem. Soc.* **1985**, *190th*, INOR 65.

(30) The moment is somewhat high for all the vanadium to be in the vanadium(IV) form since μ_{eff} for vanadyl ion is 1.7 μ_B and may suggest the continued presence of some vanadium(III).

(31) R_f values 5, 0.36; 6, 0.16. Eluting solvent 5:3:2 ethanol/toluene/methanol on silica gel plates.

(32) Although we have described the decarboxylation process as occurring through a simultaneous two-electron transfer, the alternative involving sequential one-electron transfer is equally possible.

(33) The oxo group initially on the $V^VO(EHPG)$ is probably protonated to V–OH since V(III) has little affinity for an oxo group and a proton is liberated in the decarboxylation. A second proton would be released when the open coordination site generated by the decarboxylation is filled by the previously dangling and protonated carboxyl group initially present in 5, which could further protonate V–OH to yield H_2O. Upon reoxidation of the vanadium(III) center, either by O_2 or electron transfer with vanadium(V), the oxo group would be regenerated from the water previously formed.

processes described here are graphically shown in Figure 7.

If **5** is heated in the presence of air the $V^{III}O(EHGS)$[33] initially generated could react directly with O_2 to yield $V^VO(EHGS)$ (**6**). The **6** thus formed would undergo further reaction in an analogous manner to ultimately yield **7**.

The fact that we have shown that the monodecarboxylated **6** also undergoes rapid decarboxylation under these conditions demonstrates that it is the coordinated carboxyl group that must be released. The coordinative saturation of both **5** and **6** also suggests an intramolecular rather than intermolecular reaction. Thus the mechanism we have proposed is consistent with all known observations and chemistry of these systems.

Conclusions and Relevance to Biological Systems

We have extensively investigated the coordination chemistry of vanadium in the +IV and +V oxidation states with phenolate-containing chelating ligands, with some preliminary work with vanadium(III) as well. The following general conclusions can be drawn from our results and from the complimentary work on catechols of Cooper et al.[34]

(*1*) *The chelate chemistry of vanadium(V) is not limited to the VO_2^+ moiety as had been previously supposed.* Rather it displays a rich chemistry involving VO^{3+} and bare V^{5+} as well as the ubiquitous VO_2^+ all of which have some stability in aqueous solution at physiological pH. We have also provided some of the first evidence for the protonation of the VO_2^+ group to yield initially the $VOOH^{2+}$ moiety and ultimately VO^{3+}. These transformations have previously been suggested but virtually no evidence for their existance was provided except under high acid conditions (>2 M H_2SO_4).[35] The complexes with VO^{3+}, virtually unknown in mononuclear chelate chemistry, are very stable and represent a new area of vanadium(V) coordination chemistry.

(*2*) *Vanadium(V) complexes with these ligands can be quite stable with respect to internal redox reactions.* Previous results have suggested that vanadium(V) catecholates and phenolates existed only transiently due to the oxidation of the ligands with concomitant reduction of the metal center.[36,37] While such re-

actions are indeed important under some conditions (low pH, nonchelating ligands) they are clearly not general. In fact vanadium(V) is probably the stable oxidation state of this element with phenol ligands under aerobic conditions. This is in agreement with the general observation that these types of ligands stabilize the highest available oxidation states.[34] The vanadium(III) and many of the vanadium(IV) phenolate complexes in this study are unstable in air and will spontaneously oxidize to the vanadium(V) states. However, this air oxidizability can be modulated by the nature of the solvent, with the more polar solvents stabilizing the lower, tetravalent oxidation state.

(*3*) *Bare vanadium(IV), bare vanadium(V), and the VO^{3+} ion complexed to phenolate ligands all display LMCT bands in their visible spectra giving rise to intense blue-violet colors.* These colors provide a means of distinguishing these forms of the metal from the more common VO^{2+} and VO_2^+ ions which do not have intense LMCT bands. It should be noted that it is the intensity of the bands that is characteristic here rather than the color, as many simple vanadyl complexes are blue. We have already used this information to determine that vanadium(IV) and vanadium(V) must both be bound to the tyrosinate protein transferrin,[3] as the VO^{2+} and VO_2^+ forms, respectively, as they do not display LMCT bands.

These results should aid in delineating the possible modes of coordination of vanadium with the newly isolated tunichromes from the vanadocytes of ascidians.[4] They also suggest that further study concerning the previously postulated role of these tunichromes may be required. Work in our laboratory utilizing multidentate catechol complexes as models for these extremely unstable compounds is presently directed toward that goal.

Supplementary Material Available: Complete NMR titration of the α-protons as a function of pH for the two isomers from the solubility threshold to its fully protonated form (1 page). Ordering information is given on any current masthead page.

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(37) Ferguson, J. H.; Kustin, K. *Inorg. Chem.* **1979**, *18*, 3349.