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# Novel Reactivity Patterns of (*N*,*N'*-Ethylenebis(salicylideneaminato))oxovanadium(IV) in Strongly Acidic Media

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(*N*,*N'*-Ethylenebis(salicylideneaminato))oxovanadium(IV), $V^{IV}$O(SALEN), displays a rich coordination chemistry in strongly acidic solution with the complexes being generated depending on the choice of solvent, the proton source, and the presence or absence of dioxygen. Under aerobic conditions, the addition of anhydrous HCl to an acetonitrile solution of $V^{IV}$O(SALEN) results in the protonation and dissociation of the vanadyl oxygen atom, giving the dark blue $V^{IV}Cl_2$(SALEN). This complex exhibits a reversible one-electron reduction to $V^{III}Cl_2(SALEN)^-$, at +0.05 V (vs. SCE). In contrast, when perchloric acid is added to an acetonitrile solution of $V^{IV}$O(SALEN), a different dark blue complex, $V^{V}$O(SALEN)$ClO_4$, is isolated. This material arises from a disproportionation of the $V^{IV}$O(SALEN), giving both $V^{V}$O(SALEN)$ClO_4$ and an incompletely characterized V(III) species that is oxidized to $V^{V}$O(SALEN)$ClO_4$ by dioxygen. When the identical reaction is run under anaerobic conditions, a stable, green-brown solution containing an equimolar mixture of $V^{V}$O(SALEN)$ClO_4$ and the V(III) complex is formed. Addition of chloride ion to this solution causes the redox equilibrium to shift back toward the original state, that is, the quantitative generation of an equimolar mixture of $V^{IV}$O(SALEN) and $V^{IV}Cl_2$(SALEN), indicating that chloride stabilizes the V(IV) oxidation state relative to V(III) and V(V). All the compounds in this study have been characterized by cyclic voltammetry and rotating platinum electrode voltammetry. In addition, single-crystal X-ray diffraction has structurally characterized $V^{V}$O(SALEN)$ClO_4$ [$VClO_7N_2C_{16}H_{14}$], which crystallizes in the monoclinic crystal system: space group $C2/c$, $Z = 8$, $a = 15.414$ (5) Å, $b = 8.438$ (3) Å, $c = 26.208$ (10) Å, $\beta = 90.51$ (3)°, $V = 3408$ (2) Å$^3$, $R = 0.034$, $R_w = 0.032$. It is suggested that the reactions described in this report may be relevant to the mechanism of vanadium accumulation in tunicates.

## Introduction

Unlike the situation for many of the first-row transition elements, the biochemical role of vanadium is still poorly understood.[1,2] Among the endogenous forms of vanadium falling within this category are the low-molecular-weight complex amavadin,[3] which is isolated from *Amanita muscaria*, and a recently described vanadoprotein, isolated from *Ascophyllum modosum*, which displays peroxidase activity.[4] In addition, certain sessile marine organisms (ascidians) are known to concentrate vanadium 1 000 000-fold[2] over seawater levels. While our awareness of the occurrence of vanadium in biological systems is increasing, an understanding of the structural, functional, and mechanistic properties of vanadium in them is still in its infancy. This understanding rests, in part, on further definition of the coordination chemistry of vanadium in the +3, +4, and +5 oxidation states.

In previous communications,[5–7] we have reported on the extensive coordination chemistry of vanadium–phenolate complexes. The structure and reactivity of these complexes are seminal to the understanding of vanadium biochemistry in many systems. For example, vanadyl ion has been used as a spectroscopic probe of the phenolate-containing metal binding site of the serum iron transport protein, transferrin.[8] In addition, a polyphenol natural product, tunichrome,[9] has been isolated from ascidians. It has been reported[10] that in ascidians vanadium is stored in blood cells within highly acidic vesicles. Thus, early model studies investigated vanadium coordination chemistry at low pH.[11] However, interest in this chemistry waned when a report appeared[12] that questioned whether the vanadium environment was truly acidic. The most recent data once again suggest that the pH of the environment containing the vanadium is highly acidic.[13] Thus, it seemed worthwhile to examine in greater detail the chemistry of well-defined vanadium–phenolate complexes in highly acidic media. The stability and reactivity of one such complex, $V^{IV}$O(SALEN),[14] are reported herein. A brief account of this work has already appeared.[15]

## Experimental Section

**Materials.** $V^{IV}$O(SALEN) was prepared as previously reported.[7] Acetonitrile was obtained from Burdick and Jackson, stored under nitrogen, and used without further purification. All other materials were reagent grade and used as received.

**$V^{IV}Cl_2$(SALEN) (I).** Bubbling dry hydrogen chloride gas or adding hydrogen chloride saturated acetonitrile to a 1 mM solution of the pale green $V^{IV}$O(SALEN) in acetonitrile rapidly produces a deep blue solution. Upon standing overnight, dark blue, air-stable microcrystals of I are deposited. Anal. Calcd for $VCl_2$(SALEN): C, 49.2; H, 4.1; N, 7.2; V, 13.1; Cl, 17.9. Found: C, 48.7; H, 3.6; N, 7.3; V, 13.7; Cl, 18.6.

**$V^{V}$O(SALEN)$ClO_4$ (II).** Two equivalents of perchloric acid was added to an approximately 1 mM solution of $V^{IV}$O(SALEN) in acetonitrile and the mixture stirred overnight. The dark blue solution was rotary evaporated to dryness and the residue recrystallized by slow evaporation from methanol to produce diffraction-quality crystals of compound II, as thin plates. *Warning*: Perchlorate salts of metal complexes are potentially explosive.[16]

**Methods.** Infared spectra were obtained on a Nicolet 6000 FT-IR instrument as potassium bromide pellets. Room-temperature solid-state magnetic susceptibilities were calculated from data obtained with a Faraday balance composed of a Cahn R-100 electrobalance and a Varian Fieldial Mark 1 field-regulated magnetic power supply. $Hg[Co(SCN)_4]$ was used as a standard. Solution magnetic moments were obtained by using the Evans method[17] on a Bruker 270 MHz FT-NMR instrument. Electron paramagnetic resonance spectra were run at room temperature on a Varian E-4 spectrometer operating at 9.2 GHz using a quartz flat

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(14) Abbreviations used: SALEN = *N*,*N'*-ethylenebis(salicylideneamine); EHPG = ethylenebis((*o*-hydroxyphenyl)glycine); EHGS = *N*-(2-(*o*-salicylideneamino)ethyl)(*o*-hydroxyphenyl)glycine); EDTA = ethylenediaminetetraacetic acid.
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**Table I.** Crystallographic Data for $VO(SALEN)ClO_4$

| | |
|---|---|
| formula | $VClO_7N_2C_{16}H_{14}$ |
| mol wt | 432.69 |
| *a*, Å | 15.414 (5) |
| *b*, Å | 8.438 (3) |
| *c*, Å | 26.208 (10) |
| $\beta$, deg | 90.51 (3) |
| *V*, $Å^3$ | 3408 (2) |
| cryst syst | monoclinic |
| space group | *C*2/*c* |
| $d_{calcd}$, g $cm^{-3}$ | 1.687 |
| *Z* | 8 |
| radiation | Mo K$\alpha$ |
| temp, K | 295 |
| cryst size, mm | 0.057 × 0.234 × 0.395 |
| scan speed, deg $min^{-1}$ | 2.5–12 |
| scan range, deg | 1.7 |
| bkgd/scan time ratio | 0.8 |
| $2\theta$, deg | 45 |
| abs coeff, $\mu_{abs}$, $cm^{-1}$ | 7.629 |
| data collected | 2683 ($+h,+k,\pm l$) |
| no. of unique data, $I > 3\sigma(I)$ | 1625 |
| no. of variables | 244 |
| residual, e $Å^{-3}$ | 0.22 |
| *R*, % | 0.034 |
| $R_w$, % | 0.032 |

cell. UV–visible spectra were obtained on a Perkin-Elmer 553 spectrophotometer interfaced to an Apple IIe computer. Spectral manipulations were performed by using the software developed by Hage and Taylor.[18] Analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY. Cyclic voltammetry studies were carried out with a BAS CV-1B-120 apparatus, and rotating platinum electrode studies utilized a Princeton Applied Research (PAR) 174A polarographic analyzer. All experiments employed a spherical platinum electrode and tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) as supporting electrolyte. Potentials are reported vs. the saturated calomel electrode.

**Collection and Reduction of X-ray Data.** Suitable crystals of $V^VO(SALEN)ClO_4$ were obtained as described above. Intensity data were obtained with Mo K$\alpha$ (0.71069 Å) radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The crystal and machine parameters used in the unit cell determination and in data acquisition are summarized in Table I. Intensity data were collected on a Syntex $P2_1$ diffractometer using $\theta/2\theta$ scans. The data were reduced by using the SHELX program package,[19] and the structure was solved by using the direct-methods program MULTAN.[20] Absorption correction was applied by using the SHELX program package. Atomic scattering factors were from ref 21. The function used in the least-squares minimization was $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were located but not refined and given fixed bond distances of 0.95 Å in the final least-squares refinement. All hydrogen atoms were given fixed *U* values (isotropic temperature factors) of 0.05. Unique data used and final *R* values are given in Table I.

## Results

**Aerobic Acidification of VO(SALEN).** When dry HCl gas is bubbled into an anhydrous acetonitrile solution of $V^{IV}O(SALEN)$, the pale green solution immediately turns a deep blue. The protonation and loss of the vanadyl oxygen atom in the product, I, were demonstrated by the absence of a V=O stretch in the 910–990-$cm^{-1}$ region of the IR spectrum. The addition of concentrated aqueous HCl to an acetonitrile solution of $V^{IV}O(SALEN)$ also produces I. The paramagnetic product has an intense ligand to metal charge-transfer band (LMCT) in the optical spectrum at 604 nm with an extinction coefficient of 3640 $M^{-1}$ $cm^{-1}$ (acetonitrile). Elemental analysis, mass spectrometry, conductivity, and solid-state magnetic susceptibility indicate that this material is the previously reported[22] $V^{IV}Cl_2(SALEN)$. A cyclic voltammogram (CV) of I is shown in Figure 1 and represents the reversible one-electron reduction of the vanadium(IV) complex to vanadium(III) at +0.05 V.[23]

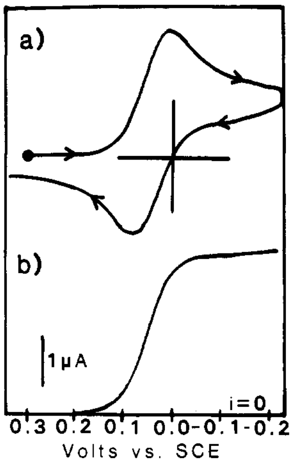

**Figure 1.** (a) Cyclic voltammogram (platinum electrode, 0.200 V $s^{-1}$) and (b) rotating platinum electrode voltammogram (0.020 V $s^{-1}$) of $V^{IV}Cl_2(SALEN)$ (each in acetonitrile containing 0.1 M tetraethylammonium chloride).

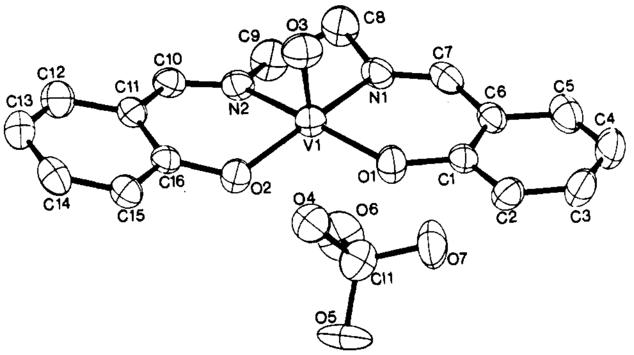

**Figure 2.** ORTEP diagram of $VO(SALEN)ClO_4$ with thermal ellipsoids of 50% probability.

**Table II.** Fractional Atomic Coordinates for Non-Hydrogen Atoms

| atom | *x* | *y* | *z* |
|---|---|---|---|
| V1 | 0.7103 (1) | 0.4776 (1) | 0.6437 (1) |
| O1 | 0.8026 (2) | 0.5946 (3) | 0.6622 (1) |
| C1 | 0.8340 (3) | 0.7415 (5) | 0.6555 (2) |
| C2 | 0.9005 (3) | 0.7960 (5) | 0.6872 (2) |
| C3 | 0.9323 (3) | 0.9477 (6) | 0.6792 (2) |
| C4 | 0.9003 (3) | 1.0436 (6) | 0.6403 (2) |
| C5 | 0.8341 (3) | 0.9882 (5) | 0.6092 (2) |
| C6 | 0.7996 (3) | 0.8369 (5) | 0.6168 (2) |
| C7 | 0.7280 (3) | 0.7857 (5) | 0.5852 (2) |
| N1 | 0.6869 (2) | 0.6544 (4) | 0.5898 (1) |
| C8 | 0.6106 (3) | 0.6272 (6) | 0.5567 (2) |
| C9 | 0.6076 (3) | 0.4540 (6) | 0.5445 (2) |
| N2 | 0.6255 (2) | 0.3689 (4) | 0.5927 (1) |
| C10 | 0.5870 (3) | 0.2362 (3) | 0.6011 (2) |
| C11 | 0.6055 (3) | 0.1349 (5) | 0.6441 (2) |
| C12 | 0.5529 (3) | 0.0019 (5) | 0.6528 (2) |
| C13 | 0.5716 (3) | −0.1014 (5) | 0.6915 (2) |
| C14 | 0.6449 (3) | −0.0777 (5) | 0.7221 (2) |
| C15 | 0.6986 (3) | 0.0486 (5) | 0.7135 (2) |
| C16 | 0.6794 (3) | 0.1565 (5) | 0.6755 (2) |
| O2 | 0.7331 (2) | 0.2788 (3) | 0.6664 (1) |
| O3 | 0.6371 (2) | 0.5299 (4) | 0.6818 (1) |
| Cl1 | 0.8679 (1) | 0.4340 (1) | 0.5390 (1) |
| O4 | 0.8096 (2) | 0.3792 (4) | 0.5782 (1) |
| O5 | 0.9422 (2) | 0.3348 (4) | 0.5392 (1) |
| O6 | 0.8247 (2) | 0.4216 (4) | 0.4909 (1) |
| O7 | 0.8915 (2) | 0.5946 (4) | 0.5484 (1) |

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**Table III.** Selected Interatomic Distances (Å) and Angles (deg) for VO(SALEN)ClO$_4$

| | | | | | |
|---|---|---|---|---|---|
| V1–O1 | 1.795 (3) | V1–O2 | 1.813 (3) | V1–O3 | 1.576 (3) |
| V1–O4 | 2.456 (3) | V1–N1 | 2.083 (3) | V1–N2 | 2.074 (3) |
| O1–V1–O2 | 105.6 (1) | O1–V1–O3 | 104.2 (1) | O1–V1–O4 | 82.9 (1) |
| O1–V1–N1 | 85.4 (1) | O1–V1–N2 | 155.5 (1) | O2–V1–O3 | 100.9 (1) |
| O2–V1–O4 | 78.2 (1) | O2–V1–N1 | 156.5 (1) | O2–V1–N2 | 85.5 (1) |
| O3–V1–O4 | 172.8 (1) | O3–V1–N2 | 96.2 (1) | O3–V1–N2 | 94.7 (1) |
| O4–V1–N1 | 82.7 (1) | O4–V1–N2 | 78.0 (1) | N1–V1–N2 | 77.0 (1) |

If HClO$_4$ (rather than HCl) is used as a proton source, a deep blue diamagnetic material, II, is formed, 1 equiv of acid being required for complete conversion (vide infra). The IR spectrum of this material retains a V=O stretch at 981 cm$^{-1}$. The cyclic voltammetric response of II is identical with that of the initial V$^{IV}$O(SALEN) ($E°$ = +0.47 V) except that anodic rather than cathodic current is passed. Structural analysis reveals II to be VO(SALEN)ClO$_4$, an oxovanadium(V) species.

**Description of the Structure of V$^V$O(SALEN)ClO$_4$.** Parameters for data collection are given in Table I and fractional atomic coordinates in Table II. The structure of V$^V$O(SALEN)ClO$_4$ (Figure 2) is very similar to that described in a previous brief report of V$^V$O(SALEN)H$_2$O$^+$, which crystallized as the counterion for Cu$_2$Cl$_4^-$.[24] In the present structure the VO$^{3+}$ unit extends 0.318 Å above the best SALEN N$_2$O$_2$ least-squares plane with a long distance, 2.456 (3) Å, to the perchlorate oxygen. A comparison of the two structures suggests that since the perchlorate ion is less coordinating than the water (2.310 Å), the distances (Table III) in V$^V$O(SALEN)ClO$_4$ more closely represent a true five-coordinate oxovanadium(V) ion. The weak trans influence also results in a shorter V=O bond length at 1.576 (3) Å, although this distance is only 0.012 Å shorter than the V=O bond for V$^{IV}$O(SALEN) (Table IV). Obviously the oxidation of the vanadium atom is scarcely reflected in the V=O bond length. Indeed, the V=O stretching frequencies (981 cm$^{-1}$) are identical for V$^{IV}$O(SALEN) and V$^V$O(SALEN)$^+$. However, the VO$^{3+}$ center does exhibit a strong preference for phenolate coordination when compared with VO$^{2+}$, which is reflected in the V–O(phenolate) bond lengths; 1.80 vs. 1.92 Å. The V–N bonds on the other hand do not differ much between the oxidized and reduced forms.

A stepped ring configuration is common to five-coordinate M(SALEN) structures.[25] That V$^V$O(SALEN)ClO$_4$ follows this pattern is illustrated by a comparison of the bond angles O1–V1–O3 and N1–V1–O3 (104.2 and 96.2°) with O2–V1–O3 and N2–V1–O3 (100.9 and 94.5°). The deviation from a planar arrangement is slight, however, since no atom deviates by more than 0.01 Å from the best N$_2$O$_2$ plane.

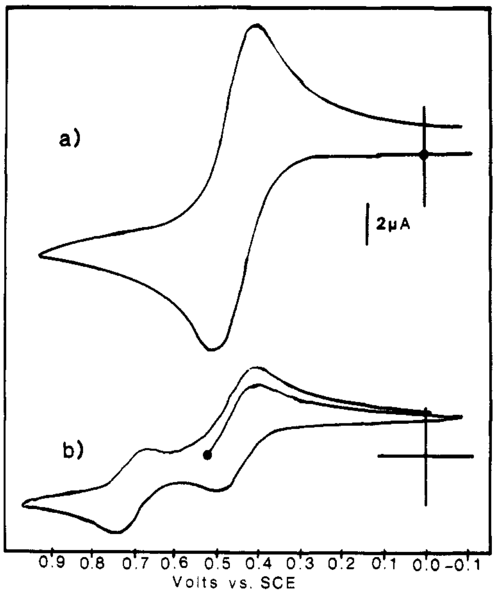

**Figure 3.** Cyclic voltammograms of V$^{IV}$O(SALEN) (in acetonitrile containing 0.1 M (TBA)PF$_6$ with a 0.200 V s$^{-1}$ scan rate at a spherical platinum electrode): (a) initial voltammogram; (b) voltammogram after addition of 2 equiv of perchloric acid.

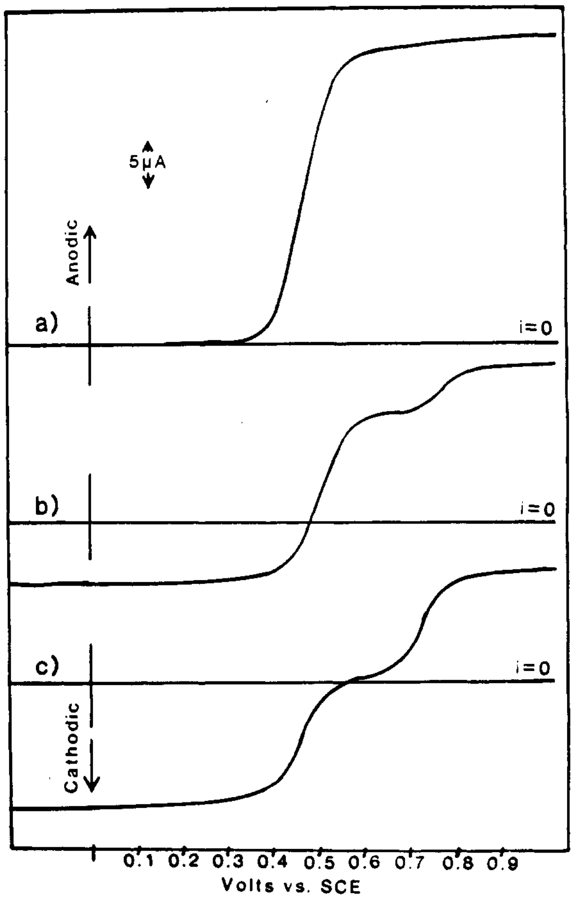

**Figure 4.** Rotating platinum electrode voltammograms of V$^{IV}$O(SALEN) (in acetonitrile containing 0.1 M (TBA)PF$_6$ with a 0.02 V s$^{-1}$ scan rate): (a) initial voltammogram; (b) voltammogram after addition of 1 equiv of perchloric acid; (c) voltammogram after addition of 2 equiv of perchloric acid.

The structure of V$^V$O(SALEN)ClO$_4$ can be compared with a number of previous X-ray structures of vanadium Schiff base and amino–carboxylate complexes[6,8,26,27] in order to gain insight concerning the coordination preferences about the VO$^{2+}$, VO$^{3+}$, and VO$_2^+$ ions (Table IV). The trend in V=O bond lengths appears to be VO$_2^+$ > VO$^{2+}$ > VO$^{3+}$ although there is only a small difference (0.013–0.031 Å) between the VO$^{2+}$ and VO$^{3+}$ ions. As expected, a strong trans effect is observed in all the complexes. If we assume that a cis V–N bond for a VO$_2^+$ ion is about 2.1–2.15 Å, the trans V–N orientation causes a 0.2–0.25-Å elongation of this bond. This compares with a 0.11-Å elongation of the trans V–N bond of V$^{IV}$O(EHPG)$^-$ or a 0.16-Å elongation of the trans V–O bond in V$^{IV}$O(EHGS)$^-$.[14] One does not observe a trans ligand in either V$^{IV}$O(SALEN) structure[6,28] while aquo and perchlorate moieties have been shown to associate with V$^V$O(SALEN)$^+$. However, the extent of trans influence appears to

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[23] VCl$_2$(SALEN) electrochemistry is reversible in the presence of excess chloride ions: $i_{pa}/i_{pc}$ = 0.97; constant current function ($i_{pc}/v^{1/2}$). The one-electron nature of the process was established by comparison, in the same cell, with V$^{IV}$O(SALEN), a well-established one-electron standard.

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**Table IV.** Comparison of Bond Lengths (Å) for V(IV) and V(V) Schiff Base and Amino–Carboxylate Complexes[a]

| | V=O(oxo) | V—O(phe)[b] | V—O(carb)[b] | V—N | ref |
|---|---|---|---|---|---|
| $V^VO(SALEN)^+$ | 1.576 | 1.795 | ... | 2.083 | this work |
| | ... | 1.813 | ... | 2.074 | |
| $V^{IV}O(SALEN)$ | 1.588 | 1.924 | ... | 2.055 | 2, 23[c] |
| | ... | 1.923 | ... | 2.051 | |
| $VO_2(H_2EDTA)$ | 1.623 | ... | 1.996 | 2.351[e] | 21 |
| | 1.657 | ... | 2.008 | 2.362[e] | |
| $VO_2(EDTA)$[f] | 1.639 | ... | 2.001 | 2.359[e] | 22 |
| | 1.657 | ... | 1.999 | 2.366[e] | |
| $V^{IV}O(EHPG)^-$[d,g] | 1.607 | 1.950 | 2.011 | 2.152 | 2 |
| | ... | ... | 2.009 | 2.264[e] | |
| $V^{IV}O(EHGS)^-$[g] | 1.606 | 1.949 | 2.285[e] | 2.126 | 2 |
| | ... | 1.943 | ... | 2.055 | |

[a] VO(SALEN) is five-coordinate. $VO(SALEN)^+$ is nearly five-coordinate with perchlorate oxygen atom at 2.456 Å. All other compounds are six-coordinate. [b] Legend: phe = oxygen atom of phenolate; carb = oxygen atom of carboxylate. [c] The vanadyl oxygen atom is coordinated to an $Na^+$ ion in this structure. [d] The $NH_4^+$ salt. [e] The ligating atom is trans to the oxo moiety. [f] The trisodium salt. [g] For ligand names see ref 14.

follow the general pattern $VO_2^+ > VO^{2+} > VO^{3+}$.

**Anaerobic Acidification of $V^{IV}O(SALEN)$.** The addition of degassed perchloric acid to an anaerobic acetonitrile solution of $V^{IV}O(SALEN)$ yields a dark green-brown solution. The optical density of this solution reaches a maximum after 2 equiv is added rather than the 1 equiv needed in the presence of air. As illustrated in Figure 3, the CV of this solution reveals that (1) the original $V^{IV/V}O(SALEN)$ couple is still present at +0.47 V and (2) there is a new reversible wave at +0.73 V. Quantitation of the redox-active species was accomplished by using a rotating platinum electrode (RPE), which allows an accurate assessment of the percentage of a species in the oxidized vs. that in the reduced form. RPE studies clearly show that upon addition of 2 equiv of $HClO_4$ to $V^{IV}O(SALEN)$ under anaerobic conditions, 50% of the total vanadium is in the form of the species with the +0.73 V redox potential, III, and 50% is in the form of oxidized $V^VO(SALEN)^+$ (Figure 4). *Thus, the oxidation of the $V^{IV}O(SALEN)$ occurs in the absence of molecular oxygen.* If oxygen is admitted to the green-brown solution, the color gradually turns dark blue and the redox couple at +0.73 V disappears. The final CV is indistinguishable from that of pure II.

An EPR titration under anaerobic conditions showed that the original eight-line signal attributed to $V^{IV}O(SALEN)$ diminishes in intensity upon addition of acid and vanishes at 2 equiv. Since half the vanadium is known to be oxidized to the diagmagnetic $V^VO(SALEN)^+$, the remaining 50% (in the form of the new species, III) must also be EPR-silent at room temperature; i.e. it must be vanadium(V), a spin-coupled dimer or oligomer of vanadium(IV), or vanadium(III). Solution susceptibility measurements confirm the oxidation state as V(III); $\mu = 3.1\ \mu_B$.[29] An optical spectrum of III was obtained by using spectral subtraction methods. If a normalized spectrum of $V^VO(SALEN)^+$ is subtracted from the spectrum of the reaction mixture, the resulting spectrum should be that attributed to the vanadium(III) species. A weak d–d band at approximately 770 nm is observed, as well as an absorbance near 400 nm, which could either be another d–d band or a perturbed $H_2SALEN$ absorbance (possibly associated with vanadium(III)).

Results identical with those described here for $HClO_4$ are also observed for other noncoordinating acids such as $HBF_4$. The intriguing difference in behavior between HCl (which yields $V^{IV}Cl_2(SALEN)$) and $HClO_4$ or $HBF_4$ (which yield oxidized $V^VO(SALEN)^+$ and the new species III) suggested the potential involvement of the coordinating anion, chloride, in the reaction paths. To test this hypothesis, we initially added 2 equiv of $HClO_4$ to $V^{IV}O(SALEN)$ under $N_2$ and then added an excess of chloride ion (as the tetraethylammonium salt) to a final concentration of ~0.01 M. Upon addition of chloride, the green-brown solution instantly turned dark blue. Monitoring the resulting solution, immediately after chloride addition, by cyclic voltammetry and RPE methods revealed (a) the disappearance of the "new" species present at +0.73 V, (b) the appearance of a wave at +0.050 V, corresponding to the oxidized form of the dichloro species $V^{IV}Cl_2(SALEN)$ (I, ~50%), and (c) a wave corresponding to $V^{IV}O(SALEN)$ (~50%) (Figure 5).[30,31]

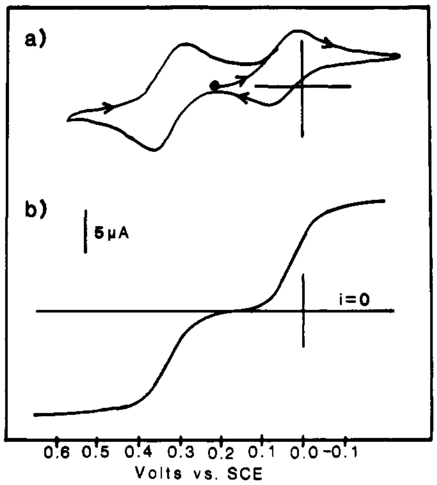

**Figure 5.** (a) Cyclic voltammogram (0.200 V $s^{-1}$) and (b) rotating platinum electrode voltammogram (0.020 V $s^{-1}$) of a solution of $V^{IV}O(SALEN)$ to which have been added 2 equiv of perchloric acid, followed by an excess of tetraethylammonium chloride.

## Discussion

$V^{IV}Cl_2(SALEN)$ has been previously prepared either by direct means from $VCl_4$ and SALEN or by dehydration of $V^{IV}O(SALEN)$ with $SOCl_2$ or $PCl_5$ in benzene.[22] We are unaware of any reports of its preparation by the simple expedient of protonation. Vanadyl porphyrins[32] are reported to be inert to protonation by hydrogen halides but are deoxygenated by $SOCl_2$. However, there is precedent for simple acid–base chemistry at

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(29) Magnetic susceptibility values corrected for 50% of the vanadium being in the diamagnetic +5 oxidation state.

(30) When this system is allowed to remain in the electrochemical cell (under $N_2$), the current at the RPE due to the oxidation of $V^{IV}O(SALEN)$ is seen to increase at the expense of the reduction current of $V^{IV}Cl_2(SALEN)$, despite the presence of protons (generated in reaction 4) and chloride ions. While there is apparently enough acid to generate $VCl_2(SALEN)$, the product disappears as quickly as it is generated under these conditions. This is probably a result of the instability of the dichloro species in the presence of water according to the equation

$$V^{IV}Cl_2(SALEN) + H_2O \rightarrow V^{IV}O(SALEN) + 2HCl$$

During this aging the solution fades to a pale green from the deep blue observed following initial chloride addition, and the final RPE voltammogram is indistinguishable from that of $V^{IV}O(SALEN)$ in the presence of a chloride-containing electrolyte.

(31) Evidence of $VCl_2(SALEN)$ instability is also presented in Seangpraserkij, R.; Riechel, T. L. *Inorg. Chem.* **1986**, *25*, 3121.

(32) Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87.

the oxovanadium center, as we have reported the protonation and subsequent loss of *one* oxygen atom in $\mathrm{VO_2^+}$ to generate $\mathrm{VO^{3+}}$ complexes.[7]

Although the formation of $\mathrm{V^{IV}Cl_2(SALEN)}$ can be understood mechanistically as a series of protonation steps, the apparent one-electron oxidation of $\mathrm{V^{IV}O(SALEN)}$ in the presence of acid is not as straightforward.[33] Specifically, the nature of the oxidant that produces II is unclear. A possible mechanism, i.e. initial protonation of $\mathrm{V^{IV}O(SALEN)}$ to yield an intermediate that is then oxidized by molecular oxygen, was examined by conducting the reaction under anaerobic conditions. However, the appearance of the vanadium(V) complex II even in the absence of $\mathrm{O_2}$ indicates that another mechanism must be in operation. We propose that, under anaerobic conditions, the initial reaction is a disproportionation of a protonated $\mathrm{V^{IV}O(SALEN)}$ to yield $^1/_2$ equiv of a vanadium(III) complex (species III) and $^1/_2$ equiv of $\mathrm{V^VO(SALEN)^+}$. This process is represented by eq 1. The overall

$$2\mathrm{V^{IV}O(SALEN)} + 4\mathrm{H^+} \rightarrow \text{“}\mathrm{V^{III}(H_2SALEN)}\text{”} + \mathrm{V^VO(SALEN)^+} + \mathrm{H_2O} \qquad (1)$$

two protons per vanadium stoichiometry of the reaction (vide supra) and the unambiguous presence of *unprotonated* $\mathrm{V^VO(SALEN)^+}$ as one of the products requires that four protons be involved with the formation of the vanadium(III) species. We hypothesize that two of the four protons are consumed in the protonation and loss of the oxo group (as water) from the now softer vanadium(III) center. The remaining two are associated with the protonation of the SALEN ligand. Whether the vanadium(III) is strongly coordinated to the now protonated ligand remains unclear, hence our representation of the product as "$\mathrm{V^{III}(H_2SALEN)}$". A reasonable intermediate that would account for the products of reaction 1 would be the formation, upon protonation, of an oxo-bridged dimer. Inner-sphere electron transfer would then yield the products.

Upon addition of oxygen, the oxidation wave seen for III is lost and the reduction wave of $\mathrm{V^VO(SALEN)^+}$ is seen to increase, consistent with the reaction

$$\text{“}\mathrm{V^{III}(H_2SALEN)}\text{”} + {}^1/_2\mathrm{O_2} \rightarrow \mathrm{V^VO(SALEN)^+} + 2\mathrm{H^+} \qquad (2)$$

The overall reaction (no mechanism implied) conducted under air is then the sum of reactions 1 and 2:

$$2\mathrm{V^{IV}O(SALEN)} + {}^1/_2\mathrm{O_2} + 2\mathrm{H^+} \rightarrow 2\mathrm{V^VO(SALEN)^+} + \mathrm{H_2O} \qquad (3)$$

Reaction 3 indicates that only 1 equiv of acid is needed when the reaction is conducted under air, as protons are regenerated in reaction 2. This 1-equiv *aerobic* stoichiometry has been quantitatively demonstrated by using UV-visible and EPR titrations (data not shown).

Chloride addition to the anaerobic reaction mixture also causes a disappearance of the species with $E° = +0.73$ V (III). This is accompanied by the *reduction* of the $\mathrm{V^VO(SALEN)^+}$ back to $\mathrm{V^{IV}O(SALEN)}$. Presumably the "$\mathrm{V^{III}(H_2SALEN)}$" is transformed in the presence of chloride to $\mathrm{V^{III}Cl_2(SALEN)^-}$, which, according to the measured redox potentials, should be readily oxidized by the $\mathrm{V^VO(SALEN)^+}$ in solution. The reduction potentials for the "$\mathrm{V^{IV}(H_2SALEN)}$"/"$\mathrm{V^{III}(H_2SALEN)}$" and the $\mathrm{V^VO(SALEN)^+/V^{IV}O(SALEN)}$ couples are +0.73 and +0.47 V, respectively, indicating that in the absence of chloride a mixture of "$\mathrm{V^{III}(H_2SALEN)}$" and $\mathrm{V^VO(SALEN)^+}$ is preferred by 0.26 V. However, when in the presence of chloride "$\mathrm{V^{III}(H_2SALEN)}$" is transformed into $\mathrm{V^{III}Cl_2(SALEN)^-}$ ($E° = +0.05$ V), the equilibrium drastically shifts in favor of $\mathrm{V^{IV}O(SALEN)}$ and $\mathrm{V^{IV}Cl_2(SALEN)}$. These reactions demonstrate that the simple addition of chloride can have a profound effect on the redox equilibrium of the system. The overall process in the presence of chloride can thus be represented by

$$\text{“}\mathrm{V^{III}(H_2SALEN)}\text{”} + \mathrm{Cl^-}(\text{excess}) \rightarrow \mathrm{V^{III}Cl_2(SALEN)^-} + 2\mathrm{H^+} \qquad (4)$$

$$\mathrm{V^{III}Cl_2(SALEN)^-} + \mathrm{V^VO(SALEN)^+} \rightarrow \mathrm{V^{IV}O(SALEN)} + \mathrm{V^{IV}Cl_2(SALEN)} \qquad (5)$$

An attractive mechanistic sequence for the electron-transfer event in eq 5 is via an inner-sphere intermediate similar to that proposed for reaction 1. Here one can envision the anion $\mathrm{V^{III}Cl_2(SALEN)^-}$ attacking the cationic $\mathrm{V^VO(SALEN)^+}$ trans to the V═O, forming the neutral precursor complex $\mathrm{(SALEN)ClV^{III}{-}Cl{-}V^VO(SALEN)}$. Electron transfer can occur through the chloro bridge, followed by dissociation of the successor complex. As observed in the structure of $\mathrm{V^VO(SALEN)ClO_4}$, even the noncoordinating $\mathrm{ClO_4^-}$ shows some tendency to occupy the trans coordination site of $\mathrm{VO^{3+}}$. A chloride ion, with a higher metal ion affinity, would be expected to engage in a stronger interaction at this site. In contrast, the $\mathrm{VO^{2+}}$ ion exhibits weaker trans-ligating tendencies than $\mathrm{VO^{3+}}$ (vide supra), which would promote dissociation of the successor complex. Proof of this mechanistic proposal awaits future kinetic studies.

**Relevance to Vanadium Accumulation in Tunicates.** The chemistry reported herein adds substantial data to the chemistry of vanadium-phenolate complexes, which are potentially relevant to the biochemistry of this element. In particular the redox chemistry accompanying vanadium uptake by the vanadocytes of the tunicates has remained obscure. It is known that the vanadium is initially transported across the membrane as vanadium(V).[2] Inside the cell the vanadium is reduced to a mixture of vanadium(IV) and vanadium(III).[2] How this reduction takes place is unclear since the most likely reductant, the tunichromes, appear, in vitro at least, only to reduce vanadium(V) to vanadium(IV).[34] A variety of data also seems to suggest that both the vanadium(III) and the vanadium(IV) within the vanadophores are unligated, although this conclusion must remain tentative.[13] Nevertheless, this would be consistent with our observations that vanadium(V) will bind to phenolate ligands similar to the tunichromes even at low pH, while the softer vanadium(III) is unable to compete with protons for these weakly basic ligands.[35]

The present work also suggests a means by which vanadium(III) could be produced from vanadium(V) with tunichromes as reductants. A speculative mechanism could have the vanadium(IV) produced by tunichrome reduction undergoing a disproportionation to produce vanadium(III) and vanadium(V). The vanadium(V) could then undergo further reduction by the tunichromes. Whether disproportionation of vanadium(IV) is a viable mechanism will depend on a variety of factors, including its ligation, the acidity, and the presence or absence of coordinating anions. It is clear however that the relative stabilities of the various oxidation states of vanadium phenolate complexes can be varied over a wide range by a number of factors and that these must be taken into account in any attempt to formulate a mechanism.

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**Supplementary Material Available:** Table V (anisotropic thermal parameters), Table VI (fractional atomic coordinates for hydrogen atoms), Table VII (bond distances), and Table VIII (bond angles) (9 pages); Table IX (structure factor amplitudes) (7 pages). Ordering information is given on any current masthead page.

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[33] As expected, $\mathrm{V^VO(SALEN)^+}$ can be generated electrochemically by a bulk oxidation requiring one electron ($E° = +470$ mV vs. SCE in acetonitrile) or by use of chemical oxidants such as $\mathrm{Fe^{3+}}$, $\mathrm{Cu^{2+}}$, and $\mathrm{Ag^+}$.

[34] Macara, I. G.; McLeod, G. C.; Kustin, K. *Biochem. J.* **1979**, *181*, 457.

[35] Carrano, C. J.; Kime-Hunt, E., unpublished observations.