in coordinated O_2. No activation barrier is found for rotation of the O–O group from the side-bonded to the linear position. The most stable bond angle in O–Fe–O is calculated to be 180°. For dissociation of the O–O bond in side-bonded FeO_2 to form O–Fe–O, an activation energy of 100 kcal/mol is calculated. Negative charge on the complex decreases the activation energy while positive charge increases it. Thus single iron atoms are a poor catalyst for dissociation of O_2, which suggests that dissociative adsorption of O_2 on iron surfaces most likely occurs on a site where the O_2 interacts with several iron atoms.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Venezuelan Government for a fellowship to support F.R.

Appendix

In order to demonstrate that the procedure can handle a wide range of compounds, we have done calculations for FeH, FeH_4, Fe_2, Fe_6, $Fe(CO)_5$, FeO, FeO_2, OFeO, NiH, NiH_2, Ni_2H_2, NiO, Ni_2, Ni_6, and $Ni(CO)_4$. While some of these calculations are still in preliminary stages, it has been possible to find satisfactory parameters in all cases even though the final optimized parameters have not been established for all these compounds. Parameters selected to give FeH a bond energy of 60 kcal/mol at an equilibrium bond length of 1.50 Å produce a calculation for FeH_4 in good agreement with an ab initio calculation by Hood, Pitzer, and Schaefer;[37] i.e., both calculations give a moderately stable $^5T_2(t_2{}^2e^2)$ ground state with a 4p orbital occupancy around 1. Parameters selected to give Fe_2 a bond energy of 30 kcal/mol[38] at an equilibrium bond length of 2.3 Å when used in a Fe_6 cluster calculation indicate a stable cluster with a "d" bandwidth of 3.5 eV, which is similar to 4.0 eV given by our Xα calculation. The $Fe(CO)_5$ calculation gives orbital energies that differ by less than 0.5 eV from the principal bands in the experimental[39] photoelectron spectrum of $Fe(CO)_5$. Having verified that the calculational procedure gives reasonable results for a wide variety of transition-metal compounds, this paper has concentrated on iron–oxygen interactions. More details about the procedure are being published.[40]

Registry No. FeO, 1345-25-1; FeO^+, 12434-84-3; FeO^-, 59700-48-0; FeO_2, 64766-39-8; Fe–O–O, 58220-66-9; $FeO_2{}^+$, 80441-12-9; $FeO_2{}^{2+}$, 80441-13-0; Fe–O–O^{2+}, 80448-79-9; $FeO_2{}^-$, 80441-11-8; O–Fe–O, 12411-15-3; O–Fe–O^+, 80434-52-2; O–Fe–O^-, 22295-36-9.

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Redox Chemistry of Metal–Catechol Complexes in Aprotic Media. 4. Synthesis and Characterization of 3,5-Di-*tert*-butylcatecholato Complexes of Vanadium(V), -(IV), and -(III)

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The disodium bis(3,5-di-*tert*-butylcatecholato)methoxyoxovanadate(V), disodium bis(3,5-di-*tert*-butylcatecholato)oxovanadate(IV), disodium dichlorobis(3,5-di-*tert*-butylcatecholato)vanadate(IV), and trisodium tris(3,5-di-*tert*-butylcatecholato)vanadate(III) complexes have been synthesized and isolated. These and related species have been characterized by cyclic voltammetry and controlled-potential electrolysis as well as by UV-visible, IR, proton NMR, and EPR spectroscopy and magnetic susceptibility measurements in aprotic media. The vanadium(III) and -(IV) species are oxidized to vanadium(V) by protic substrates. This is in contrast to the pyrocatechol complexes of vanadium(V), -(IV), and -(III), where vanadium(IV) is the stable oxidation state.

Although vanadium is present in the human body at a level of 0.03 ppm,[1] its biological function is unknown. Vanadium(V) reacts with L-ascorbate to produce vanadium(IV) and dehydroascorbic acid.[2] Vanadium(V) ion also acts as an inhibitor for (Na,K)-ATPase,[3-5] dynein ATPase, and LAD-1.[6] The inhibition is reversed by the addition of catechol (1,2-dihydroxybenzene) or catecholamine. A study of the reaction of norepinephrine (a catecholamine) with vanadium(V) indicates that norepinephrine first complexes and then reduces the vanadium.[7]

The reaction of catechol and its derivatives with various oxidation states of vanadium in protic solvents (water and methanol) has been extensively investigated. Solution studies of vanadium(III) with catechol indicate that the formation of mono, bis, and tris complexes is dependent on pH.[8-10] Vanadium(IV) reacts with catechol to yield $V^{IV}(cat)_3{}^{2-}$, when isolated from solution.[11,12] In solution, the principal species

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appears to be $VO(cat)_2^{2-}$.[13] A bis complex, $V^{IV}(cat)_2$, also has been reported.[14] Vanadium(V) oxidizes catechol to *o*-quinone, and the resulting vanadium(IV) reacts with any remaining catechol to form a blue species.[15-17] In solutions of low acidity, vanadium(IV)–catechol complexes are partially oxidized to vanadium(V) species.[18]

A primary motivation for the present study was to confirm the formation of a bis(3,5-di-*tert*-butylcatecholato)vanadium(IV) complex that had been reported by our group[14] and to extend the characterization of its solution chemistry. *Unfortunately, we have been unable to duplicate the synthesis and isolation of this purported tetrahedral* $V^{IV}(DTBC)_2$ *complex. Hence, the reported reversible adducts of* O_2*, CO, and NO with the complex represent spurious results, and the spectral and structural interpretations are believed to be fallacious.* A contemporary investigation of vanadium–catechol complexes by Cooper, Koh, and Raymond[25] includes a particularly insightful and almost certainly correct rationalization for these spurious results and interpretations. We believe their investigation in combination with the present study provides a reasonably complete characterization of vanadium–catechol complexes in nonaqueous media.

The pH dependence of many of the reactions of vanadium with catechol has prompted an investigation of vanadium–catechol species that are formed in aprotic media. Several vanadium(V), -(IV), and -(III) complexes have been synthesized by use of disodium 3,5-di-*tert*-butylcatecholate in aprotic media. The isolated complexes have been characterized, and their redox properties, as well as those of similar complexes synthesized in methanol, have been determined.

Experimental Section

Equipment and Techniques. Cyclic voltammetric and controlled-potential electrolysis measurements were made with a Princeton Applied Research Corporation Model 173/175/179 potentiostat/galvanostat, Universal Programmer, and Digital Coulometer. The electrochemical cell was equipped with a Beckman platinum-inlay working electrode (area, 0.23 cm^2), a platinum-flag auxiliary electrode, and an Ag/AgCl reference electrode filled with an aqueous tetramethylammonium solution and adjusted to 0.000 V vs SCE. The latter was contained in a Pyrex tube with a soft-glass cracked tip; this electrode was placed inside a luggin capillary. For controlled-potential electrolysis, a platinum-mesh working electrode and auxiliary were employed. The supporting electrolyte for the electrochemical studies was 0.1 M tetraethylammonium perchlorate or 0.2 M tetra-*n*-butylammonium perchlorate.

The UV-visible spectra for solutions of the complexes were recorded with a Cary Model 17D or Model 219 spectrophotometer. Infrared spectra of the complexes, as KBr disks or as solutions in NaCl cells, were recorded with a Perkin-Elmer Model 283 infrared spectrophotometer. Proton nuclear magnetic resonance spectra were recorded with a Varian EM 390 NMR spectrometer. Electron spin resonance spectra were obtained with a Varian Model V4500 spectrometer. All spectra were referenced vs. DPPH ($g = 2.0037$). Magnetic susceptibility measurements were made by use of a Faraday balance or by the NMR method.[19] The measurements were corrected for diamagnetism.

All syntheses and preparations of solutions were performed inside a Vacuum Atmospheres Corp. Dri-Train He-193-1 DriLab glovebox filled with purified nitrogen. Sample cells for spectroscopic measurements were filled inside this glovebox and then sealed in the appropriate cell with rubber stopples or wax before being exposed to ambient air.

Reagents. 3,5-Di-*tert*-butylcatechol, 3,5-di-*tert*-*o*-benzoquinone (Aldrich Chemical Co.), V^VOCl_3 (Alfa), and vanadium(IV) and -(III) and pentanedione (acac) complexes were employed to synthesize the vanadium–catechol complexes. The $V^{IV}O(acac)_2$ complex was synthesized from $V^{IV}OSO_4\cdot 2H_2O$ (Eastman) and 2,4-pentanedione (Hacac) (Aldrich);[20] $V^{III}(acac)_3$[21] and $V^{IV}Cl_2(acac)_2$[22] were synthesized by established methods. A 25% solution of tetraethylammonium hydroxide (TEAOH) in methanol (Eastman) was used as a source of base. Syntheses were performed in reagent grade CH_2Cl_2 (dried with Linde 5-Å Molecular Sieves), anhydrous diethyl ether, or anhydrous methanol (Mallinckrodt).

Solutions for spectroscopic or electrochemical measurements were prepared by use of Burdick and Jackson "distilled in glass" CH_2Cl_2, acetonitrile (MeCN), and dimethyl sulfoxide (Me_2SO). For the NMR measurements Me_2SO-d_6 (99 atom %D) and $CDCl_3$ (99.8 atom %D) were used.

The disodium salt of 3,5-di-*tert*-butylcatechol (Na_2DTBC) was prepared by addition of excess sodium metal (approximately 2 g) to a solution of 4 g of 3,5-di-*tert*-butyl-*o*-quinone in 250 mL of ether; the mixture was stirred for several minutes every hour. (The reaction was too vigorous if stirred continuously.) After 2 h, the green quinone color was replaced by the dark blue color of the semiquinone radical; the solution became viscous. After 1 week, the solution turned yellow and lost its high viscosity. The solution was filtered and dried under vacuum.

The product from the combination of V^VOCl_3 and Na_2DTBC, formulated as $Na_2[V^VO(OCH_3)(DTBC)]$, was prepared by slowly adding 461 μL (0.005 mol) of $VOCl_3$ (diluted in 10 mL of CH_2Cl_2) to 2.66 g (0.01 mol) of $Na_2(DTBC)$ (dissolved in 40 mL of CH_2Cl_2). The reaction mixture was stirred for 1 h and then 0.2 g of $NaOCH_3$ in 20 mL of MeOH was added and the solution filtered. The filtrate was evaporated at room temperature under vacuum to isolate the pure material.

Disodium Salt of Bis(3,5-di-*tert*-butylcatecholato)oxovanadium(IV), $Na_2[V^{IV}O(DTBC)_2]$. This complex was prepared by adding 1.33 g (0.005 mol) of freshly prepared $V^{IV}O(acac)_2$ in 40 mL of CH_2Cl_2 to 2.66 g (0.01 mol) of Na_2DTBC in 40 mL of CH_2Cl_2. The reaction mixture was stirred for 1 day and then filtered to remove Na(acac). The filtrate was evaporated at room temperature under vacuum to isolate the pure material.

Disodium Salt of Dichlorobis(3,5-di-*tert*-butylcatecholato)vanadium(IV), $Na_2[V^{IV}Cl_2(DTBC)_2]$. This material was synthesized by the same procedure as for $Na_2V^{IV}O(DTBC)_2$, but $V^{IV}Cl_2(acac)_2$ was used in place of $V^{IV}O(acac)_2$. Alternatively, the same product was obtained by the addition of a stoichiometric amount of $SOCl_2$ to a solution of $Na_2V^{IV}O(DTBC)_2$ in CH_2Cl_2; the product was isolated by solvent evaporation.

Trisodium Salt of Tris(3,5-di-*tert*-butylcatecholato)vanadium(III), $Na_3[V^{III}(DTBC)_3]$. This complex was prepared by adding 1.74 g of (0.005 mol) of $V^{III}(acac)_3$ in 30 mL of CH_2Cl_2 to 3.99 g (0.015 mol) of Na_2DTBC in 60 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h and then filtered to remove Na(acac). The filtrate was evaporated to dryness at room temperature to isolate the pure material.

Results

$Na[V^VO(DTBC)_2]$. The addition of 1 equiv of $VOCl_3$ to 2 equiv of Na_2DTBC in CH_2Cl_2 results in a vigorous reaction that leads to the isolation of dark blue crystals. The crystals are soluble in a variety of solvents, including Me_2SO and MeCN. Figure 1 illustrates the absorption spectrum for this complex; the peak at 680 nm is assigned to a charge-transfer band. The same spectrum is observed in Me_2SO and MeCN. (However, when the crystals are dissolved in MeOH, the maximum absorbance shifts to 640 nm.) There is no spectroscopic evidence for the formation of quinone from the reaction, and magnetic susceptibility measurements confirm that the product is diamagnetic. Hence, a reasonable assumption

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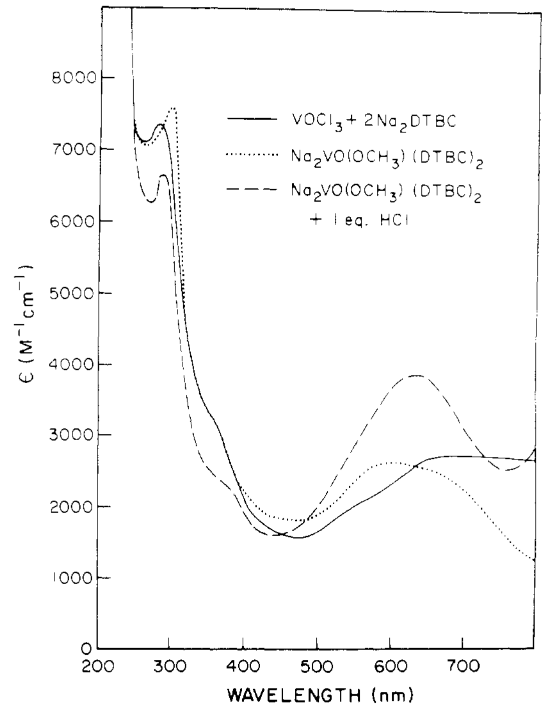

Figure 1. Absorption spectra in CH_2Cl_2 of 1 mM solutions of (a) the reaction product from the 1:2 combination of V^VOCl_3 and Na_2DTBC, (b) $Na_2VO(OCH_3)(DTBC)_2$, and (c) $Na_2VO(OCH_3)(DTBC)_2$ plus 1 equiv of HCl in Me_2SO (ε based on apparent total vanadium concentration).

is that the product is simply $NaV^VO(DTBC)_2$. However, the proton NMR spectra in various solvents indicate that the compound is not a simple monomeric species.

Although the UV–visible spectrum for this product is not solvent dependent (with the exception of MeOH), its proton NMR spectrum is affected by the medium. In Me_2SO-d_6 four *tert*-butyl resonances for two nonequivalent DTBC ligands are observed at 1.48, 1.53, 1.57, and 1.64 ppm vs. Me_4Si. The proton resonance for Me_2SO-d_6 is centered at 2.79 ppm as compared with 2.47 ppm for pure Me_2SO, and the individual resonances are not as sharp. This implies that Me_2SO binds to the sixth coordination site of the complex.

The proton NMR spectra for the product species in CCl_4 and MeCN-d_3 are broad with a series of sharp resonances superimposed. For CCl_4, these occur at 1.40, 1.48, and 1.61 ppm and for MeCN at 1.18, 1.23, 1.26, and 1.38 ppm. Peak broadening in NMR often results from exchange mechanisms. Alternatively, what appears to be a single broad peak may actually be the composite of many slightly nonequivalent resonances such as would be found in a polymer. That ligand exchange would occur readily in MeCN and CCl_4 but not in Me_2SO is unreasonable and makes the second explanation more tenable.

An examination of the electrochemistry of the product species, tentatively identified as $[NaV^VO(DTBC)_2]$, in Me_2SO, MeCN, and CH_2Cl_2 indicates that the material probably is polymeric. The cyclic voltammograms for the complex in the three solvents are illustrated by Figure 2. The extremely small current values are consistent with extensive polymerization. In Me_2SO, the two oxidation peaks correspond to ligand oxidations. Controlled-potential electrolysis at +0.38 V vs. SCE results in a four-electron oxidation to produce two quinone (DTBQ) molecules; an initial positive scan of the product solution reveals that all of the DTBC has been oxidized.

Controlled-potential electrolysis of the reduction peak at −0.45 V vs. SCE (Figure 2) requires one electron per vanadium and yields a product with a vanadium(IV) EPR signal. Reversal of an initial negative scan results in the appearance of a new oxidation peak at −0.38 V vs. SCE. This peak also is present for an initial positive scan after controlled-potential electrolysis at −0.55 V vs. SCE and is due to the oxidation of vanadium(IV). The electrochemistry of the complex in MeCN and CH_2Cl_2 is similar to that in Me_2SO, although the peaks are not as well-defined.

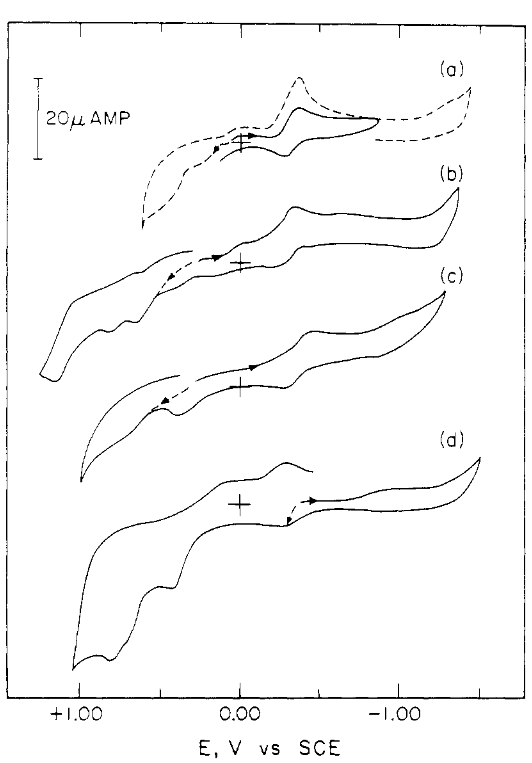

Figure 2. Cyclic voltammograms for 1 mM solutions of the reaction product from the 1:2 combination of V^VOCl_3 and Na_2DTBC in (a) Me_2SO, (b) MeCN, and (c) CH_2Cl_2, and for (d) 1 mM $Na_2V^VO(OCH_3)(DTBC)_2$ in CH_2Cl_2 (scan rate 0.01 V s^{-1}; Pt working electrode (area 0.23 cm^2)).

$Na_2V^VO(OCH_3)(DTBC)_2$. The change in the visible spectrum of $[NaV^VO(DTBC)_2]_n$ in MeOH is more indicative of a chemical reaction than a solvent shift. The addition of methoxide to the sixth coordination site to form $Na_2V^V(OCH_3)(DTBC)_2$ is a reasonable possibility under these conditions. This compound, which has been synthesized (see Experimental section), has a spectrum in CH_2Cl_2 that is illustrated in Figure 1. When 1 equiv of HCl is added to the solution, the absorption maximum at 600 nm shifts to 640 nm. A reasonable assumption is that the latter peak is due to $Na_2V^V(OH)(OCH_3)(DTBC)_2$. Attempts to isolate this product, either by dissolving the vanadium(V) polymer in MeOH or by adding HCl to $Na_2V^VO(OCH_3)(DTBC)_2$, consistently result in a mixture of products. Although a contemporary X-ray crystallographic investigation reports the synthesis and isolation of a crystalline $Et_3NH[V^V(DTBC)_3]$ complex,[25] electrochemical measurements indicate that $V^V(DTBC)_3^-$ is not a stable species in solution.

The cyclic voltammogram for $Na_2V^VO(OCH_3)(DTBC)_2$ is shown in Figure 2. In contrast to $[NaV^VO(DTBC)_2]_n$, a reduction of vanadium(V) to -(IV) does not occur. Comparison with the electrochemistry for the $V^{III}(DTBC)_3^{3-}$ complex (Table I) confirms that the $V^V(DTBC)_3^-$ complex is not stable in this solution (a reduction peak at +0.37 V vs. SCE would be observed). On the basis of controlled-potential electrolysis experiments, each of the oxidation peaks represents a two-electron process to form DTBQ.

Spectroscopic measurements confirm that $Na_2V^VO(OCH_3)(DTBC)_2$ is stable in air. If HCl is added to the solution, it gradually turns purple in the presence of air (λ_{max} 510 nm).

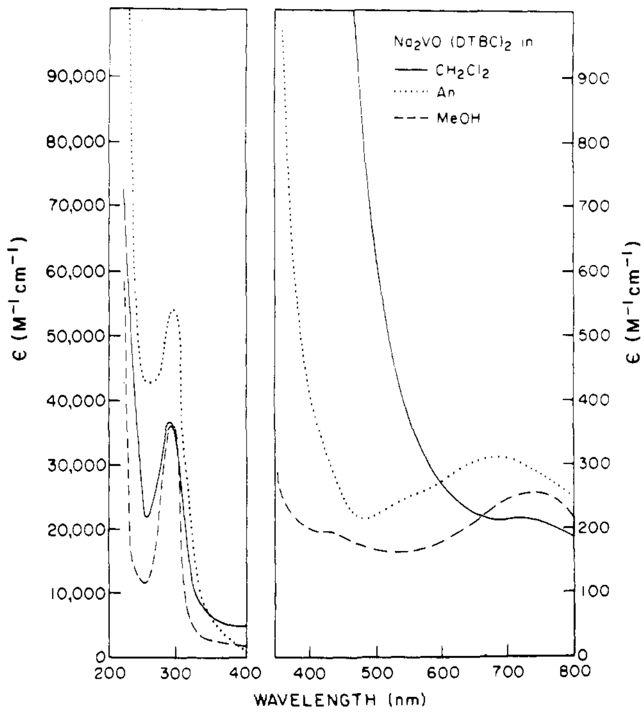

Figure 3. Absorption spectra for 1 mM solutions of Na$_2$V^{IV}O(DTBC)$_2$ in (a) CH$_2$Cl$_2$ and (b) MeCN.

This process is not reversible. On the basis of its electrochemistry, such an oxygenated solution appears to contain bound semiquinone ligands. Addition of V^{V}OCl$_3$ to the semiquinone of DTBQ (DTBSQ$^{-}\cdot$) in MeOH or MeCN results in the formation of a purple solution, but attempts to isolate a product result in the formation of DTBQ and vanadium–DTBC complexes. Thus, the purple complex probably is a vandium(V)–DTBSQ$^{-}\cdot$ species.

Na$_2$V^{IV}O(DTBC)$_2$. When 1 equiv of V^{IV}O(acac)$_2$ is added to 2 equiv of Na$_2$DTBC in CH$_2$Cl$_2$, an immediate reaction occurs to form a red-bronze solution. If this solution is allowed to stir several hours, a white precipitate of Na(acac) forms, which can be removed from the solution by filtration. When the filtrate is evaporated, coffee-colored crystals of pure Na$_2$V^{IV}O(DTBC)$_2$ result; their absorption spectrum is illustrated by Figure 3.

Most vanadyl compounds exhibit three low-intensity bands in the visible region at room temperature that are attributed to d → d* transitions.[23,24] The spectrum of Na$_2$V^{IV}O(DTBC)$_2$ is dominated by the presence of an intense charge-transfer band at 283 nm (ϵ 36 300 M^{-1} cm^{-1}), which results in a bronze-colored CH$_2$Cl$_2$ solution. This band extends into the visible region and obscures most of the region in which d → d* transitions occur; there is a slight shoulder at 710 nm which may be due to such a transition. Solutions of Na$_2$V^{IV}O(DTBC)$_2$ in MeCN are blue-green, and the charge-transfer band at 290 nm is much more intense (ϵ 53 300 M^{-1} cm^{-1}) and less broad. As a result some of the d → d* transitions become more apparent. These spectral changes must result from the coordination of MeCN to the unfilled sixth coordination site. Unfortunately, this could not be verified for other coordinating solvents (such as Me$_2$SO or DMF) because of rapid hydrolysis reactions.

The EPR spectrum of Na$_2$V^{IV}O(DTBC)$_2$ also exhibits a significant solvent effect, which is illustrated by Figure 4. In CH$_2$Cl$_2$, Na$_2$V^{IV}O(DTBC)$_2$ exhibits a typical vanadium(IV) EPR spectrum of eight lines. The spectrum is centered at g = 1.96 and has a peak-to-peak separation of 95 G. The spectrum in MeCN has additional splittings of the original eight lines and is narrower, with a peak-to-peak separation of 90 G. The cause of the additional hyperfine splittings is not known but may be due to the nitrogen of a bound MeCN. Electron hyperfine splittings of vanadium(IV) signals by other nuclei rarely are observed.[24] The spectrum recorded in MeCN-d_3 is identical with the spectrum in MeCN, which confirms that the protons of MeCN are not responsible for the splitting.

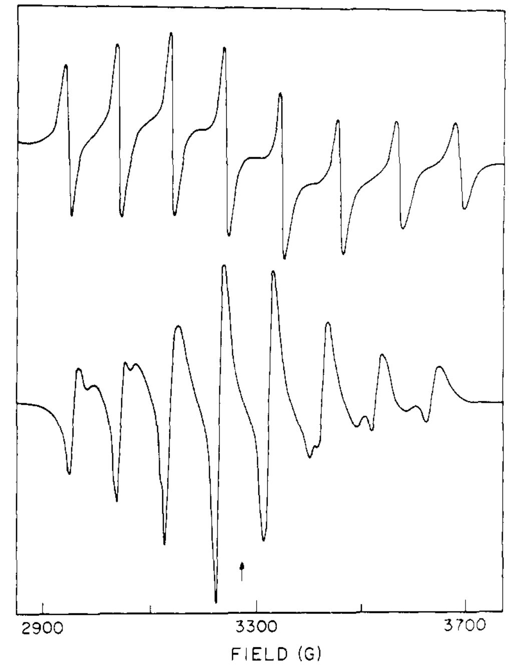

Figure 4. EPR spectra of 0.01 M Na$_2$V^{IV}O(DTBC)$_2$ in (a) CH$_2$Cl$_2$ (upper spectrum) and (b) MeCN (lower spectrum). Position of DPPH resonance is indicated by the arrow.

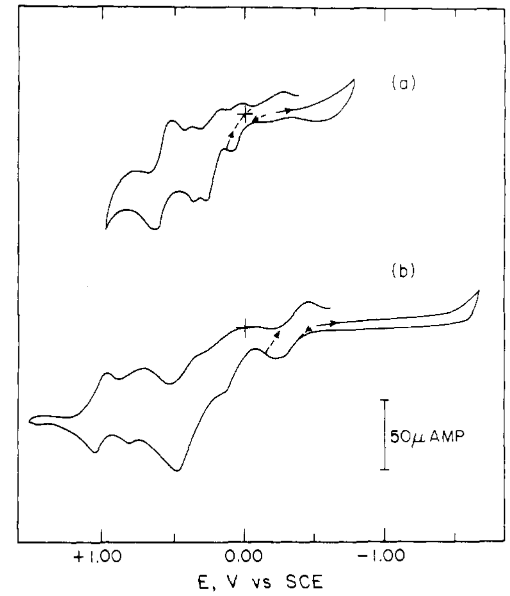

Figure 5. Cyclic voltammograms for 1 mM solutions of Na$_2$V^{IV}O(DTBC)$_2$ in (a) CH$_2$Cl$_2$ and (b) MeCN (scan rate 0.10 V s^{-1}; Pt working electrode (area 0.23 cm^2)).

The cyclic voltammograms for Na$_2$V^{IV}O(DTBC)$_2$ in CH$_2$Cl$_2$ and MeCN are shown in Figure 5. Although both systems have the same general appearance, the potentials for the various electrochemical processes are different. Vanadium(IV) is not reduced, but several oxidative processes occur.

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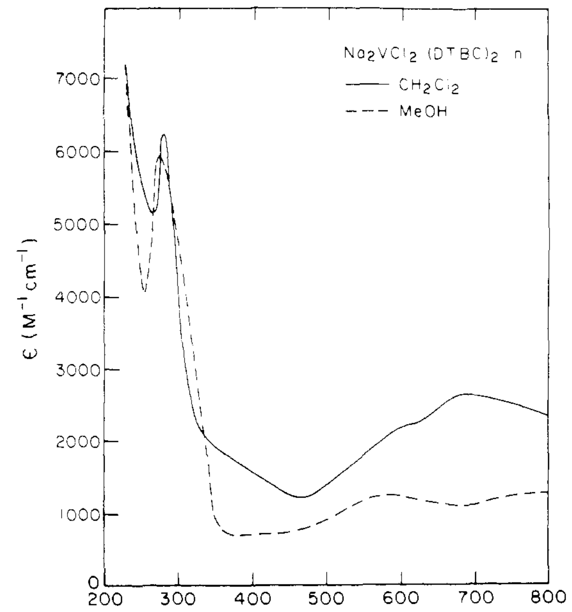

Figure 6. Absorption spectra of 1 mM solutions of $Na_2V^{IV}Cl_2(DTBC)_2$ in (a) CH_2Cl_2 and (b) MeOH.

The first anodic peak is at +0.18 V vs. SCE in CH_2Cl_2 and at −0.13 V in MeCN. Reversal of the scan after this peak results in a reduction peak at −0.52 V in CH_2Cl_2 and at −0.40 V in MeCN. Controlled-potential electrolysis at the peak potential removes one electron per complex to yield a product solution with the same UV–visible spectrum in CH_2Cl_2 and MeCN [λ_{max} 770 (ϵ 3000) and λ_{max} 280 (ϵ 29 000)]. The product does not exhibit an EPR spectrum nor any evidence for the formation of DTBQ. Hence, this species appears to be a monomeric vanadium(V) complex, $NaV^{V}O(DTBC)_2$. Controlled-potential electrolysis at the potentials for the remaining oxidation peaks removes two electrons per complex for each; spectroscopy and electrochemistry confirm that DTBQ is formed from these oxidations.

The properties of $Na_2V^{IV}O(DTBC)_2$ in MeOH also have been studied. Fresh solutions are green and their UV–visible spectra are identical with that for the product from electrochemical oxidation of $Na_2[V^{IV}O(DTBC)_2]$ (see preceding paragraph). During a period of several days, the solution gradually turns blue and the wavelength of maximum absorption shifts to 640 nm. If $Na_2V^{IV}O(DTBC)_2$ is dissolved in MeOH and then isolated by solvent evaporation, it yields a product that forms blue solutions (λ_{max} 640 nm) in Me_2SO, is EPR silent, and exhibits two broad proton NMR peaks at 1.2 and 1.6 ppm. The peak width for the Me_4Si reference of the latter is 5 Hz, which indicates that the solution is only slightly paramagnetic. These observations confirm that the majority of the vanadium in $Na_2V^{IV}O(DTBC)_2$ can be oxidized by the protons of MeOH.

$Na_2VCl_2(DTBC)_2$. When 1 equiv of $SOCl_2$ is added to 1 equiv of $Na_2V^{IV}O(DTBC)_2$ in CH_2Cl_2, the solution immediately changes color from bronze to blue. Previous work has shown that $SOCl_2$ can be used to deoxygenate vanadium(IV) compounds.[22]

$$VO(acac)_2 + SOCl_2 \rightarrow VCl_2(acac) + SO_2 \qquad (1)$$

The reaction of $Na_2V^{IV}O(DTBC)_2$ with $SOCl_2$ is rapid at room temperature and represents a simple substitution of two chlorides for the oxo group, which is analogous to the reaction of $SOCl_2$ with $V^{IV}O(acac)_2$. The blue crystals isolated by solvent evaporation also can be formed by use of the same procedure for the synthesis of $Na_2V^{IV}O(DTBC)_2$, but with $V^{IV}Cl_2(acac)_2$ in place of $V^{IV}O(acac)_2$. The direct reaction of $SOCl_2$ with $Na_2V^{IV}O(DTBC)_2$ is simpler and produces a pure product.

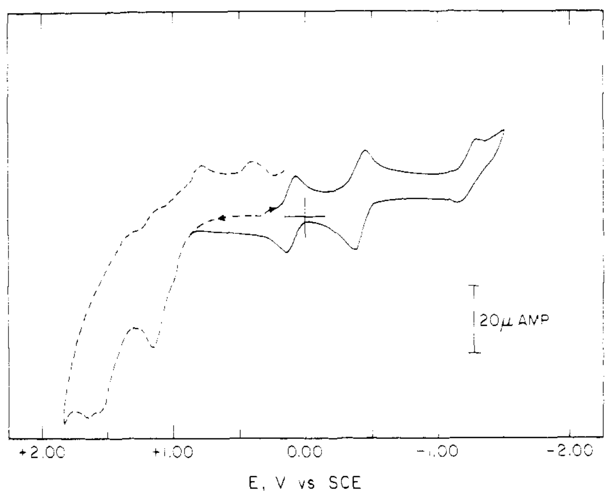

Figure 7. Cyclic voltammetry for a 1 mM solution of $Na_2V^{IV}Cl_2(DTBC)_2$ in CH_2Cl_2 (scan rate 0.10 V s^{-1}; Pt working electrode (area 0.23 cm^2)).

The UV–visible spectrum for $Na_2V^{IV}Cl_2(DTBC)_2$ in CH_2Cl_2 is illustrated by Figure 6. The same spectrum is obtained in a variety of coordinating and noncoordinating nonoxygenated solvents such as MeCN and benzene. This invariance is believed to be due to the six-coordinate nature of $Na_2V^{IV}Cl_2(DTBC)_2$ and is added evidence that the spectral changes observed for $Na_2V^{IV}O(DTBC)_2$ in MeCN are due to solvent coordination. The visible spectrum of $Na_2V^{IV}Cl_2(DTBC)_2$ is dominated by a charge-transfer band at 690 nm (ϵ 5260 m^{-1} cm^{-1}) with a slight shoulder at 600 nm, which may represent a d → d* transition.

A comparison of the infrared spectra for $Na_2V^{IV}O(DTBC)_2$ and $Na_2V^{IV}Cl_2(DTBC)_2$ clearly indicates that the vanadium–terminal oxygen band for $Na_2V^{IV}O(DTBC)_2$ occurs at 880 cm^{-1}.

The magnetic moment of $Na_2V^{IV}Cl_2(DTBC)_2$ in CH_2Cl_2 is 1.75 μ_B, which confirms that oxidation of the vanadium center has not occurred. The species exhibits an eight-line EPR spectrum centered at $g = 1.96$, with a peak-to-peak separation of 100 G. The effect of the oxygen of the vanadyl unit on the spectrum is minimal. Neither the magnetic moment nor the EPR spectrum is solvent dependent in nonoxygenated solvents.

The cyclic voltammetry for $Na_2V^{IV}Cl_2(DTBC)_2$ is illustrated by Figure 7. An initial negative scan yields three reduction peaks, each coupled to oxidation peaks that appear with a reverse scan. The first peak occurs at +0.08 V vs. SCE and is coupled to an oxidation at +0.13 V. Likewise, the reduction peaks at −0.44 and −1.25 V are coupled to oxidation peaks at −0.38 and −1.20 V, respectively. Controlled-potential electrolysis establishes that each peak represents a one-electron reduction, presumably at the metal center because they do not correspond to ligand reductions.

$$V(IV) \xrightarrow{1e^-} V(III) \xrightarrow{1e^-} V(II) \xrightarrow{1e^-} V(I) \qquad (2)$$

Although the reversibility of these peaks indicates that the products are stable within the cyclic voltammetric time frame, the reduced solutions that are formed by controlled-potential electrolysis are not sufficiently stable to characterize. The formation of V(I) is unprecedented, but a V(II)–catechol complex has been proposed.[26]

Three oxidation peaks are observed for an initial positive scan of a $Na_2V^{IV}Cl_2(DTBC)_2$ solution: at +1.13 V, +1.51 V,

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(26) Shilov, A. E. *Biol. Aspects Inorg. Chem., Symp., 1976* **1977**, 197.

Table I. Redox Chemistry of the Vandium(V), -(IV), and -(III) Complexes Formed by Disodium 3,5-Di-*tert*-butylcatecholate

reaction	V vs. SCE[a]			solvent
	$E^{\circ\prime}$	$E_{p,c}$	$E_{p,a}$	
$(1/n)[NaV^{V}O(DTBC)_2]_n \xrightarrow{-4e^-} V^{V} + 2DTBQ$			+0.30	Me_2SO
$(1/n)[NaV^{V}O(DTBC)_2]_n \xrightarrow{+1e^-} V^{IV}O(DTBC)_2{}^{2-}$		−0.45		Me_2SO
$Na_2V^{V}O(OCH_3)(DTBC)_2 \xrightarrow{-2e^-} V^{V}O(OCH_3)(DTBC) + DTBQ$			+0.43	Me_2SO
$\xrightarrow{-4e^-} V^{V} + 2DTBQ$			+0.78	Me_2SO
$Na_2V^{IV}O(DTBC)_2 \xrightarrow{-1e^-} NaV^{V}O(DTBC)_2$			+0.18	CH_2Cl_2
			−0.13	MeCN
$\xrightarrow{-3e^-} NaV^{V}O(DTBC) + DTBQ$			+0.35 +0.46	CH_2Cl_2 MeCN
$\xrightarrow{-5e^-} V^{V} + 2DTBQ$			+0.61 +1.12	CH_2Cl_2 MeCN
$Na_2V^{IV}Cl_2(DTBC)_2 \xrightarrow{+1e^-} NaV^{III}(DTBC)_2$	+0.11			CH_2Cl_2
$\xrightarrow{+2e^-} Na_2V^{II}(DTBC)_2{}^{b}$	−0.41			CH_2Cl_2
$\xrightarrow{+3e^-} V^{I\ b}$	−1.23			
$Na_2V^{IV}Cl_2(DTBC)_2 \xrightarrow{-2e^-}$ oxidation products			+1.13	CH_2Cl_2
$Na_3V^{III}(DTBC)_3 \xrightarrow{-1e^-} Na_2V^{IV}(DTBC)_3$	+0.11			CH_2Cl_2
$\xrightarrow{-2e^-} NaV^{V}(DTBC)_3$	+0.37			CH_2Cl_2
$\xrightarrow{-7e^-} V^{V} + 3DTBQ$			+1.18	CH_2Cl_2

[a] $E^{\circ\prime}$ represents the formal potential for reversible processes and is the mean of the cathodic peak potential ($E_{p,c}$) and the anodic peak potential ($E_{p,a}$) for a scan rate of 0.1 V s^{-1} at a platinum electrode. [b] Tentative.

and +1.63 V. In contrast to the cathodic peaks, the anodic electrochemistry is completely irreversible. Controlled-potential electrolysis at +1.25 V removes two electrons per complex but does not yield quinone or semiquinone. This peak probably is due to the oxidation of bound chloride to chlorine. The resulting product does not resemble any of the previously studied vanadium–catechol complexes.

Although spectroscopic measurements indicate that solutions of $Na_2V^{IV}Cl_2(DTBC)_2$ in CH_2Cl_2 are stable in air for several minutes, the compound reacts immediately with water or oxygenated solvents. The spectrum of the complex in MeOH is shown in Figure 6. When crystals that have been dissolved in MeOH are recovered by solvent evaporation, they no longer exhibit an EPR spectrum but have a proton NMR spectrum in Me_2SO-d_6 with four sharp resonances at 1.18, 1.30, 2.01, and 2.05 ppm. The UV–visible spectrum of methanolic solutions of $Na_2V^{IV}Cl_2(DTBC)_2$ is strikingly similar to that for $Na_2VO(OCH_3)(DTBC)_2$ (Figure 1). The strong affinity of vanadium(IV) for oxygen apparently promotes a rapid reaction with methanol.

$$Na_2V^{IV}Cl_2(DTBC)_2 + MeOH \rightarrow V^{V}(OCH_3)(DTBC)_2 + 0.5H_2 + 2NaCl \quad (3)$$

$Na_3V^{III}(DTBC)_3$. When 3 mol of Na_2DTBC is added per 1 mol of $V^{III}(acac)_3$ in CH_2Cl_2, an immediate reaction occurs in which the solution changes from brown to olive green. After several hours of stirring, a white precipitate of Na(acac) forms, which can be removed by filtration. Evaporation of the filtrate yields dark green crystals of $Na_3V^{III}(DTBC)_3$. Exposure of the solid compound or of solutions in CH_2Cl_2 to air results in a color change from green to blue within seconds, which is irreversible.

The spectrum of $Na_3V^{III}(DTBC)_3$ in CH_2Cl_2 exhibits an absorption band at λ_{max} 284 (ϵ 49 000); dilute solutions are bronze and similar in appearance to solutions of $Na_2V^{IV}O(DTBC)_2$. More concentrated solutions (0.01 M) are olive green. Like $Na_2V^{IV}O(DTBC)_2$, the spectrum of $Na_3V^{III}(DTBC)_3$ is dominated by an intense absorbance [λ_{max} 284 nm (ϵ 49 000 M^{-1} cm^{-1})]. The $Na_3V^{III}(DTBC)_3$ complex, which does not exhibit a vanadium–oxygen vibrational band in its IR spectrum, has a magnetic moment of 2.93 μ_B. Thus, despite the spectral similarities of $Na_2V^{IV}O(DTBC)_2$ and $Na_3V^{III}(DTBC)_3$, two distinct complexes have been isolated.

The anodic electrochemistry of $Na_3V^{III}(DTBC)_3$ in CH_2Cl_2 is similar to that of $Na_2V^{IV}Cl_2(DTBC)_2$ with two reversible one-electron couples at +0.13 and +0.40 V plus several irreversible peaks in the region of +1.0 V. Controlled-potential electrolysis at +0.13 V removes one electron per complex and yields a blue solution. The potential of the first oxidation peak is the same as that observed for the reverse scan of a $Na_2V^{IV}Cl_2(DTBC)_2$ reduction. Oxidative electrolysis of the remaining peaks results in the formation of DTBQ. Unlike $Na_2V^{IV}Cl_2(DTBC)_2$, no reductive electrochemistry is observed for the vanadium(III) complex. The large negative charge of the complex may preclude reduction within the solvent window. The lability of the chloride ligand may allow $Na_2V^{IV}Cl_2(DTBC)_2$ to be reduced to $Na_2V^{III}(DTBC)_2{}^+ + 2Cl^-$. The stronger interaction between the catecholate anion and V(III) prevents a similar process for $Na_3V^{III}(DTBC)_3$.

In MeOH the UV–visible spectrum for the vanadium(III) complex is substantially different from that in CH_2Cl_2 with the appearance of a peak at 385 nm. When the complex is dissolved in MeOH and then recovered by solvent evaporation, the resulting material is blue instead of olive green (even when redissolved in CH_2Cl_2). The proton NMR spectrum of this material in Me_2SO-d_6 has resonances at 1.21 and 1.53 ppm, which are 5 Hz in width; thus the solution is not completely diamagnetic. However, the amount of paramagentism is much less than would be expected if the material were vanadium(III) or even a vanadium(IV) species. The solution appears to

Table II. Spectroscopic Properties of Vanadium(V), -(IV), and -(III) Catecholate Complexes

complex	solvent	UV-vis[a] (ϵ, M^{-1} cm^{-1})	μ_{eff}, μ_B	proton NMR[b]	EPR g	EPR A, G
$[NaV^{V}O(DTBC)_2]_n$	Me_2SO	700 (2700)		1.43, 1.53		
		282 (7350)		1.57, 1.64		
	MeCN	680 (3550)	diamagnetic	1.18, 1.23		
		271 (6550)		1.26, 1.38		
	CH_2Cl_2	680 (3720)		1.40, 1.47		
		274 (7180)		1.61		
$Na_2V^{V}O(OCH_3)(DTBC)_2$	Me_2SO	600 (2600)	diamagnetic	1.49, 1.61		
		295 (7570)				
$Na_2V^{IV}O(DTBC)_2$	CH_2Cl_2	283 (36 300)	1.72		1.96	95
	MeCN	290 (53 300)	1.73		1.96	90
$Na_2V^{IV}Cl_2(DTBC)_2$	CH_2Cl_2	690 (5260)	1.75		1.96	100
		287 (6310)				
$Na_3V^{III}(DTBC)_3$	CH_2Cl_2	284 (49 000)	2.93			

[a] Absorptions given in nm. ϵ values are based on the weight of isolated complex and do not take into account any solvent of crystallization. [b] Chemical shifts given in ppm vs. Me_4Si.

contain mainly vanadium(V) with traces of the lower oxidation states. Hence, $Na_3V^{III}(DTBC)_3$ is not stable in MeOH.

Discussion and Conclusions

The oxidation–reduction reactions and spectroscopic properties of the vanadium–catechol complexes are summarized in Tables I and II. On the basis of the magnetic data in Table II, stable vanadium–catechol complexes can be prepared without an accompanying change of oxidation state in aprotic media. Addition of protons in the form of MeOH (or H_2O) results in the conversion of the lower oxidation states to vanadium(V). This is in contrast to previous studies of vanadium pyrocatechol complexes in which vanadium(IV) appears to be the stable oxidation state in MeOH.[11-18] The reason for this discrepancy is not clear.

Because $Na_2V^{IV}O(DTBC)_2$ is unstable in the presence of methanol and is oxidized at +0.18 V vs. SCE, a concerted redox reaction probably occurs:

$$V^{IV}O(acac)_2 + 2DTBCH_2 + CH_3OH \rightarrow V^{V}(OH)(OCH_3)(DTBC)_2 + 2H(acac) + 0.5H_2 + H^+ \quad (4)$$

The initial reaction of vanadium(IV) with $DTBCH_2$ results in the formation of a vanadium(IV) complex, which is oxidized by the free protons released by the ligand. Hence, vanadium(IV) that is bound to DTBC is easier to oxidize than that bound to pyrocatechol.

The effect of the terminal oxygen of the vanadyl unit on the properties of the vanadium(IV)–DTBC complexes is illustrated by a comparison of $Na_2V^{IV}O(DTBC)_2$ and $Na_2V^{IV}Cl_2(DTBC)_2$. The EPR spectra of the two complexes are similar to g values of 1.96. The vanadium–oxalate complex $K_2V^{IV}O(ox)_2$ and $VOSO_4$ in sulfuric acid have the same value,[23] which confirms that the in-plane ligands dominate the energetics of the unpaired electron. Although the terminal oxygen does not affect the magnetic spectra, it has a significant influence on the electrochemistry. The $Na_2V^{IV}O(DTBC)_2$ complex is not reducible, but is does exhibit quasi-reversible oxidation to vanadium(V). In contrast, the $Na_2V^{IV}Cl_2(DTBC)_2$ complex undergoes three one-electron reversible reductions but no oxidation to vanadium(V). The reduction products are highly unstable and may even react with the nitrogen present in the "inert" atmosphere of the electrolysis cell.

The vanadium(III) complex $[Na_3V^{III}(DTBC)_3]$ exhibits the same electrochemical reversiblity as $Na_2V^{IV}Cl_2(DTBC)_2$ because of the absence of the vanadyl moity. It cannot be reduced because of its high negative charge density but is oxidized by one electron to form a blue species.

In summary, the results of the present investigation confirm that stable complexes of vanadium(V), –(IV), and –(III) with DTBC can be synthesized in aprotic media, but in protic media only vanadium(V) complexes are stable. For the vanadium–DTBC system metal ion oxidations always occur before ligand oxidation. Hence, the only semiquinone complex which can be formed electrochemically is with vanadium(V).

The inhibition by the terminal oxo group to reversible electron transfer undoubtedly is important to the design of small molecules as models for redox enzymes such as nitrogenase. The similarlity of vanadium and molybdenum chemistry indicates that the effect of terminal oxygen atoms on molybdenum electrochemistry should be determined.

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Registry No. $Na_2[V^{V}O(OCH_3)(DTBC)_2]$, 80243-45-4; $Na_2[V^{IV}O(DTBC)_2]$, 80243-46-5; $Na_2[V^{IV}Cl_2(DTBC)_2]$, 80262-57-3; $Na_3[V^{III}(DTBC)_3]$, 80262-58-4; $[NaV^{V}O(DTBC)_2]_n$, 80243-48-7; $V^{IV}O(acac)_2$, 3153-26-2; $V^{IV}Cl_2(acac)_2$, 38991-25-2; $V^{III}(acac)_3$, 13476-99-8.