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Catecholate and Semiquinone Complexes of Vanadium. Factors That Direct Charge Distribution in Metal-Quinone Complexes

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Semiquinone and catecholate complexes of vanadium have been studied with tetrachloroquinone and 3,5-di-*tert*-butylquinone ligands. Crystallographic characterization has been carried out on the sodium salt of $V(DBCat)_3^-$, obtained as the methanol solvate, $Na[V(DBCat)_3]\cdot 4CH_3OH$. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 12.020$ (3) Å, $b = 15.842$ (3) Å, $c = 15.521$ (4) Å, $\alpha = 105.04°$, $\beta = 104.94$ (2)°, $\gamma = 110.72$ (4)°, and $V = 2461.7$ (8) Å^3. Spectral characterization on $Na[V(Cl_4Cat)_3]$ indicates that it has a similar charge distribution. In the solid state, neutral $V(Cl_4SQ)_3$ has the tris(semiquinonato)vanadium(III) charge distribution found also with the Cr and Fe analogues. Electrochemical reduction of this complex occurs reversibly in acetonitrile solution, pointing to a change in charge distribution. Under these conditions the form of the complex appears to be $V(Cl_4SQ)(Cl_4Cat)_2$, containing mixed-charge quinone ligands and related to the solid-state form by transfer of two electrons from the metal to the quinones. Parameters that influence charge distribution in metal-quinone complexes include solvation effects and overall charge of the complex in addition to effects that directly alter d-orbital energy at the metal.

Introduction

The π-electronic levels of *o*-quinones appear to be similar in energy to transition-metal d orbitals. Quinones complex with metals in three localized electronic forms. Within the neutral, isoelectronic metal-quinone complex unit, limiting forms are metal-benzoquinone and metal-catecholate related by transfer of two electrons between quinone and metal. An intermediate form containing the partially reduced semiquinone also exists and has been found to occur commonly with metals of the first transition series. Studies are being carried out to identify parameters that stabilize one mode of coordination over another and to develop the reactivity of these compounds.

Vanadium complexes containing catecholate and semiquinone ligands have been of particular interest. Several reports have described the complicated solution and redox chemistry of vanadium-catechol systems.[1-4] Other studies have focused on applying the strong reductive property of vanadium(II)-catechol mixtures to reactions that reduce acetylenes to olefins, CO to methanol, and N_2 to ammonia.[5,6] We have described the reaction between $V(CO)_6$ and benzoquinones, which leads to neutral V(III)-semiquinonate complexes of form $V(SQ)_3$.[7] The tris(3,5-di-*tert*-butyl-1,2-semiquinonato)vanadium(III) complex was observed to react with molecular oxygen to form dimeric [VO(3,5-DBSQ)(3,5-DBCat)]$_2$, a complex containing mixed-charge ligands and vanadium(V). This result suggested that nucleophilic reactivity accompanied by internal transfer of charge may occur as an important and unique aspect of the chemistry of vanadium-quinone systems. In related work, $V(Cat)_3^-$ complexes have been formed by treating V(V) with catecholate ligands.[2,7] An interesting difference in charge distribution exists between $V(SQ)_3$ and $V(Cat)_3^-$ such that the one-electron redox process relating the two species must be accompanied by transfer of two electrons between metal and quinone ligands. Ironically, *reduction* of the neutral complex results in *oxidation* of the metal ion. In this report we describe some of the chemical and physical properties of the $V(SQ)_3$ and $V(Cat)_3^-$ complexes prepared with tetrachloro-1,2-benzoquinone and 3,5-di-*tert*-butyl-1,2-benzoquinone.

Table I. Infrared Bands in the 900-1600-cm^{-1} Region for $M(Cl_4SQ)_3$ and $M(Cl_4Cat)_3$ Complexes

complex	bands, cm^{-1}
$V(Cl_4SQ)_3$	1495 (s), 1465 (s), 1333 (m), 1268 (m), 1205 (s), 1005 (s)
$Cr(Cl_4SQ)_3$	1470 (s), 1435 (s), 1330 (m), 1270 (m), 1208 (s), 980 (s)
$Fe(Cl_4SQ)_3$	1483 (s), 1445 (s), 1339 (m), 1273 (m), 1212 (s), 970 (s)
$V(Cl_4Cat)_3^-$	1535 (m), 1390 (m), 1260-1240 (b, s), 990 (s)
$[Mo(Cl_4Cat)_3]_2$	1530 (m), 1380 (m), 1260-1230 (b, s), 970 (s)

Experimental Results

Both $V(DBSQ)_3$ and $V(Cl_4SQ)_3$ have been prepared by treating $V(CO)_6$ with the respective benzoquinone.[7,8] In the presence of trace quantities of O_2, $V(DBSQ)_3$ reacts to form dimeric [VO(DBSQ)(DBCat)]$_2$; however, solutions of $V(Cl_4SQ)_3$ are air-stable. We have attempted to look further at the chemistry of $V(DBSQ)_3$ but have found that it fails to react with H_2O, S_8, acetylenes including Ph_2C_2 and $(CF_3)_2C_2$, and CH_3I. These observations were made by treating toluene solutions of the complex with reagent and observing no change in the characteristic EPR spectrum of $V(DBSQ)_3$. Apparently, oxygen sensitivity is not associated with general nucleophilic reactivity in this case.

More reduced forms of the di-*tert*-butylquinone complex have recently been reported by Cooper et al.[2] formed by treating higher oxidation state vanadium complexes with the catechol form of the ligand.

$$VO_3^- + H_2DBCat \rightarrow V(DBCat)_3^-$$

$$VO(acac)_2 + H_2DBCat \rightarrow V(DBCat)_3^{2-}$$

$$VCl_3 + H_2Cat \rightarrow V(Cat)_3^{3-}$$

In related chemistry, we have investigated the Shilov V(II)/catechol system by using di-*tert*-butylcatechol.[5] As with unsubstituted catechol, in methanol solution the V(II)-DBCat mixture produces hydrogen gas. Complex products of this reaction include $V(DBSQ)_3$, observed in solution by EPR, and $V(DBCat)_3^-$, which crystallized from the methanol solution as $Na[V(DBCat)_3]\cdot 4CH_3OH$. Studies on V(II) reactions with substituted catechols will be presented separately. In this report we focus on the neutral and monoanionic complexes, specifically on the difference in charge distribution between $V(SQ)_3$ and $V(Cat)_3^-$. To facilitate

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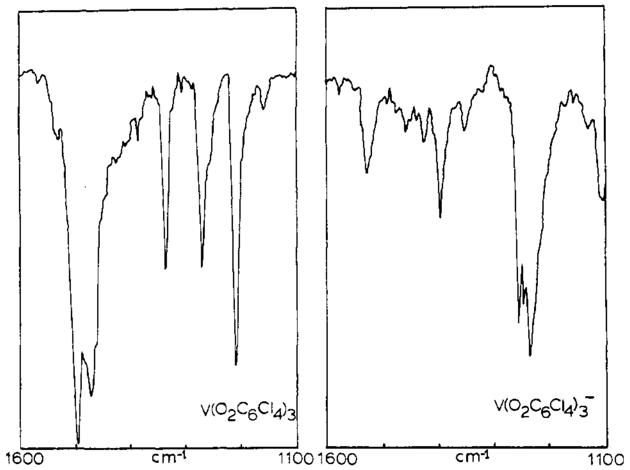

Figure 1. Infrared spectra on $V(Cl_4SQ)_3$ and $Na[V(Cl_4Cat)_3]$ in the 1100–1600-cm^{-1} region, recorded as KBr pellets. Spectra show differences that appear diagnostic of semiquinone and catecholate coordination for the tetrachloroquinone ligand.

this study a new route to the $V(Cat)_3^-$ complexes has been developed, beginning with $V(CO)_6^-$ and the respective benzoquinone. This procedure is general for a wide variety of *o*-benzoquinones, and the product complex can be isolated in high yield directly from the reaction mixture. In the Experimental Section synthetic routes to $V(DBCat)_3^-$ and $V(Cl_4Cat)_3^-$ are described. Both complexes are stable in air as solids but undergo gradual air oxidation to $[VO(DBSQ)(DBCat)]_2$ and $V(Cl_4SQ)_3$ in solution, as shown by the appearance of characteristic EPR spectra for these products.

Spectroscopic Properties of the $V(SQ)_3$ and $V(Cat)_3^-$ Complexes. Infrared spectra on tetrachlorocatecholate and tetrachlorosemiquinone complexes appear diagnostic of charge distribution. The spectrum of $V(Cl_4SQ)_3$ shown in Figure 1, apart from slight shifts in band position, is identical with spectra obtained on $Cr(Cl_4SQ)_3$, characterized crystallographically,[9] and $Fe(Cl_4SQ)_3$, shown by Mössbauer spectroscopy to contain ferric iron (Table I).[10] All three complexes prepared by the same procedure in benzene solution crystallize as tetrabenzene solvates with the same space group and crystal structure. In the presence of solvate benzene molecules, resolution of the IR spectrum is poor. Under vacuum much of the benzene can be removed, resulting in sharp spectral bands. Prominent features of the spectra on these complexes above 1000 cm^{-1} include a sharp, intense band near 1000 cm^{-1}, an intense band near 1210 cm^{-1}, bands of medium intensity near 1270 and 1350 cm^{-1}, and a strong, broad band near 1460 cm^{-1}, which can be resolved into at least two separate bands.

The tetrachlorocatecholate complexes $Na[V(Cl_4Cat)_3]$ and $[Mo(Cl_4Cat)_3]_2$[11] have similar spectra and differ from the semiquinone complexes in intensity pattern (Figure 1). These complexes show a sharp, intense band at 1000 cm^{-1}, a strong, broad band near 1250 cm^{-1}, and two bands of medium intensity at 1380 and 1530 cm^{-1}. The methanol-solvated sodium salt of $V(Cl_4Cat)_3^-$ shows two additional bands at 1110 and 1080 cm^{-1} of weak intensity, which appear associated with the cation.

Optical spectra of the neutral and anionic complexes show strong bands in the 600-nm region resulting in an intense blue-violet color for the compounds. $V(DBCat)_3^-$ and $V(Cl_4Cat)_3^-$ have bands at 650 (15 000) and 678 nm (21 000), respectively; $V(Cl_4SQ)_3$ has a strong absorption at 590 nm (5300) in acetone solution, which shifts to 620 nm in toluene. Surprising properties of $Na[V(DBCat)_3]\cdot 4CH_3OH$ are its solubility in nonpolar solvents (toluene) and its volatility. The complex shows a simple electron-impact mass spectrum with a parent ion peak at m/e 734 for $Na[V(DBCat)_3]$. The NMR spectrum of the anion consists of two sharp *tert*-butyl resonances at 1.22 and 1.08 ppm, indicating symmetrical equivalence of the three catecholate ligands in $CDCl_3$.

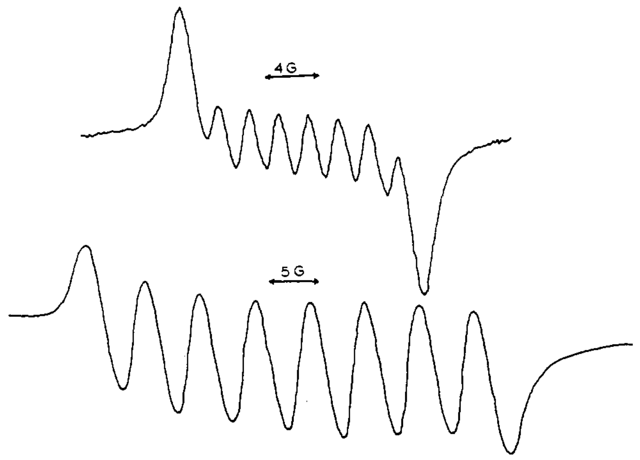

Figure 2. EPR spectra recorded on $V(Cl_4SQ)_3$ in toluene solution (upper) and diethyl ether (lower) (T = 23 °C). Both spectra are centered at a $\langle g \rangle$ value of 2.0028 (3) and show ^{51}V hyperfine coupling values of 2.1 and 5.6 G, respectively.

EPR spectra recorded on $V(Cl_4SQ)_3$ at room temperature shown in Figure 2 consist of eight lines centered at g = 2.0028 (3), due to coupling to the $I = {}^7/_2$ ^{51}V nucleus. The magnitude of the coupling in toluene solution is 2.1 G, clearly indicating that spin density is concentrated on the semiquinone ligands. Octahedral, paramagnetic vanadium complexes generally show metal coupling constants greater than 80 G, and even the highly delocalized complexes $V(bpy)_3$, $V(C_6H_6)_2$, and $V(S_2C_2Ph_2)_3$ have values of 83, 63, and 62 G, respectively.[12-14] Spectra recorded on $V(Cl_4SQ)_3$ have been observed to show a solvent dependence (Figure 2). Vanadium coupling in diethyl ether solution is 5.6 G. This could be related to changes in solvate structure and/or to a change in electronic structure of the complex.

Crystallographic Characterization of $V(Cl_4SQ)_3$ and $Na[V(DBCat)_3]\cdot 4CH_3OH$. Violet crystals of $V(Cl_4SQ)_3$ can be obtained directly from the $V(CO)_6$/tetrachloro-1,2-benzoquinone reaction mixture when the synthesis is carried out in benzene solution. Crystals form as tetrabenzene solvates and lose solvent molecules of crystallization immediately upon separation from solution. A crystal isolated directly from the reaction mixture was coated with an amorphous resin and studied by using single-crystal X-ray diffraction methods. Photographs taken by using Weissenberg and precession cameras indicated that the space group and crystal structure were identical with those of the Cr and Fe analogues, $M(Cl_4SQ)_3\cdot 4C_6H_6$, studied previously.[10] All three complexes crystallize in the acentric tetragonal space group $P4_32_12$ (or $P4_12_12$) with four formula units per unit cell.[15] The complex molecule lies along a 2-fold rotational axis in the unit cell with the metal atom close to the origin. In the acentric unit cell only one enantiomeric form can exist for the complex. False inversion symmetry at the origin has made it difficult to locate atoms of the complex and has made refinement of atom positions impossible. With $Cr(Cl_4SQ)_3$, recrystallization from CS_2 gave mixed-solvate crystals, $Cr(Cl_4SQ)_3\cdot CS_2\cdot 0.5C_6H_6$ in the triclinic crystal system, which produced a satisfactory crystallographic result.[9] Mössbauer spectra recorded on $Fe(Cl_4SQ)_3\cdot 4C_6H_6$ verified the presence of ferric iron for this complex and a similar charge distribution to the Cr analogue.[10] Structural studies on quinone complexes solvated with aromatic molecules have shown that solvate mole-

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(15) Unit cell data for the compounds $M(O_2C_6Cl_4)_3\cdot 4C_6H_6$ (M = V, Cr, Fe): tetragonal, space group $P4_32_12$ or $P4_12_12$; Z = 4. M = V: a = 13.524 (6) Å, c = 24.841 (6) Å. M = Fe: a = 13.567 (6) Å, c = 25.022 (6) Å. M = Cr: a = 13.555 (2) Å, c = 25.055 (3) Å.

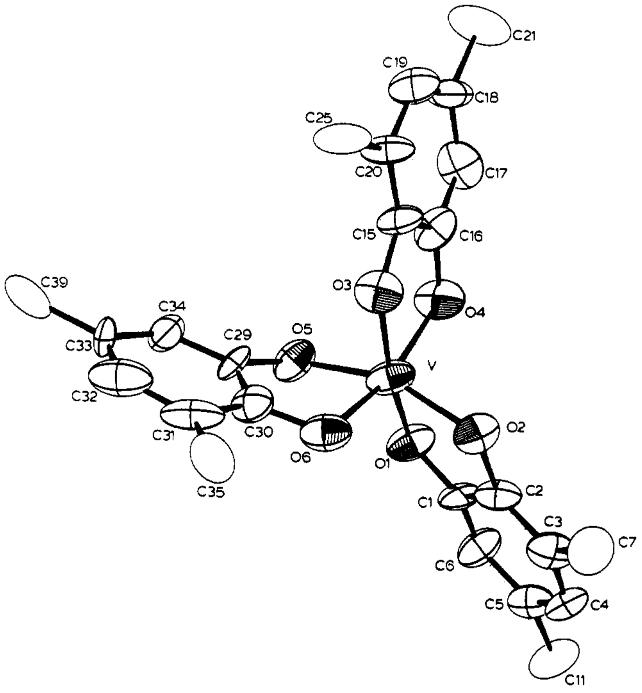

Figure 3. ORTEP plot showing the coordination geometry of the $V(DBCat)_3^-$ anion.

cules of crystallization interact, often strongly, with planar quinone ligands. To the extent that solvate interactions are sensitive to charge distribution in the complex molecule, it is likely that the form of the vanadium complex is similar to the Fe and Cr analogues as $V^{III}(Cl_4SQ)_3$. This conclusion appears confirmed by the similarity of infrared spectra for the three complexes.

Violet crystals of $Na[V(DBCat)_3]$ were obtained directly from a V(II)/3,5-di-*tert*-butylcatechol reaction carried out in methanol and were obtained as methanol solvates. As the solubility of $Na[V(DBCat)_3]$ in nonpolar solvents might suggest, there is close association between the sodium cation and the complex anion. The anion consists of a V(V) center chelated by three di-*tert*-butylcatecholate ligands with substituents positioned to give the facial, D_3, isomeric structure shown in Figure 3. Bond distances and angles for the structure are given in Table II. The sodium cation is bound to catecholate oxygens O1 and O4 of one complex anion, O1 and O5 of an adjacent anion, and two of the disordered methanol solvate molecules. Sodium and complex ions are located about an inversion center forming the neutral, dimeric unit shown in the stereoview given in Figure 4. Examples of V(V) coordination without strongly bound oxo ligands are quite rare. However, the $Mo(Cat)_3$ complexes formed by treating $Mo(CO)_6$ with tetrachloro-1,2-benzoquinone,[11] 9,10-phenanthrenequinone,[16] or 3,5-di-*tert*-butyl-1,2-benzoquinone[17] demonstrate the property of catecholate ligands to form stable complexes with high-oxidation-state metal ions. The combination of a high-oxidation-state metal with ligands that readily form semiquinone upon exposure to oxygen in solution and are regarded to be reasonably strong reducing agents is an unusual situation. Like oxo ligands, the catecholates serve as strong π donors, an effect that stabilizes metal and ligand without a change in formal charge. The average C–O bond length of the anion is 1.34 (1) Å, consistent with values found in other catecholate structures, and the average ring C–C length of 1.39 (1) Å is typical of aromatic rings. An interesting comparison can be made between the V–O bond lengths of $V(DBCat)_3^-$ and values reported by Raymond for $V(Cat)_3^{2-}$ and $V(Cat)_3^{3-}$ given in Table III.[2] A consistent decrease in length occurs with an increase in metal charge and decrease in metal ion radius. Bonds between catecholate oxygen atoms and the sodium ion are relatively strong and influence the V–O bonds. The V–O1 length is the longest (1.956 (9) Å) of the structure with O1 bridging two Na^+ ions. Lengths to O4 and O5 are 0.07 Å longer than distances to O2, O3, and O6. Two methanol solvate molecules are bonded to the sodium ion, and two others are hydrogen-bonded to these. All show some measure of disorder and have contributed to limiting the quality of the structure determination.

Table II. Selected Bond Lengths and Angles for $Na[V(O_2C_6H_2(t\text{-}Bu)_2)_3]\cdot 4CH_3OH$

	Bond Lengths, Å		
V–O1	1.956 (9)	V–O4	1.947 (10)
V–O2	1.876 (9)	V–O5	1.939 (9)
V–O3	1.856 (9)	V–O6	1.872 (10)
Na–O1	2.543 (11)	Na–O8	2.417 (27)
Na–O4	2.323 (10)	Na–O1′	2.421 (10)
Na–O7	2.375 (25)	Na–O5′	2.384 (11)
	Ligand 1		
O1–C1	1.33 (2)	C4–C5	1.43 (2)
O2–C2	1.35 (2)	C5–C6	1.38 (2)
C1–C2	1.40 (2)	C6–C1	1.38 (2)
C2–C3	1.39 (2)	C3–C7	1.50 (2)
C3–C4	1.41 (2)	C5–C11	1.54 (2)
	Ligand 2		
O3–C15	1.36 (2)	C18–C19	1.40 (2)
O4–C16	1.33 (2)	C19–C20	1.38 (2)
C15–C16	1.41 (2)	C20–C15	1.34 (2)
C16–C17	1.39 (2)	C18–C21	1.56 (2)
C17–C18	1.39 (2)	C20–C25	1.55 (2)
	Ligand 3		
O5–C29	1.35 (2)	C32–C33	1.40 (2)
O6–C30	1.34 (2)	C33–C34	1.41 (2)
C29–C30	1.42 (2)	C34–C29	1.30 (2)
C30–C31	1.41 (2)	C31–C35	1.52 (2)
C31–C32	1.36 (2)	C33–C39	1.50 (2)
	Angles, deg		
O1–V–O2	79.7 (4)	O2–C2–C1	110.8 (13)
O3–V–O4	79.9 (4)	V–O3–C15	119.0 (8)
O5–V–O6	81.3 (4)	V–O4–C16	115.2 (8)
O1–V–O3	165.4 (4)	O3–C15–C16	110.7 (12)
O2–V–O5	158.0 (4)	O4–C16–C15	114.5 (13)
O4–V–O6	164.3 (4)	V–O5–C29	110.6 (8)
V–O1–C1	113.8 (8)	V–O6–C30	111.6 (9)
V–O2–C2	118.2 (8)	O5–C29–C30	111.8 (13)
O1–C1–C2	115.9 (13)	O6–C30–C29	114.8 (14)

Electrochemistry of $V(Cl_4SQ)_3$ and $V(Cl_4Cat)_3^-$. Solutions prepared with $V(Cl_4Cat)_3^-$ and $V(Cl_4SQ)_3$ in acetonitrile were studied by using cyclic voltammetry and constant-potential coulometry and were found to behave in the same way. The anionic complex undergoes one-electron oxidation and reduction reactions reversibly as shown in Figure 5. Reduction occurs at −0.85 V vs. the Fc/Fc^+ couple (ΔE = 86 mV, $i_a/i_c = 1$), a potential that is considerably more negative than the corresponding $V(Cat)_3^-/V(Cat)_3^{2-}$ couple reported to occur at −0.035 V vs. SCE.[2] Oxidation occurs at +0.31 V (ΔE = 78 mV, $i_a/i_c = 1$). The oxidation product was generated coulometrically at a potential of +0.6 V and found to give the weakly coupled EPR signal of the neutral complex. At +0.86 V the neutral product undergoes irreversible two-electron oxidation to give a species that can be reduced irreversibly by two electrons at −0.13 V. Further coulometry at +1.1 V gave a dark green product upon oxidation by two units of charge and a yellow-orange solution upon further oxidation. Characterization of these products has not been carried out.

If both the neutral and anionic complexes retain in solution the charge distributions found in the solid state, irreversible electrochemistry would be expected. Oxidation of the anion must occur at one ligand and a two-electron-transfer step is required to give $V(Cl_4SQ)_3$ (eq 1). This assumes that intramolecular electron

$$V^{V}(Cl_4Cat)_3^- \xrightleftharpoons{-e^-} V^{V}(Cl_4SQ)(Cl_4Cat)_2 \rightarrow V^{III}(Cl_4SQ)_3 \quad (1)$$

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Table III. Vanadium–Oxygen Bond Lengths for Tris(catecholato)vanadium Complexes of Different Charge

	$K_3[V(O_2C_6H_4)_3]$	$(Et_3NH)_2[V(O_2C_6H_4)_3]$	$Na[V(O_2C_6H_2(t\text{-}Bu)_2)_3]$
metal ion	V(III)	V(IV)	V(V)
ionic radius, Å	0.78	0.72	0.68
V–O bond lengths, Å	1.984 (1), 1.993 (1), 2.012 (1), 2.029 (1), 2.036 (1), 2.206 (1)	1.921 (3), 1.925 (3), 1.931 (3), 1.944 (2), 1.961 (3), 1.971 (2)	1.858 (9), 1.872 (10), 1.876 (9), 1.939 (9), 1.947 (10), 1.956 (9)
$V\text{–}O_{av}$	2.013 (9)	1.942 (8)	1.91 (4)
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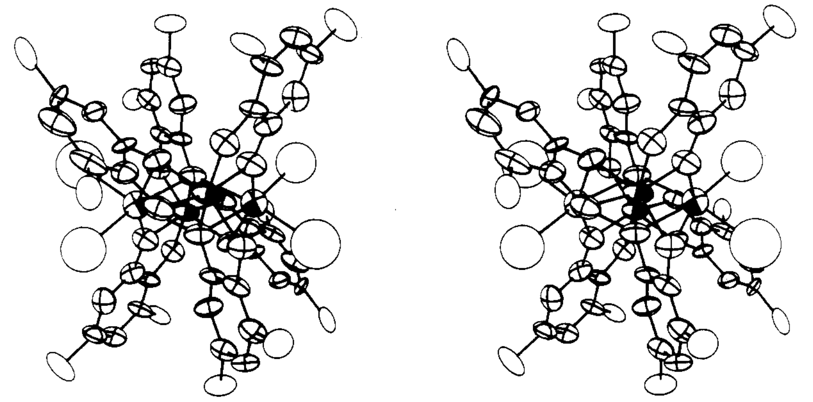

Figure 4. Stereoview showing cation–anion interactions within the unit cell of $Na[V(DBCat)_3]\cdot4CH_3OH$. Oxygen atoms of the two methanol solvate molecules bonded to each sodium cation are shown as open ellipsoids. The remaining two solvate molecules of each unit are hydrogen-bonded to the coordinated methanol molecules.

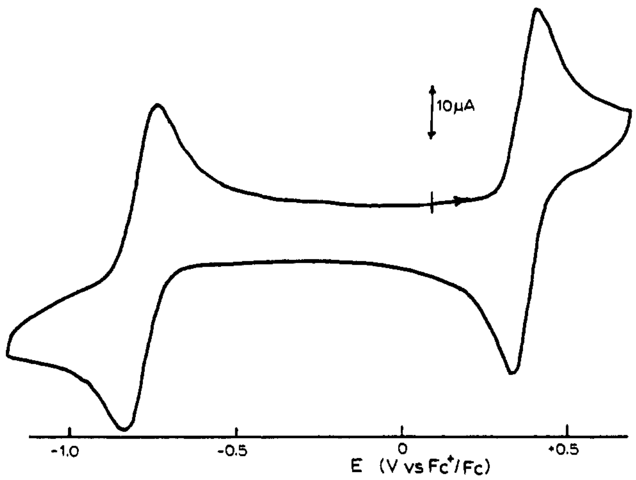

Figure 5. Cyclic voltammogram on $V(Cl_4Cat)_3^-$ in acetonitrile recorded at a scan rate of 200 mV/s. The anion undergoes reversible reduction to $V(Cl_4Cat)_3^{2-}$ at −0.85 V (Fc/Fc$^+$) and reversible oxidation to $V(Cl_4Cat)_2(Cl_4SQ)$ at +0.31 V.

transfer occurs rapidly on the electrochemical time scale for these systems. Reduction of the neutral form would likely occur at the metal as an ec process also requiring an electron-transfer step (eq 2). Restricting charge on the metal to V(III), V(IV), and V(V),

$$V^{III}(Cl_4SQ)_3 \xrightleftharpoons{e^-} V^{III}(Cl_4SQ)_2(Cl_4Cat)^- \rightarrow V^V(Cl_4Cat)_3^- \quad (2)$$

there exist three forms for both the neutral and anionic complexes, related by transfer of charge between ligand and metal. For the neutral complex these forms would be $V(SQ)_3$, $V(SQ)_2(Cat)$, and $V(SQ)(Cat)_2$; the anion could exist as $V(SQ)_2(Cat)^-$, $V(SQ)(Cat)_2^-$, and $V(Cat)_3^-$. Several redox processes occurring reversibly at either the ligand or the metal can be envisioned to relate different forms of the complex. If one assumes that the dianion contains V(IV), $V^{IV}(Cl_4Cat)_3^{2-}$, a charge distribution consistent with characterization obtained on related complexes prepared with catecholate and 3,5-di-*tert*-butylcatecholate ligands,[2] the selection of reversible two-step redox processes is limited to two. Both begin with the V(V) form of the neutral complex, implying a difference in charge distribution in acetonitrile solution relative to solid state. Both contain redox steps at the ligand and at the metal but differ in order. The sequence described in eq 3 has ligand reduction occurring first; eq 4 shows reduction occurring first at the metal.

$$V^V(Cl_4SQ)(Cl_4Cat)_2 \xrightleftharpoons{e^-} V^V(Cl_4Cat)_3^- \xrightleftharpoons{e^-} V^{IV}(Cl_4Cat)_3^{2-} \quad (3)$$

$$V^V(Cl_4SQ)(Cl_4Cat)_2 \xrightleftharpoons{e^-} V^{IV}(Cl_4SQ)(Cl_4Cat)_2^- \xrightleftharpoons{e^-} V^{IV}(Cl_4Cat)_3^{2-} \quad (4)$$

Neither of these redox sequences can be eliminated with the information at hand, but the process described by eq 3 appears more plausible. Reduction of free tetrachloro-1,2-benzoquinone occurs at a positive potential so that ligand reduction at +0.31 V is not unreasonable. The product of this process is similar in charge distribution to the form of $V(DBCat)_3^-$ characterized crystallographically and the solid form of $Na[V(Cl_4Cat)_3]$ characterized spectrally. Further reduction to form the dianion occurs at a potential more negative than that found with the unsubstituted catecholate ligand. This is most characteristic of a metal-based redox process. Tetrachlorocatechol is more effective at stabilizing high-oxidation-state metal ions, and redox processes of unsubstituted catechol occur at negative potentials.

With these assumptions, we conclude that the form of the neutral complex investigated electrochemically in solution is different in charge distribution from the form characterized in the solid state and that eq 3 best describes the redox behavior of the complex.

Discussion

Crystallographic characterization on $V(O_2C_6Cl_4)_3$ and solid-state infrared spectra indicate that the complex is similar to Cr and Fe analogues with semiquinone ligands chelated to a trivalent metal ion, $V^{III}(Cl_4SQ)_3$. Similar characterization on the anionic complexes indicates that they are of form $V^V(Cat)_3^-$. This is different from the Cr analogues, where the metal remains trivalent in the mixed-charge ligand complexes, such as $Cr^{III}(Cat)(SQ)_2^-$.[18] The reversibility of the oxidation couple of $V(O_2C_6Cl_4)_3^-$ indicates that the product obtained in acetonitrile solution is $V^V(Cl_4Cat)_2(Cl_4SQ)$ since an additional, rapid two-electron-transfer step to give $V^{III}(Cl_4SQ)_3$ would result in irreversibility. The neutral complex therefore appears to exist in two tautomeric electronic

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(18) Downs, H. H.; Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1736–1740.

Table IV. Crystal Data and Details of the Structure Determination for $Na[V(O_2C_6H_2(t\text{-}Bu)_2)_3]\cdot 4CH_3OH$

Crystal Data

formula	$VNaO_{10}C_{46}H_{76}$	vol, Å^3	2461.7 (8)
mol wt	863.03	Z	2
space group[a]	$P\bar{1}$	d_{calcd}, g cm^{-3}	1.17
		d_{exptl}, g cm^{-3}	1.24 (3)
cryst syst	triclinic	$F(000)$	836
a, Å[b]	12.020 (3)	μ, cm^{-1}	2.51
b, Å	15.842 (3)	cryst dimens, mm	0.52 × 0.33 × 0.25
c, Å	15.521 (4)		
α, deg	105.04 (3)		
β, deg	104.94 (2)		
γ, deg	110.72 (4)		

Data Collection and Reduction

diffractometer	Syntex $P\bar{1}$
data collected	$+h,\pm k,\pm l$
radiation (λ, Å)	Mo Kα (0.71069)
monochromator angle, deg	12.2
temp, K	294–296
scan technique	θ–2θ
scan range (2θ), min–max, deg	3.0–40.0
scan speed, deg/min	4.0
scan range, deg	0.7 below Kα_1 and 0.7 above Kα_2
background	stationary cryst–stationary counter; background time = 0.5(scan time)
no. of unique reflecns measd	4994
no. of obsd reflecns	1910
criterion	$F > 6\sigma(F)$

Structure Determination and Refinement

programs used	SHELX[c]
scattering factors	neutral atoms[d]
R_1, R_2[e]	0.067, 0.070
weight	$1/(\sigma(F)^2 + 0.0005F^2)$
no. of parameters	499
ratio of observations to parameters	3.83

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 20 reflections with 2θ in the range 15–20°. [c] Sheldrick, G. M. "SHELX76, A Program for Crystal Structure Determination", University of Cambridge, England. [d] *International Tables for X*-rray *Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4., pp 55–60, 99–101, 149–150. [e] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

forms related by transfer of two electrons between the metal and the quinone ligands, with intramolecular charge distribution determined by the physical environment of the complex.

Ligand–metal electron transfer is a difficult process to study due to the short lifetime of intermediates and the absence of systems where it occurs reversibly. Quinone ligands have vacant electronic levels that are similar in energy to metal d orbitals. This similarity is illustrated by the sensitivity of the charge distribution within the metal–quinone complex to subtle effects that influence both metal and ligand orbital energies. The donation property of other ligands bonded to the metal is important. Hard nitrogen donor counterligands result in oxidized metal–reduced quinone charge distributions in the complexes (bpy)Cu(Cat) and Mn(py)$_2$(Cat)$_2$. In the related compounds (diphos)Cu(SQ) and [Mn(SQ)$_2$]$_4$, soft phosphorus donor ligands or weak bridging interactions of quinone oxygen atoms result in a charge distribution with the metal in a reduced oxidation state.[19,20] Forms of Co(bpy)(DBSQ)(DBCat) and Mn(py)$_2$(DBCat)$_2$ related by transfer of one or two electrons between quinone ligand and metal have been studied in thermal equilibrium in solution.[20,21]

$$\mathrm{Co^{III}(bpy)(DBSQ)(DBCat)} \rightleftarrows \mathrm{Co^{II}(bpy)(DBSQ)_2}$$

$$\mathrm{Mn^{IV}(py)_2(DBCat)_2} \rightleftarrows \mathrm{Mn^{II}(py)_2(DBSQ)_2}$$

Table V. Atomic Positional and Derived Isotropic Thermal Parameters for $Na[V(O_2C_6H_2(t\text{-}Bu)_2)_3]\cdot 4CH_3OH$

atom	x	y	z	U_{eq}, Å^2
V	−0.0042 (2)	0.1871 (1)	0.0226 (1)	0.050 (1)
Na	−0.1643 (5)	−0.0519 (3)	0.0019 (3)	0.064 (3)
O1	−0.0363 (8)	0.0599 (5)	−0.0656 (6)	0.053 (5)
O2	−0.1411 (8)	0.1655 (5)	−0.0855 (6)	0.054 (5)
O3	0.0108 (7)	0.2894 (5)	0.1238 (6)	0.054 (5)
O4	−0.0944 (8)	0.1137 (5)	0.0867 (6)	0.055 (5)
O5	0.1583 (8)	0.1931 (5)	0.0947 (5)	0.046 (5)
O6	0.106 (1)	0.2843 (6)	−0.0050 (6)	0.057 (5)
C1	−0.116 (1)	0.0328 (9)	−0.1550 (9)	0.040 (8)
C2	−0.177 (1)	0.0918 (8)	−0.169 (1)	0.044 (8)
C3	−0.259 (1)	0.0772 (9)	−0.259 (1e	0.060 (9)
C4	−0.288 (1)	−0.0082 (9)	−0.3350 (8)	0.045 (8)
C5	−0.236 (1)	−0.0742 (8)	−0.3221 (9)	0.048 (8)
C6	−0.151 (1)	−0.0521 (9)	−0.231 (1	0.051 (8)
C7	−0.313 (1)	0.1480 (9)	−0.270 (1)	0.054 (9)
C8	−0.197 (1)	0.2484 (9)	−0.242 (1)	0.09 (1)
C9	−0.390 (2)	0.157 (1)	−0.208 (1)	0.13 (1)
C10	−0.400 (2)	0.118 (1)	−0.376 (1)	0.11 (1)
C11	−0.279 (2)	−0.1653 (9)	−0.4125 (9)	0.06 (1)
C12	−0.224 (1)	−0.2336 (9)	−0.3870 (9)	0.065 (9)
C13	−0.426 (1)	−0.2247 (9)	−0.451 (1)	0.07 (1)
C14	−0.242 (2)	−0.137 (1)	−0.491 (1)	0.10 (1)
C15	−0.029 (1)	0.2697 (8)	0.1942 (9)	0.042 (7)
C16	−0.090 (1)	0.1677 (8)	0.170 (1)	0.044 (7)
C17	−0.139 (1)	0.1343 (9)	0.233 (1)	0.069 (8)
C18	−0.123 (1)	0.202 (1)	0.3184 (9)	0.058 (9)
C19	−0.061 (1)	0.3014 (9)	0.3377 (9)	0.052 (8)
C20	−0.012 (1)	0.3370 (8)	0.2758 (9)	0.053 (8)
C21	−0.182 (2)	0.163 (1)	0.387 (1)	0.10 (1)
C22	−0.074 (2)	0.220 (1)	0.493 (1)	0.15 (2)
C23	−0.216 (2)	0.058 (1)	0.369 (1)	0.13 (1)
C24	−0.285 (2)	0.191 (1)	0.394 (2)	0.19 (2)
C25	0.060 (1)	0.4486 (8)	0.3025 (9)	0.055 (8)
C26	0.069 (1)	0.5077 (8)	0.4018 (9)	0.077 (8)
C27	−0.011 (1)	0.4734 (9)	0.225 (1)	0.076 (9)
C28	0.198 (1)	0.4734 (9)	0.3079 (9)	0.062 (9)
C29	0.256 (1)	0.2827 (9)	0.1228 (9)	0.030 (8)
C30	0.224 (2)	0.3338 (9)	0.065 (1)	0.044 (9)
C31	0.315 (2)	0.428 (1)	0.082 (1)	0.08 (1)
C32	0.428 (2)	0.467 (1)	0.160 (1)	0.08 (1)
C33	0.462 (1)	0.418 (1)	0.217 (1)	0.042 (9)
C34	0.369 (1)	0.3221 (9)	0.1933 (9)	0.040 (8)
C35	0.279 (1)	0.486 (1)	0.025 (1)	0.07 (1)
C36	0.166 (1)	0.505 (1)	0.040 (1)	0.10 (1)
C37	0.242 (2)	0.431 (1)	−0.081 (1)	0.13 (1)
C38	0.393 (2)	0.588 (1)	0.058 (1)	0.11 (1)
C39	0.588 (2)	0.467 (1)	0.303 (1)	0.07 (1)
C41	0.682 (2)	0.566 (1)	0.317 (1)	0.09 (1)
C42	0.560 (1)	0.476 (1)	0.3963 (9)	0.08 (1)
O7	−0.253 (2)	−0.130 (1)	0.097 (1)	0.184 (8)
C43[a]	−0.375 (6)	−0.179 (4)	0.055 (4)	0.22 (1)
C44[a]	0.310 (8)	−0.200 (5)	0.126 (5)	0.22 (1)
O8	−0.371 (3)	−0.067 (2)	−0.090 (1)	0.245 (8)
C45	−0.47 (1)	−0.031 (9)	−0.060 (8)	0.23 (1)
O9	−0.616 (5)	−0.158 (4)	−0.113 (4)	0.19 (1)
C46[a]	−0.425 (5)	0.115 (4)	0.005 (4)	0.20 (1)
C47[a]	−0.655 (5)	−0.219 (4)	−0.065 (4)	0.19 (1)
C48[a]	0.05 (1)	0.18 (1)	0.74 (1)	0.23 (2)
O10[a]	−0.06 (1)	−0.098 (9)	0.27 (1)	0.24 (2)
C49[a]	−0.086 (7)	−0.148 (6)	0.320 (6)	0.23 (2)
O11[a]	−0.134 (9)	−0.181 (7)	0.207 (7)	0.25 (2)

[a] Atoms refined with occupancy factors of 0.5, $U_{eq} = {}^1/_3 \sum U_{11}$.

In solution V(Cl$_4$SQ)$_3$ appears to show properties similar to those of the Mn complex. In polar solvents at room temperature both exist in the oxidized metal–reduced quinone form, Mn(py)$_2$(DBCat)$_2$ and V(Cl$_4$Cat)$_2$(Cl$_4$SQ). The dependence of ^{51}V hyperfine coupling on solvent polarity may indicate a change in charge distribution in nonpolar solvents. Spectral and crystallographic data on the compound in the solid state strongly point to the V^{III}(SQ)$_3$ formulation.

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Parameters that influence charge distribution within metal–quinone complexes include effects of solvation and overall charge in addition to changes in d-orbital energy of the metal resulting from a counterligand effect.

Experimental Section

$Na(diglyme)_2[V(CO)_6]$ was obtained from Strem Chemical Co., and $V(CO)_6$ was prepared by literature procedures.[22] Tetrachloro-1,2-benzoquinone, 3,5-di-*tert*-butyl-1,2-benzoquinone, and 3,5-di-*tert*-butylcatechol were obtained from Aldrich Chemical Co. and recrystallized prior to use. Neutral $V(O_2C_6H_2(t\text{-}Bu)_2)_3$ was prepared by procedures described earlier.[7]

$V(O_2C_6Cl_4)_3$. Tetrachloro-1,2-benzoquinone (2.00 g, 8.2 mmol) in 50 mL of benzene was added dropwise to freshly prepared $V(CO)_6$ (0.55 g, 2.5 mmol) in 50 mL of diethyl ether under Ar. Reaction occurred immediately, giving the dark blue product. The reaction mixture was heated at reflux for 1 h and reduced to half-volume. Dark blue crystals of $V(O_2C_6Cl_4)_3$ separated from solution over a period of several hours as the solution cooled. Analytical data obtained immediately upon isolation of crystals from solution indicated that they form as benzene solvates.

Anal. Calcd for $V(O_2C_6Cl_4)_3 \cdot 4C_6H_6$: C, 45.4; H, 2.2; Cl, 38.3; V, 4.7. Found: C, 45.6; H, 2.3; Cl, 38.5; V, 4.6.

$[Na(CH_3OH)_4][V(O_2C_6Cl_4)_3]$. A solution of $[Na(diglyme)_2][V(CO)_6]$ (0.51 g, 1.0 mmol) in 15 mL of CH_3OH was added dropwise to tetrachloro-1,2-benzoquinone (1.23 g, 5.0 mmol) dissolved in 20 mL of toluene. Reaction occurred immediately to give the dark blue microcrystalline product. The volume of the solution was reduced to 20 mL, and the product (0.87 g, 0.87 mmol) was isolated by filtration.

Anal. Calcd for $[Na(CH_3OH)_4][V(O_2C_6Cl_4)_3]$: C, 26.4; H, 1.7; Na, 2.3; Cl, 42.5; V, 5.1. Found: C, 26.3; H, 1.8; Na, 2.2; Cl, 41.8; V, 5.3.

$[Na(CH_3OH)_4][V(O_2C_6H_2(t\text{-}Bu)_2)_3]$. This complex was prepared by the procedure above substituting 3,5-di-*tert*-butyl-1,2-benzoquinone for tetrachlorobenzoquinone.[23]

Anal. Calcd for $[Na(CH_3OH)_4][V(O_2C_6H_2(t\text{-}Bu)_2)_3]$: C, 64.0; H, 8.9; Na, 2.7; V, 5.9. Found: C, 63.2; H, 8.7; Na, 2.8; V, 5.9.

Physical Measurements. Infrared spectra were recorded on a Beckman IR 4250 spectrometer with samples prepared as KBr pellets. UV–vis spectra were recorded on a Cary 219 spectrophotometer. Electron paramagnetic resonance spectra were obtained by using a Varian E-109 spectrometer with DPPH used as the g value standard. Cyclic voltammograms were obtained with a PAR Model 174A potentiostat at scan rates ranging from 50 to 1000 mV/s. A platinum-wire working electrode and a platinum-coil auxiliary electrode were used. TBAP was used as the supporting electrolyte, a Ag/AgCl reference electrode was used, and the ferrocene/ferrocenium couple was used as an internal standard. $E_{1/2}$ for oxidation for 10^{-3} M ferrocene vs. Ag/AgCl is 0.52 V.

Crystallographic Structure Determination on $[Na(CH_3OH)_4][V(O_2C_6H_2(t\text{-}Bu)_2)_3]$. The crystal used for this investigation was obtained from a reaction of V^{2+} with 3,5-di-*tert*-butylcatechol in a CH_3OH solution containing $NaOCH_3$. Crystals formed as large parallelepipeds directly from solution. These crystals were determined to be identical with crystals obtained by using the synthetic procedure above. Even though a relatively large crystal was used for data collection, it was observed to diffract very poorly. This is often related to molecular disorder, and such was found to be the case in this structure determination. Carbon atoms of catecholate *tert*-butyl groups refined with elongated anisotropic thermal parameters due to apparent rotational disorder. Methanol solvate molecules associated with the sodium ion suffered from severe positional disorder. Two of the solvate molecules are coordinated to the cation to give a slightly distorted octahedron of oxygen atoms about the Na^+ ion. The remaining two methanol molecules are hydrogen-bonded to those coordinated to the sodium. The locations of the V atom and other atoms of the inner coordination sphere were determined by direct methods. Details of procedures used for data collection and structure determination are given in Table IV. Final positional and isotropic thermal parameters for all atoms are listed in Table V. Tables containing anisotropic thermal parameters and structure factors are available as supplementary material.

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Registry No. $V(O_2C_6Cl_4)_3 \cdot 4C_6H_6$, 103935-66-6; $[Na(CH_3OH)_4][V(O_2C_6Cl_4)_3]$, 103935-64-4; $V(CO)_6$, 14024-00-1; $[Na(diglyme)_2][V(CO)_6]$, 15531-13-2; $[Na(CH_3OH)_4][V(O_2C_6H_2(t\text{-}Bu)_2)_3]$, 104011-74-7; tetrachloro-1,2-benzoquinone, 2435-53-2; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9.

Supplementary Material Available: A table containing anisotropic thermal parameters (2 pages) for the $Na[V(DBCat)_3] \cdot 4CH_3OH$ structure determination; a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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[23] This general synthetic procedure has also been used to prepare related complexes of 1,2-naphthoquinone and 9,10-phenanthrenequinone.

Contribution from the Laboratoire de Chimie des Polymères Inorganiques, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France, and Laboratoire de Cinétique Chimique, Université Pierre et Marie Curie, 75005 Paris, France

Derivatives of Tetrathiotungstate(VI). Synthesis and Structure of $[W_2(S)_2(SH)(\mu\text{-}\eta^3\text{-}S_2)(\eta^2\text{-}S_2)_3]^-$

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Acidification (HCl in CH_3CN) of a solution of $[PPh_4]_2WS_4$ in CH_3CN leads to the formation of the dinuclear anion $[W_2S_{11}H]^-$. The complex crystallizes in the space group $C2/c$ ($Z = 4$) with unit cell dimensions $a = 13.126$ (1) Å, $b = 23.272$ (2) Å, $c = 11.499$ (6) Å, and $\beta = 96.83$ (4)°; final $R = 0.0505$ based on 5225 reflections collected and 1849 used. Each tungsten is ligated by six sulfur atoms in approximatively pentagonal-pyramidal coordination geometry. The two pyramids share a corner with a W–S(3)–W bridge angle of 90.0 (2)°. The axial position of each pyramid is occupied by a terminal sulfido group, and the equatorial positions are occupied by a bridging and simultaneous side-on disulfido (S_2^{2-}) group, a terminal disulfido group, and an SH^- ligand. ^1H NMR spectra reveal indirectly the thiol proton. Electronic spectral assignments are proposed.

Interest in sulfur-containing compounds of Mo and W has grown with respect to their implications in bioinorganic chemistry[1] and catalysis.[2] "Soluble metal sulfides"[3] $M_nS_m^{2-}$ (M = Mo, W) constitute a new class of transition-element compounds. The chemistry of binary soluble Mo–S anions is by far the most highly developed, showing a wide range of stoichiometries: MoS_9^{2-},[4] $Mo_2S_8^{2-}$,[5] $Mo_2S_{10}^{2-}$,[6] $Mo_2S_{12}^{2-}$,[7] $Mo_3S_9^{2-}$,[8] and $Mo_3S_{13}^{2-}$.[9] With

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