and data statistics are given in Table VII. Final positional and thermal parameters with estimated standard deviations are given in Tables VIII and XIS (S indicates supplementary material), respectively.

6. Single crystals of **6** were obtained by slow evaporation of a CH_2Cl_2/hexane solution at ambient temperature under N_2 atmosphere. X-ray data were collected[46] and the structure solved as described above. An absorption correction was not performed. Crystal and data statistics are given in Table VII. Final positional and thermal parameters with estimated standard deviations are given in Tables IX and XIIS, respectively.

9. Single crystals of **9** were obtained by slow cooling of a CH_2Cl_2/hexane solution to −5 °C. X-ray data were collected[46] and solved for heavy atoms with MULTAN.[47] Remaining atoms were located in subsequent difference maps, and all non-hydrogen atoms were refined to anisotropic convergence.[47,48] Hydrogen atom positions were calculated but were kept fixed during the final cycles of refinement. An absorption correction was not employed. Crystal and data statistics are given in Table VII. Final positional and thermal parameters with estimated standard deviations are given in Tables X and XIIIS, respectively.

4a. Single crystals of **4a** were obtained by slow diffusion of hexane into a saturated CH_2Cl_2 solution at ambient temperature. Our unit cell constants and spectroscopic data were in good agreement with those reported.[23a]

4w. Single crystals of **4w** were obtained by slow diffusion of hexane into a saturated toluene solution at ambient temperature. Determination of unit cell parameters ($a = 18.00$, $b = 8.35$, $c = 16.03$ Å; $\beta = 114.3°$) indicated that the crystals were isomorphous with the analogous Mo butterfly cluster **4a**.

7. Single crystals of **7** were obtained by slow diffusion of hexane into a saturated CH_2Cl_2 solution at ambient temperature. Our unit cell parameters and spectroscopic data were in good agreement with those reported.[27]

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Supplementary Material Available: For **3b**, **6**, and **9**, Tables XIS–XIIIS, listing thermal parameters (B_{ij}), and, for **3b**, Figures 6 and 7, showing cyclic voltammograms (5 pages); for **3b**, **6**, and **9**, Tables XIV–XVIS, listing F_o and F_c (31 pages). Ordering information is given on any current masthead page.

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(48) Refinement entailed minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ were the observed and calculated structure factor amplitudes. The weighting factors w were taken as $w = 4F_o^2/(\sigma^2(F_o^2) + (PF_o^2)^2)$, where P, the factor preventing overweighting of strong reflections, was set equal to 0.04. The agreement indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2\sum wF_o^2)^{1/2}$ were used to evaluate the refinement.

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Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27695-8204

Syntheses and Characterization of Two Vanadium Tris Complexes of the 1,2-Dithiolene 5,6-Dihydro-1,4-dithiin-2,3-dithiolate. Crystal Structure of $[(C_4H_9)_4N][V(DDDT)_3]$[1]

Jane Hanna Welch, Robert D. Bereman,* and Phirtu Singh

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The reaction between VCl_3 and the dipotassium salt of the new dithiolene 5,6-dihydro-1,4-dithiin-2,3-dithiolate, $DDDT^{2-}$, resulted in the isolation of $V(DDDT)_3^-$ as the tetraalkylammonium salt. This reaction, under oxygen-free conditions, yields the dianion, $V(DDDT)_3^{2-}$, also isolated as the tetraalkylammonium salt. A single-crystal structural study of the tetrabutylammonium salt of $V(DDDT)_3^-$ has been performed and is the first reported crystal structure of a monoanionic vanadium dithiolene. The salt crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 10.425$ (4) Å, $b = 19.596$ (9) Å, and $c = 38.53$ (2) Å. The large unit cell contains eight cations and eight anions with two complete molecules in the asymmetric unit. In each of the unique anions, the six ligated sulfur atoms form a slightly distorted trigonal prism about the vanadium with average V–S distances of 2.338 (4) and 2.343 (4) Å, respectively. Two parameters relevant to trigonal-prismatic coordination are an average S–V–S (trans) angle of 135.5 (2)° and an average twist angle of 3.7°. While the formal oxidation states of $V(DDDT)_3^-$ and $V(DDDT)_3^{2-}$ are V and IV, respectively, evidence presented here indicates that the monoanion is more correctly formulated as a V(III) complex with the ligands being intermediate between dithiodiketone and dithiolate.

Introduction

The coordination chemistry of transition-metal dithiolenes has been an area of great interest for a number of years. Yet, the first analytically pure tris(dithiolene), $Mo[S_2C_2(CF_3)_2]_3$, was prepared by King[2] in 1963. This class of compounds yielded the highly unusual trigonal-prismatic (TP) geometry in the structures of $Mo(S_2C_2H_2)_3$, $Re(S_2C_2Ph_2)_3$, and $V(S_2C_2Ph_2)_3$.[3-5] It is known that tris complexes like their bis counterparts undergo reversible one-electron-transfer reactions resulting in stable species differing in oxidation state. These observations brought about a flurry of research on tris(dithiolenes).[6-10]

Since the initial report of the synthesis of the new dithiolene potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate[11] (K_2DDDT) shown in Figure 1, only the chemistry with the latter transition metals Ni, Pd, Pt, Cu, and Au has been investigated.[12,13] In our efforts to more fully understand the coordination chemistry of the

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* To whom correspondence should be addressed.

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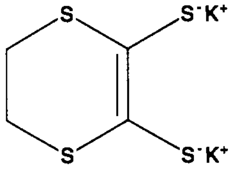

Figure 1. K_2DDDT.

new ligand, two new vanadium complexes representing a redox pair have been isolated as tetraalkylammonium salts.

Syntheses of the Cu and Ni group complexes begin with metal(II) salts and yield oxidized products, $M(DDDT)_2^-$, in the presence of oxygen. Under an Ar atmosphere, no oxidation occurs. The reaction of VCl_3 and K_2DDDT exposed to air yields $(R_4N)[V(DDDT)_3]$. This result was not surprising in view of the previous examples. However, the same reaction under oxygen-free conditions also yielded an oxidized product, $(R_4N)_2[V(DDDT)_3]$.

Simple assignment of an oxidation state in metal dithiolenes, assuming the ligands to be 1,2-dithiolates, can often be incorrect.[14,15] The ligands can themselves be oxidized to dithiodiketones. Considering both possibilities, the formulations for each complex could be

metal oxidation	ligand oxidation
$[V^{V}L^{2-}{}_3]^-$	$[V^{III}L^0L^{2-}{}_2]^-$
$[V^{IV}L^{2-}{}_3]^{2-}$	$[V^{III}L^-L^{2-}{}_2]^{2-}$

The reaction product obtained in the presence of air is a V(V) complex if the metal oxidizes, and the ligands retain dithiolate character or a V(III) metal if one of the ligands undergoes a two-electron oxidation to a dithiodiketone. Similarly, the reaction under Ar yields a V(IV) product with dithiolate ligands or a V(III) metal where one of the ligands is oxidized by a single electron. ESR data, structural data, and a molecular orbital diagram are considered here in an attempt to identify the most accurate formulation of each anion.

Only three vanadium structures have been reported. The neutral compound, $V(S_2C_2Ph_2)_3$, has a slightly distorted trigonal-prismatic coordination while both dianions, $V[S_2C_2(CN)_2]_3^{2-}$ and $V(dmit)_3^{2-}$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate), have distorted octahedral VS_6 cores.[5,16,17] The crystal structure of $[(C_4H_9)_4N][V(DDDT)_3]$ is the first example in which the complex anion is mononegative.

Experimental Section

Reagents. Potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2DDDT) was prepared by literature methods[11] and characterized by IR and NMR. Anhydrous vanadium trichloride, tetraethylammonium bromide, tetrabutylammonium iodide, and Gold Label solvents, acetonitrile and dimethylformamide, were purchased from Aldrich Chemical Co. Tetraethylammonium bromide was recrystallized twice from ethanol and stored over phosphorus pentoxide. Tetraethylammonium perchlorate was purchased from Southwestern Analytical Chemicals. Tetrahydrofuran, purchased from Fisher Scientific Co., was dried over Na/benzophenone and distilled prior to use. Ethyl alcohol was purchased from Aaper Alcohol and Chemical Co. Argon was purchased from Air Products Inc. Unless otherwise stated, all chemicals were used without further purification.

Procedures. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

Syntheses. **$[(C_2H_5)_4N][V(S_4C_4H_4)]_3$.** Under an Ar atmosphere and with use of standard Schlenk techniques, 1.5 g of K_2DDDT and 0.3 g of VCl_3 were added to 30 mL of THF. The mixture was stirred for 1 h, during which time the solution changed color from purple to green. After filtration to remove any residue, 0.8 g of tetraethylammonium bromide in 30 mL of EtOH was added to the filtrate, causing immediate precipitation. The mixture was stirred for 5 min and then filtered in the open atmosphere by suction. The crude weight was 1.0 g (75%). The product appeared green at the initial stages of filtration; however, as the process continued, it developed a blue color. The solid was stirred in room-temperature acetonitrile, the mixture was filtered, and the product was then recrystallized in hot acetonitrile giving a deep blue solution that yielded 0.2 g (15%) of blue crystals upon slow cooling and evaporation: mp >325 °C; ^{1}H NMR (Me_2SO-d_6) 3.26 (s, SCH_2CH_2S), 3.21 (q, CH_2), 1.06 ppm (t, CH_3); IR (KBr) 1480 (m), 1405 (m), 1365 (s), 1280 (s), 1170 (m), 1000 (m), 920 (m), 865 (m), 775 (m), 430 (m), 385 (w) cm^{-1}. Anal. Calcd for $VC_{20}H_{32}NS_{12}$: C, 33.26; H, 4.47; N, 1.94; S, 53.28. Found: C, 33.33; H, 4.49; N, 1.92; S, 53.36.

$[(C_4H_9)_4N][V(S_4C_4H_4)_3]$. The above procedure was followed with the substitution of tetrabutylammonium iodide for tetraethylammonium bromide to precipitate the product. This salt was synthesized for the structural determination, and no other analyses were performed.

$[(C_2H_5)_4N]_2[V(S_4C_4H_4)_3]$. The procedure followed was identical with that for the 1:1 salt above through the addition of tetraethylammonium bromide. The product was then filtered but under Ar and dried under vacuum. Recrystallization from acetonitrile was carried out under Ar to yield a green crystalline product (0.4 g, 25%). This compound is stable in air for a short time as a solid yet very sensitive to oxidation in solution. IR (KBr): 1475 (m), 1445 (s), 1390 (m), 1365 (s), 1280 (s), 1180 (w), 1170 (m), 1000 (m), 915 (w), 870 (w), 775 (m), 345 (s), 325 (sh) cm^{-1}. Anal. Calcd for $VC_{28}H_{52}N_2S_{12}$: C, 39.45; H, 6.15; N, 3.29; S, 45.14. Found: C, 39.25; H, 6.08; N, 3.23; S, 44.95.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1}. UV/vis/near-IR spectra were recorded on a Cary 2300 spectrophotometer in DMF. ESR spectra were recorded on a Varian E-3 spectrometer at room temperature (solution) or at 100 K with DMF as a solvent. The field was calibrated with $VO(acac)_2$ and DPPH. All electrochemical measurements were performed by using a BAS CV-27. A platinum wire was employed for both the working and auxiliary electrodes, and either a SCE or a Ag/AgCl electrode, as the reference electrode. The solutions used for all techniques consisted of 0.1 M tetraethylammonium perchlorate as supporting electrolyte in DMF with metal complex concentrations of 10^{-3} M. Solutions were degassed with Ar for 15 min prior to making measurements.

Single-Crystal X-ray Analysis. A representative crystal was surveyed, and cell dimensions were obtained by a least-squares fit of setting angles of 19 high-angle reflections ($2\theta > 20°$). A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$ Å). Systematic absences indicated that the crystal belonged to the orthorhombic space group $P2_12_12_1$ ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). Two check reflections collected every 48 reflections revealed no unexpected variation in intensity. Six thousand twenty-six unique reflections in the range $3° < 2\theta < 45°$ were recorded. Three thousand two hundred sixty-one of these (having $I > 2\sigma(I)$) were used in the structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption owing to the low absorption coefficient (9.0 cm^{-1}). Atomic scattering factors for all atoms were taken from ref 18. Pertinent crystal, data collection, and refinement parameters are summarized in Table I.

The vanadium and sulfur atoms were located by the direct-methods subroutine RANT of the crystallographic program package SHELXTL.[19] The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the block-diagonal least-squares technique using SHELXTL on the Data General Microeclipse computer. The quantity minimized was $\sum w(\Delta F)^2$, where $w = 1/(\sigma_F{}^2 + 0.00030F^2)$. The non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon atom and were not refined. The final R indices are given in Table I. A final difference Fourier map revealed no missing or misplaced electron density. Hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material.

The refined structure was plotted by using the SHELXTL graphics package. Figure 2 shows one of the anions in the asymmetric unit. Bond distances and selected bond angles of the anions are given in Table II. Atom coordinates are given in Table III. Bond lengths and angles of the tetrabutylammonium counterions, all remaining angles of the anions, and a stereoview of the molecular packing are available as supplementary material.

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Table I. Single-Crystal X-ray Crystallographic Analysis

	Crystal Parameters
formula	$VC_{28}H_{48}NS_{12}$
mol wt	834.41
crystn medium	acetonitrile
cryst size, mm	0.80 × 0.24 × 0.04
cryst color	blue
cryst habit	thin plate
cell dimens	a = 10.425 (4) Å b = 19.596 (9) Å c = 38.53 (2) Å
volume	7872 (7) Å^3
space group	$P2_12_12_1$
molecules/unit cell	8
density (calcd), g/cm^3	1.41
F(000)	3504 e
	Data Collection Parameters
temp	298 K
2θ range	3–45°
scan type	ω
scan speed	variable; 4–29.3°/min
octants collected	*hkl*
bkgd measurement	half of total scan time at beginning and end of each scan
linear abs coeff	9.0 cm^{-1}
	Refinement Parameters[a]
final R index	R = 0.062 R_w = 0.054
goodness of fit	GOF = 1.34
largest shift/esd	0.6
data/parameter ratio	4.2

[a] The data fit criteria (based on reflections having $I > 2\sigma(I)$) were

$$R = \sum||F_o| - |F_c||/\sum F_o = 0.062$$

$$R_w = [\sum w(\Delta F)^2/\sum F_o^2]^{0.5} = 0.054$$

$$\mathrm{GOF} = \sum(w[|F_o| - |F_c|]^2/[N_o - N_v])^{0.5} = 1.34$$

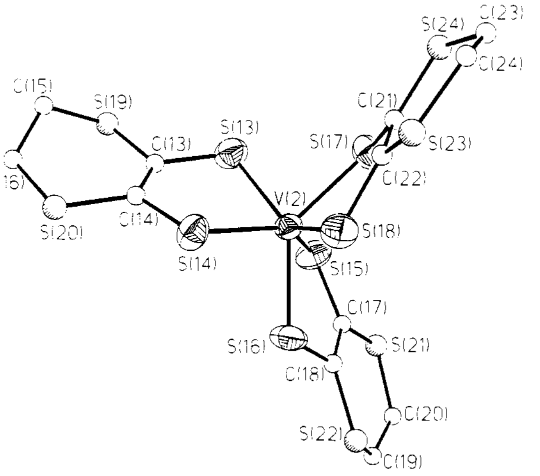

Figure 2. Structure of V(DDDT)$_3^-$ showing the numbering scheme. Hydrogen atoms are not shown. Thermal ellipsoids (50% probability) for the vanadium and six coordinated sulfur atoms only are shown. All other atoms are shown as spheres for clarity.

The carbon–carbon bonds in the $-CH_2-CH_2-$ fragment of the ligand are quite different from the expected value. The same is true for some of the bonds in the carbon chains of the counterions. These uncharacteristic bond lengths are the result of disorder and high anisotropic temperature factors for these carbons (Table III). This type of disorder is common in large bulky complex ions as well as long carbon chains.

Table II. Bond Distances (Å) and Selected Bond Angles (deg) of the V(DDDT)$_3^-$ Anions

	Bond Lengths		
V(1)–S(1)	2.365 (4)	V(1)–S(2)	2.323 (4)
V(1)–S(3)	2.335 (4)	V(1)–S(4)	2.331 (4)
V(1)–S(5)	2.336 (4)	V(1)–S(6)	2.335 (4)
S(1)–C(1)	1.682 (13)	S(2)–C(2)	1.703 (13)
S(3)–C(6)	1.715 (16)	S(4)–C(5)	1.696 (14)
S(5)–C(9)	1.736 (12)	S(6)–C(10)	1.667 (12)
S(7)–C(1)	1.734 (14)	S(7)–C(3)	1.775 (18)
S(8)–C(2)	1.742 (13)	S(8)–C(4)	1.774 (21)
S(9)–C(5)	1.747 (14)	S(9)–C(7)	1.744 (19)
S(10)–C(6)	1.742 (16)	S(10)–C(8)	1.778 (18)
S(11)–C(9)	1.748 (12)	S(11)–C(12)	1.700 (19)
S(12)–C(10)	1.748 (13)	S(12)–C(11)	1.748 (18)
C(1)–C(2)	1.424 (18)	C(3)–C(4)	1.233 (26)
C(5)–C(6)	1.382 (21)	C(7)–C(8)	1.267 (29)
C(9)–C(10)	1.399 (18)	C(11)–C(12)	1.260 (24)
V(2)–S(13)	2.339 (5)	V(2)–S(14)	2.342 (4)
V(2)–S(15)	2.342 (4)	V(2)–S(16)	2.342 (4)
V(2)–S(17)	2.348 (4)	V(2)–S(18)	2.347 (4)
S(13)–C(13)	1.708 (13)	S(14)–C(14)	1.712 (13)
S(15)–C(17)	1.688 (14)	S(16)–C(18)	1.696 (14)
S(17)–C(21)	1.783 (13)	S(18)–C(22)	1.710 (13)
S(19)–C(13)	1.762 (13)	S(19)–C(15)	1.698 (18)
S(20)–C(14)	1.769 (13)	S(20)–C(16)	1.810 (19)
S(21)–C(17)	1.773 (15)	S(21)–C(20)	1.695 (17)
S(22)–C(18)	1.742 (15)	S(22)–C(19)	1.733 (17)
S(23)–C(22)	1.758 (14)	S(23)–C(24)	1.772 (26)
S(24)–C(21)	1.737 (13)	S(24)–C(23)	1.763 (22)
C(13)–C(14)	1.358 (18)	C(15)–C(16)	1.435 (26)
C(17)–C(18)	1.400 (19)	C(19)–C(20)	1.348 (23)
C(21)–C(22)	1.303 (18)	C(23)–C(24)	1.238 (30)
	Bond Angles		
S(1)–V(1)–S(2)	81.0 (1)	S(1)–V(1)–S(3)	81.7 (1)
S(2)–V(1)–S(3)	129.5 (2)	S(1)–V(1)–S(4)	139.8 (2)
S(2)–V(1)–S(4)	82.7 (2)	S(3)–V(1)–S(4)	80.9 (2)
S(1)–V(1)–S(5)	81.1 (1)	S(2)–V(1)–S(5)	139.0 (2)
S(3)–V(1)–S(5)	83.5 (1)	S(4)–V(1)–S(5)	132.0 (2)
S(1)–V(1)–S(6)	132.6 (2)	S(2)–V(1)–S(6)	83.6 (1)
S(3)–V(1)–S(6)	139.3 (2)	S(4)–V(1)–S(6)	81.2 (2)
S(5)–V(1)–S(6)	81.9 (1)	S(13)–V(2)–S(14)	81.7 (1)
S(13)–V(2)–S(15)	81.7 (2)	S(14)–V(2)–S(15)	134.8 (2)
S(13)–V(2)–S(16)	138.1 (2)	S(14)–V(2)–S(16)	83.2 (1)
S(15)–V(2)–S(16)	81.7 (1)	S(13)–V(2)–S(17)	81.3 (1)
S(14)–V(2)–S(17)	135.6 (2)	S(15)–V(2)–S(17)	82.3 (1)
S(16)–V(2)–S(17)	133.6 (2)	S(13)–V(2)–S(18)	134.4 (2)
S(14)–V(2)–S(18)	81.7 (1)	S(15)–V(2)–S(18)	136.7 (2)
S(16)–V(2)–S(18)	81.1 (1)	S(17)–V(2)–S(18)	81.5 (1)

Description of Structure

The unit cell for the complex $[(C_4H_9)_4N][V(S_4C_4H_4)_3]$ contains eight cations and eight anions. The structure of the entire asymmetric unit with labeling of all atoms is very congested and does not provide useful information. The numbering of the other anion is similar to that in Figure 2, with sulfurs 1–6 coordinated to vanadium 1. The remaining atoms on a ligand are numbered sequentially starting with the atoms composing the ligand containing sulfurs 1 and 2, then sulfurs 3 and 4, and finally sulfurs 5 and 6. The counterions contain nitrogens 1 and 2 with bonded *n*-butyl carbons 25–40 and 41–56, respectively. The hydrogen atoms have the same number as their attached carbon atom.

The six sulfurs coordinate to the vanadium in a slightly distorted trigonal-prismatic (TP) array, with an average V–S distance of 2.340 (4) Å. The two triangular faces in Figure 2 are defined by S(13), S(15), S(17) and by S(14), S(16), S(18). Another view of this anion (Figure 3), down the approximate 3-fold axis, illustrates the TP geometry. Here, the slight distortion is apparent. Two criteria that have been established to describe the distortion in TP complexes are the S–M–S (trans) angle and the trigonal twist angle.[20] In all previously reported TP complexes the S–M–S (trans) angle has a value of approximately 136°. The average value in V(DDDT)$_3^-$ is 135.5 (2)°. Three trigonal twist angles of one anion are 6.1, 6.4, and 4.3°. Those of the other unique anion are slightly smaller at 1.4, 2.7, and 1.2°. The average value of all six is 3.7°. In this work, a twist angle for each ligand is defined as the dihedral angle between the planes of the centroids of the triangular faces with each coordinated sulfur of a ligand.

Table IV compares these values, the S–M–S (bite) angle, and selected distances to those of the other three vanadium structures

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Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*[a]		*x*	*y*	*z*	*U*[a]
V(1)	5523 (2)	2945 (1)	1143 (1)	35 (1)	C(17)	12810 (14)	8064 (7)	1500 (3)	51 (6)
S(1)	4737 (4)	2077 (2)	773 (1)	49 (1)	C(18)	12848 (13)	7829 (7)	1157 (4)	53 (6)
S(2)	5229 (4)	3588 (2)	642 (1)	51 (1)	C(19)	15489 (15)	7837 (11)	1175 (4)	145 (11)
S(3)	7059 (4)	2112 (2)	1265 (1)	51 (1)	C(20)	15462 (14)	7909 (13)	1523 (4)	186 (14)
S(4)	7316 (4)	3646 (2)	1205 (1)	59 (2)	C(21)	8208 (12)	6683 (7)	1683 (3)	46 (5)
S(5)	4296 (4)	2340 (2)	1546 (1)	46 (1)	C(22)	8255 (13)	6512 (7)	1357 (3)	51 (6)
S(6)	4538 (4)	3874 (2)	1412 (1)	49 (1)	C(23)	6844 (27)	5542 (11)	1858 (5)	143 (13)
S(7)	2932 (5)	1954 (3)	198 (1)	86 (2)	C(24)	6676 (31)	5451 (12)	1543 (6)	243 (20)
S(8)	3625 (6)	3622 (3)	23 (1)	95 (2)	N(1)	7748 (11)	1621 (6)	2427 (3)	55 (5)
S(9)	10086 (4)	3613 (3)	1134 (2)	117 (3)	C(25)	6356 (15)	1490 (7)	2321 (3)	70 (7)
S(10)	9753 (4)	1849 (3)	1146 (1)	103 (2)	C(26)	5915 (14)	759 (7)	2303 (4)	76 (7)
S(11)	3354 (4)	2522 (2)	2253 (1)	68 (2)	C(27)	4633 (15)	660 (7)	2137 (4)	82 (7)
S(12)	3791 (6)	4243 (2)	2112 (1)	87 (2)	C(28)	4297 (18)	−50 (8)	2066 (5)	109 (9)
C(1)	3958 (14)	2456 (7)	443 (3)	52 (6)	C(29)	8093 (14)	1247 (10)	2761 (3)	97 (9)
C(2)	4200 (12)	3160 (7)	377 (3)	44 (5)	C(30)	7327 (20)	1329 (10)	3051 (4)	141 (11)
C(3)	2878 (23)	2372 (9)	−210 (4)	166 (13)	C(31)	7735 (23)	958 (12)	3387 (5)	191 (15)
C(4)	2963 (28)	2993 (9)	−255 (4)	201 (16)	C(32)	8681 (20)	476 (12)	3399 (6)	193 (16)
C(5)	8649 (11)	3158 (8)	1162 (3)	58 (6)	C(33)	7922 (16)	2388 (7)	2483 (4)	80 (7)
C(6)	8542 (15)	2456 (8)	1185 (3)	62 (6)	C(34)	7578 (19)	2843 (8)	2186 (4)	98 (9)
C(7)	11248 (15)	2988 (10)	1203 (7)	203 (15)	C(35)	7812 (17)	3587 (8)	2245 (5)	110 (9)
C(8)	11136 (15)	2373 (10)	1105 (6)	155 (12)	C(36)	9065 (19)	3798 (11)	2230 (6)	167 (13)
C(9)	3949 (11)	2911 (6)	1878 (3)	34 (5)	C(37)	8563 (14)	1349 (8)	2143 (3)	64 (7)
C(10)	4108 (12)	3606 (7)	1806 (3)	45 (5)	C(38)	9983 (15)	1494 (8)	2178 (4)	85 (8)
C(11)	3032 (22)	3830 (8)	2458 (4)	150 (12)	C(39)	10807 (18)	993 (11)	1984 (5)	140 (12)
C(12)	2937 (27)	3196 (9)	2506 (5)	208 (16)	C(40)	10800 (19)	291 (10)	2123 (7)	182 (15)
V(2)	9787 (2)	7953 (1)	1317 (1)	36 (1)	N(2)	1379 (11)	9356 (6)	−39 (3)	60 (5)
S(13)	8636 4)	8816 (2)	1599 (1)	54 (2)	C(41)	189 (21)	9445 (10)	−373 (8)	317 (24)
S(14)	8673 (4)	8378 (2)	836 (1)	50 (1)	C(42)	−572 (25)	9408 (13)	−283 (8)	305 (23)
S(15)	11436 (4)	8367 (2)	1673 (1)	51 (1)	C(43)	−1665 (19)	9601 (11)	−656 (5)	171 (13)
S(16)	11479 (4)	7863 (2)	920 (1)	53 (1)	C(44)	−2630 (24)	9191 (11)	−582 (5)	177 (15)
S(17)	9235 (4)	7356 (2)	1824 (1)	49 (1)	C(45)	1258 (23)	9594 (12)	328 (4)	158 (13)
S(18)	9234 (4)	6907 (2)	1062 (1)	51 (1)	C(46)	1457 (35)	9931 (15)	538 (5)	463 (33)
S(19)	7429 (5)	10125 (2)	1448 (1)	83 (2)	C(47)	1360 (17)	10140 (8)	869 (4)	115 (9)
S(20)	7445 (5)	9625 (2)	594 (1)	77 (2)	C(48)	2454 (22)	10171 (14)	1069 (7)	207 (16)
S(21)	14185 (4)	8141 (2)	1768 (1)	76 (2)	C(49)	1514 (21)	8610 (9)	−49 (6)	150 (13)
S(22)	14199 (4)	7557 (3)	930 (1)	109 (2)	C(50)	1122 (29)	8067 (10)	−135 (7)	236 (19)
S(23)	7398 (5)	5828 (2)	1174 (1)	99 (2)	C(51)	1374 (18)	7367 (8)	−105 (4)	82 (8)
S(24)	7387 (5)	6324 (2)	2030 (1)	78 (2)	C(52)	290 (22)	6944 (9)	7 (5)	138 (12)
C(13)	8095 (13)	9362 (7)	1286 (3)	46 (5)	C(53)	2412 (23)	9713 (14)	−195 (4)	238 (17)
C(14)	8067 (12)	9159 (7)	949 (3)	42 (5)	C(54)	3312 (23)	10046 (11)	−169 (6)	204 (17)
C(15)	6286 (18)	10311 (8)	1149 (4)	87 (8)	C(55)	4331 (15)	10391 (9)	−347 (4)	107 (9)
C(16)	6773 (21)	10372 (9)	802 (5)	119 (11)	C(56)	5346 (24)	10485 (16)	−140 (7)	258 (21)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Comparison of Distances (Å) and Angles (deg) of Vanadium Dithiolenes[a]

complex	M–S	S–S (intra)	S–S (inter)	S–C	C–C	ref
$V(DDDT)_3^-$	2.340 (4)	3.055	3.074	1.708 (6)	1.378 (21)	this work
$V(S_2C_2Ph_2)_3$	2.337 (6)	3.061 (12)	3.07 (13)	1.69 (1)	1.41 (2)	5
$V[S_2C_2(CN)_2]_3^{2-}$	2.36 (1)	3.14 (4)	3.20 (23)	1.72 (3)	1.33 (3)	16
$V(dmt)_3^{2-}$	2.375 (3)	3.196 (3)	3.421 (3)	1.723 (8)	1.375 (18)	17

complex	S–M–S (bite)	S–M–S (trans)	twist angle	coordination
$V(DDDT)_3^-$	81.5 (1)	135.5 (2)	3.7	TP
$V(S_2C_2Ph_2)_3$	81.7 (2)	136	8.5[b]	TP
$V[S_2C_2(CN)_2]_3^{2-}$		158.6	twisted[c]	dist Oh
$V(dmt)_3^{2-}$	84.6 (1)	164.3 (1)	twisted[c]	dist Oh

[a] Standard deviations of average values are those given in the original paper or the larger of the individual standard deviations. [b] Reference 20. [c] No twist angle given.

reported to date. The coordination of the MS_6 core is also given. The similarities among the distances for the two TP structures are apparent and contrast with those of the two distorted octahedral complexes. The same is true for the S–M–S (trans) angle.

An interesting feature of the coordination of dithiolene ligands to a metal is the bending of the ligand planes with respect to the MS_2 planes seen in all TP structures except those with stilbene-1,2-dithiolene ($S_2C_2Ph_2$). This folding is attributed to the increased stability afforded by greater π overlap of the metal and ligand orbitals. This type of overlap is similar to that proposed for stabilizing TP coordination.[21] In complexes that approach the octrahedral limit, the ligand and MS_2 planes are essentially coplanar. In $V(DDDT)_3^-$, the tetrathioethylene unit is planar with the $-CH_2CH_2-$ fragment puckering above and below this plane. The dihedral angles were calculated for only the planar portion of the ligand, the average value being 20.5°. This compares with the values of 18° for $Mo(S_2C_2H_2)_3$, 21.4° for $Mo(S_2C_6H_4)_3$, and 22.4° for $Nb(S_2C_6H_4)_3^-$.[3,22,23] Therefore, DDDT can be added to the group of dithiolene ligands that exhibit bending in TP coordination, those being $S_2C_2H_2$, $S_2C_6H_4$, and the diselenolene $Se_2C_2(CF_3)_2$. The lack of folding in the $S_2C_2Ph_2$ complexes has

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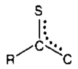
[21] Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2956.

[22] Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1976**, *15*, 1584.

[23] Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1976**, *15*, 1589 and references therein.

Table V. Comparison of IR Band Positions of Vanadium Dithiolenes[a]

complex	C–C	C–S		M–S	M–S	ref
$V(DDDT)_3^-$	1406	1165	865	430	385	this work
$V(DDDT)_3^{2-}$	1445	1170	870	345	325 (sh)	this work
$V(S_2C_2Ph_2)_3$	1372	1150	892	406	346	24
$V(S_2C_2Ph_2)_3^-$	1428	1165	869	398	349	24
$V(S_2C_2H_2)_3$	1347	1113	894	385	361	24
$V(S_2C_2H_2)_3^-$	1416	1118	849	392	363	24
$V(S_2C_2H_2)_3^{2-}$	1494	952	799	367	350	24

[a] All data obtained as KBr pellets. Values in cm^{-1}.

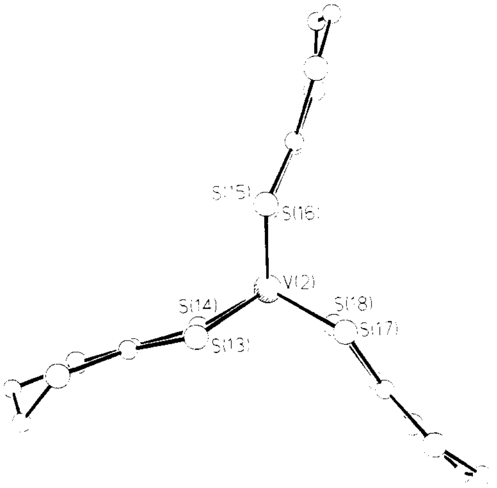


Figure 3. View of $V(DDDT)_3^-$ projected down the approximate 3-fold axis.

been postulated as resulting from steric interactions between the bulky phenyl groups.[23]

Results and Discussion

Both of the complexes, $V(DDDT)_3^-$ and $V(DDDT)_3^{2-}$, display IR spectra with all characteristic metal dithiolene absorptions present.[6] These bands are listed in Table V along with those of other vanadium dithiolenes for comparison. The shifts in the band positions of the $DDDT^{2-}$ complexes follow the general trends expected as the total charge on the complex becomes more negative. That is, the C–C frequency increases and the V–S frequencies decrease as the ligand shifts from dithiodiketonic to dithiolate character. Theoretically, the S–C and the R–C(S)–C frequencies should decrease. However, these bands are seen to flunctuate, probably due to coupling with other modes.

The ^1H NMR spectrum of the $V(DDDT)_3^-$ anion shows a singlet due to the ligand protons and a quartet and triplet resulting from the tetraethylammonium counterion. The presence of a proton signal and the absence of an ESR signal for this anion are evidence that this complex is diamagnetic.

A cyclic voltammogram of the monoanion reveals three well-defined reversible waves at 0.39, –0.51, and –1.44 V, corresponding to the neutral to monoanion, monoanion to dianion, and dianion to trianion reductions of the complex. Table VI compares these values to those of other vanadium dithiolenes. The first observation is that the $DDDT^{2-}$ complex is the only one to show three distinct redox waves. Also, it is more easily reduced than the stilbene dithiolene yet more difficult to reduce than the others shown. These potentials are an indication of the ability of the ligand to accept electron density as the charge on the complex decreases. For the $-1 \rightleftharpoons -2$ process, this ability increases in the order Ph < SCH_2CH_2S < CF_3 < CN, where these groups are the substituent (R) on the ligand $S_2C_2R_2$ or the ring-closing substituent of $DDDT^{2-}$. These potentials have also been correlated with the charge of the most stable species.[26]

Table VI. Cyclic Voltammetry Parameters for $[VL_3]^n$ Dithiolene Complexes

complex	electrode process[a] $0 \rightleftharpoons -1$	$-1 \rightleftharpoons -2$	$-2 \rightleftharpoons -3$	ref
$V(DDDT)_3$	+0.39	–0.51	–1.44	this work
$V(S_2C_2Ph_2)_3$	+0.30	–0.71		25
$V[S_2C_2(CN)_2]_3$		+0.66	–0.49	25
$V(S_2C_6H_3CH_3)_3$			–0.18	25
$V(S_2C_6H_4)_3$			–0.12	25
$V[S_2C_2(CF_3)_2]_3$		+0.47		25

[a] Values in volts vs SCE.

Table VII. ESR Results for Vanadium Dithiolenes (Solution)

complex	$\langle g \rangle$[a]	$\langle A \rangle$, G[b]	ref
$V(DDDT)_3^{2-}$	1.9917	67.2	this work
$VS_6C_6(C_6H_5)_6^{2-}$	1.9811	63.9	25
$VS_6C_6(C_6H_5)_6$	1.9900	61.5	25
$V(S_2C_6H_3CH_3)_3^{2-}$	1.9782	65.8	25
$V(S_2C_6H_4)_3^{2-}$	1.9779	65.2	25
$VS_6C_6(CN)_6^{2-}$	1.980	63.3	25
$VS_6C_6(CF_3)_6^{2-}$	1.9829	62.4	25
$VS_6C_6H_6^{2-}$	1.981	67.8	24
$VS_6C_6H_6$	1.991	62.6	24
$V(dmit)_3^{2-}$	1.979	63.9	17
$V(dmt)_3^{2-}$	1.978	61.9	17

[a] Accuracy ≤±0.002. [b] Accuracy ≤±0.5.

An interesting property of the electrochemical behavior appeared after bulk electrolysis of $V(DDDT)_3^-$ to $V(DDDT)_3^{2-}$ at –1.00 V. The electrolysis was performed to obtain solutions of the dianion for analysis before it was synthesized directly. Repeating the cyclic voltammogram, we noted that the $0 \rightleftharpoons -1$ redox wave was chemically irreversible. The same is true of solutions made from the salt of the dianion. Electrolysis of the dianion solution at 0.00 V to regain the monoanion resulted in a blue solution giving a cyclic voltammogram identical with the original one. The implication of this behavior will be discussed in more detail later in this section. Attempts at electrolysis to obtain either the trianionic or the neutral species were unsuccessful.

The electronic spectra of the vanadium complexes were recorded over the range 33 000–10 500 cm^{-1}. The spectrum of the monoanion shows three absorptions. The energies are 25 100 (3800), 15 850 (11 700), and 12 250 cm^{-1} (11 800), with molar absorptivities in parentheses. The dianion's spectrum contains two absorptions and a shoulder on the solvent edge. They appear at 29 000 sh, 24 450 (5600), and 15 150 cm^{-1} (6100). While the spectral bands are similar in energy and intensity to those of $V(S_2C_2Ph_2)_3^-$ and $V[S_2C_2(CN)_2]_3^{2-}$, no assignments can be made at this time.[24,27]

The ESR spectrum of the dianion in solution shows the characteristic eight-line pattern of vanadium ($I = {}^7/_2$). The

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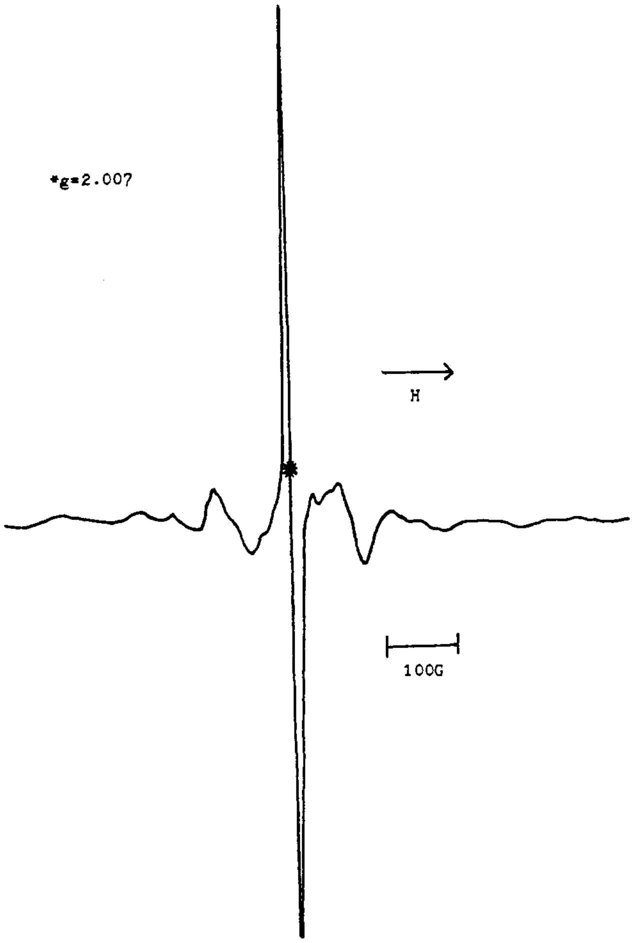

Figure 4. Frozen-glass ESR spectrum of $[(C_2H_5)_4N]_2[V(DDDT)_3]$.

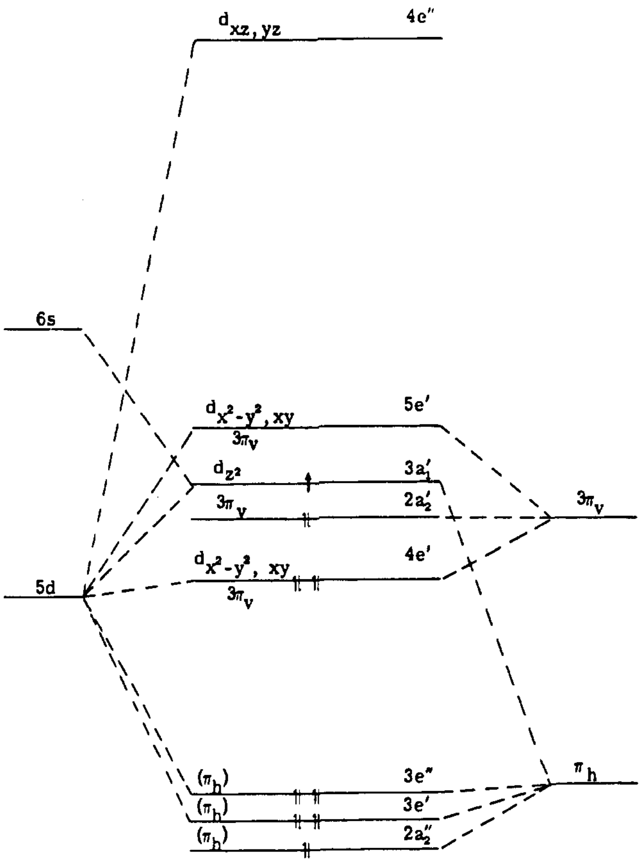

Figure 5. MO diagram for tris(dithiolenes). Electron configuration for $V(DDDT)_3{}^{2-}$ is shown.

isotropic g and A values are 1.9917 and 67.2 G, respectively. These values are compared to those of other vanadium dithiolenes in Table VII. A unique signal (Figure 4) was recorded for the frozen-glass spectrum. It is characterized by an intense line centered at a g value of 2.007. There is clear evidence of metal hyperfine splitting on either side of this line, but it has not been resolved. A very recent report[17] shows a similar spectrum for $V(dmit)_3{}^{2-}$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate), where the authors state the spectrum to be nonaxial and described by a rhombic-symmetric spin Hamiltonian. They compare their results to those of a study[28] on $V[S_2C_2(CN)_2]_3{}^{2-}$, which concludes that the single unpaired electron lies in an a_1 orbital of predominantly d_{z^2} metal character but with substantial delocalization due to overlap of the metal orbital with lone-pair orbitals (π_h) on the sulfurs. This latter study extends their findings to all ESR-active tris(dithiolenes). Therefore, it seems appropriate to conclude that the vanadium in $V(DDDT)_3{}^{2-}$ is best described as a d^1 V(IV) metal center.

In an attempt to gain a better understanding of the electronic structure of these complexes, a knowledge of the molecular orbital ordering is important. The molecular orbital scheme presented by Gray and co-workers[21] for trigonal-prismatic dithiolenes is preferred over that of Schrauzer and Mayweg[24] because of better correlation with optical and ESR spectra.[6,28] This scheme is reproduced in Figure 5. The levels of interest are 4e', a bonding orbital of d metal and π_v ligand character, $2a_2'$, a nonbonding orbital localized on the ligand, $3a_1'$, an antibonding orbital of d metal and π_h ligand character, and 5e', an antibonding orbital of d metal and π_v ligand character. The electron configuration shown is that of $V(DDDT)_3{}^{2-}$. If the 4e' level is considered to be predominantly ligand in character, then the metal is more correctly described as a vanadium(IV) d^1 metal center, which corresponds to the electron in the $3a_1'$ level. Upon removal of one electron to obtain the configuration of $V(DDDT)_3{}^-$, the HOMO would be $2a_2'$. Again, if the 4e' level is composed of predominantly ligand character, this would describe the metal as a d^0 vanadium(V). In these cases, the ligands are true 1,2-dithiolates.

It has been shown[28] that the $3a_1'$ and $2a_2'$ levels will invert as the charge on a vanadium dithiolene changes from −2 to 0. This inversion results from increased stabilization of metal orbitals over ligand orbitals as the positive charge on the complex increases. If the inversion has occurred between the −2 and −1 charged complexes, then the HOMO of the monoanion would be $3a_1'$. Assuming the electrons in the 4e' level to be located primarily on the ligand, the vanadium in $V(DDDT)_3{}^-$, is a d^2 V(III) ion. In this case, two of the ligands would be dithiolates. The third is oxidized by two electrons to a dithiodiketone. Evidence for the inversion is found in structural data. Referring back to Table IV, we see that the structural parameters for $V(DDDT)_3{}^-$ and $V(S_2C_2Ph_2)_3$ are very similar and inversion of the electronic levels is established for the neutral complex. The comparison is made between two different ligands, yet the similarities cannot be overlooked. The best comparison of structural data would be among those for tris(dithiolenes) of the $DDDT^{2-}$ ligand, and further studies are in progress. The unusual electrochemical behavior previously described could be related to inversion of the levels in the MO diagram and the oxidation state of the vanadium. The initial voltammogram of the monoanion shows three reversible waves. If the vanadium is considered to be V(III) with two d electrons, the two reversible waves negative of the initial potential correspond to placing two electrons in the $2a_2'$ level with their subsequent removal. The reversible wave at 0.39 V involves the $3a_1'$ orbital of metal character. If the oribtal energies remained unchanged for the dianion, the irreversibility of the wave in the positive region is difficult to explain. We suggest the inversion of these orbitals renders the lower lying $2a_2'$ chemically irreversible to electron transfer in cyclic voltammetry. A definitive explanation

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of this observation requires further investigation and is forthcoming.

The trigonal-prismatic structure of V(DDDT)$_3^-$ was not unexpected. Gray et al.[21] attribute the stability of trigonal-prismatic coordination to two π-bonding interactions. First, the overlap of the π_h orbitals of the sulfurs with the d_{z^2} orbital of the metal gives rise to the $2a_1'$ bonding orbital, which is always filled, and the $3a_1'$ antibonding orbital. Second, the interaction between the π_v ligand orbitals and the metal $d_{x^2-y^2}$ and d_{xy} forms 4e' and 5e', which are bonding and antibonding, respectively. The crossover point for TP to octahedral coordination is not well-defined but balances on the occupation of the bonding and antibonding orbitals. The vanadium dianions have one electron in $3a_1'$ and a filled $2a_2'$. Although Re(S$_2$C$_2$Ph$_2$)$_3$ is isoelectronic with these dianions and exhibits TP geometry, the destabilization of the vanadium species to a distorted octahedral structure is attributed to the small size of the metal and the occupation of the nonbonding orbital resulting in weakening of the π overlap. The neutral and monoanion have one and two electrons in $3a_1'$, respectively, and an empty $2a_2'$ due to the inversion of these levels. The π-bonding interactions outweigh the effect of one or two electrons in the $3a_1'$ antibonding level, and TP coordination results. On the basis of these arguments, V(DDDT)$_3^{2-}$ is predicted to have a distorted octahedral structure. However, recent reports[29,30] of two Mo dithiolene structures indicate that there are factors other than the occupation of the bonding and antibonding levels contributing to the coordination. The authors suggest the substituents attached to the dithiolene carbons play a role. Therefore, a full explanation of the coordination preference must be obtained by examining tris complexes of the same ligand, and several structural studies of complexes with the DDDT^{2-} ligand are in progress.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank the National Science Foundation for funds toward upgrading our diffractometer (Grant CHE-8307022), John Cooper for assistance in collection of UV/vis/near-IR spectra, and Jack Trexler for assistance with computer software.

Registry No. [(C$_2$H$_5$)$_4$N][V(DDDT)$_3$], 115244-54-7; [(C$_4$H$_9$)$_4$N][V(DDDT)$_3$], 115269-49-3; [(C$_2$H$_5$)$_4$N]$_2$[V(DDDT)$_3$], 115244-56-9; V(DDDT)$_3$, 115269-50-6; V(DDDT)$_3^{3-}$, 115244-57-0.

Supplementary Material Available: Cyclic voltammogram of [(C$_2$H$_5$)$_4$N][V(S$_4$C$_4$H$_4$)$_3$], solution ESR spectrum of [(C$_2$H$_5$)$_4$N]$_2$[V(S$_4$C$_4$H$_4$)$_3$], stereoview of the molecular packing for [(C$_4$H$_9$)$_4$N][V(S$_4$C$_4$H$_4$)$_3$], a table of bond lengths and bond angles, and listings of hydrogen coordinates and anisotropic temperature factors (9 pages); a listing of calculated and observed structure factors (34 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Queen's University, Kingston, Ontario, Canada K7L 3N6

Ligand Substitution Reactions of Dirhodium(II) Tetraacetate with Water-Soluble Phosphines

Manuel A. S. Aquino and Donal H. Macartney*

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The kinetics of the axial ligand substitution reactions of the diaqua adduct of dirhodium(II) tetraacetate, Rh$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$, with a series of water-soluble alkyl- and arylphosphines (PR$_3^{n+}$) of various charges have been investigated. The rate-determining formation of the Rh$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)PR$_3^{n+}$ adducts occurs with rate constants (25.0 °C, $I = 0.10$ M) in the range of (1.3–8.9) × 10^5 M^{-1} s^{-1} ($\Delta H^\ddagger = 8.0$–10.3 kcal mol^{-1}, $\Delta S^\ddagger = -5$ to 0 cal K^{-1} mol^{-1}), with the rate constant decreasing with an increase in the absolute charge on the ligand. A dissociative mechanism is proposed for the substitution of the axially coordinated water molecules, and the rate parameters are compared with values reported for substitutions by nitrogen heterocyclic ligands. The acid dissociation constants of the protonated phosphonium ligands and the stability constants of the phosphine mono and bis adducts have been measured at 25 °C.

Introduction

Dirhodium(II) tetrakis(μ-carboxylate) complexes have been the subject of numerous investigations in recent years.[1,2] Their interesting structural and spectroscopic properties, together with the observed catalytic[3] and antitumor activities,[4] have prompted studies of the rhodium–rhodium and rhodium–ligand interactions. These complexes contain a rhodium–rhodium single bond with four equatorial bridging carboxylate ions that are inert to substitution (k_1(acetate) = 7.2 × 10^{-4} s^{-1} at 38 °C).[5] The two axial positions may be occupied by donor solvents that can undergo rapid ligand exchange to yield adducts with a variety of ligand species.[2] We have recently reported the rate and activation parameters for the formation of phosphine and phosphite adducts of dirhodium(II) tetrakis(μ-acetate) in acetonitrile.[6] The kinetic behavior is consistent with the rate-determining formation of the mono adduct by a dissociative ligand substitution mechanism. The rate constant for the formation of the mono adduct was found to be independent of the nature of the phosphine ligand, with $k_1(25\ ^\circ\text{C}) = (1.05 \pm 0.05) \times 10^5$ M^{-1} s^{-1}, $\Delta H^\ddagger = 10.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = 1 \pm 2$ cal K^{-1} mol^{-1}. Bear and co-workers[7-10] have determined the kinetic and thermodynamic parameters associated with the formation of mono and bis adducts of dirhodium(II) tetrakis(μ-carboxylate) complexes with nitrogen heterocyclic ligands in aqueous solution. The rate constants (k_1, 25 °C, $I = 0.10$ M) for the formation of the mono adducts, measured by temperature-jump techniques, ranged from 4 × 10^5 M^{-1} s^{-1} (histidine) to 6.2 × 10^6 M^{-1} s^{-1} (imidazole), with the formation of the bis

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