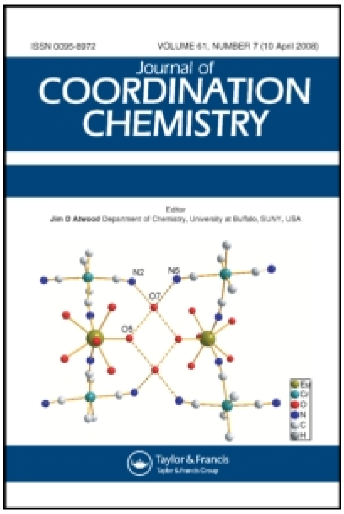


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE SYNTHESIS OF A TRIS(1,4-BUTANEDIYLDITHIOETHYLENE-1,2-DITHIOLATE) COMPLEX OF VANADIUM. STRUCTURE AND ELECTRONIC PROPERTIES

Geewon Chung[a]; Robert Bereman[a]; Phirtu Singh[a]
[a] Department of Chemistry, Box 8204, North Carolina State University, Raleigh, North Carolina

To cite this Article Chung, Geewon , Bereman, Robert and Singh, Phirtu(1994) 'THE SYNTHESIS OF A TRIS(1,4-BUTANEDIYLDITHIOETHYLENE-1,2-DITHIOLATE) COMPLEX OF VANADIUM. STRUCTURE AND ELECTRONIC PROPERTIES', Journal of Coordination Chemistry, 33: 4, 331 — 346

To link to this Article: DOI: 10.1080/00958979408024293

URL: http://dx.doi.org/10.1080/00958979408024293

J. Coord. Chem., 1994, Vol 33, pp. 331–346
Reprints available directly from the publisher
Photocopying permitted by license only

THE SYNTHESIS OF A TRIS(1,4-BUTANEDIYLDITHIOETHYLENE-1,2-DITHIOLATE) COMPLEX OF VANADIUM. STRUCTURE AND ELECTRONIC PROPERTIES

GEEWON CHUNG, ROBERT BEREMAN* and PHIRTU SINGH

Department of Chemistry, Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204

(Received April 21, 1994; in final form July 21, 1994)

A monoanionic vanadium complex has been isolated from the reaction of vanadium(III) chloride and the dipotassium salt of the dithiolene, 1,4-butanediyldithioethylene-1,2-dithiolate (BDDT). The complex, isolated as the tetraethylammonium salt and recrystallized from acetone, produced dark blue crystals suitable for an X-ray structural study. The material crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.798(11)$ Å, $b = 19.244(30)$ Å, $c = 36.370(42)$ Å, $\beta = 92.23(7)°$, $V = 7552(12)$ Å^3, $z = 8$, and $R = 0.1106$. Extended Hückel molecular orbital calculations suggest that this is best described as a V(V) complex. In contrast, however, a comparison of the MO calculation with the tris-vanadium complex of 1,2-ethanediyldithioethylene-1,2-dithiolate (DDDT) suggests this latter system is more appropriately described as a lower oxidation state of vanadium with a partially oxidized ligand. The structural data also suggest this interpretation.

KEYWORDS: vanadium, dithiolate, chelate, electronic properties

INTRODUCTION

The coordination chemistry of transition metal dithiolenes has been an area of great interest for a number of years. However, there has been relatively little work on the tris(dithiolene) complexes. The first analytically pure tris(dithiolene) complex, $Mo[S_2C_2(CF_3)_2]_3$, was prepared by King in 1963.[1] This class of compounds yielded the highly unusual trigonalprismatic (TP) geometry in the structures of $Mo(S_2C_2H_2)_3$ and $Re(S_2C_2Ph_2)_3$.[2-4] It is known that tris complexes, like their bis counterparts, undergo reversible one-electron transfer reactions resulting in stable species differing in apparent oxidation states. These observations brought about a flurry of research on tris(dithiolenes) more recently.[5-9]

Since the initial report of the synthesis of the new dithiolene potassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate[10] (K_2DDDT) shown in Figure 1, only the chemistry of the late transition metals Ni, Pd, Pt, Cu, and Au has been investigated

---

* Author for correspondence.

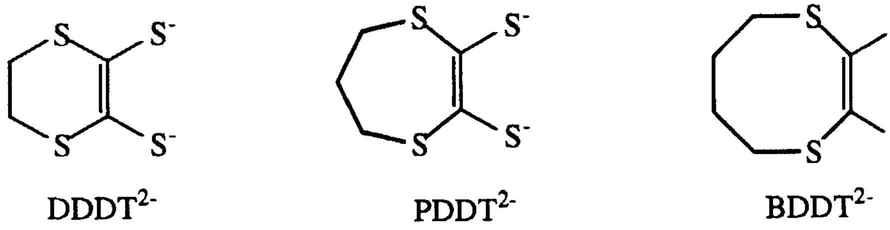


Figure 1 Lewis structures of DDDT^{2-}, PDDT^{2-}, and BDDT^{2-}.

in detail.[11,12] Several years ago, Welch *et al.*[13] reported a tris-vanadium complex of this ligand.

In our efforts to more fully understand the coordination chemistry of the transition metal complexes of the newly synthesized BDDT^{2-} ligand, a new vanadium complex has been isolated as the tetraethylammonium salt.

The 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 themselves can be oxidized to dithioketones. Considering both possibilities, the formal oxidation state of $\mathrm{V(BDDT)}_{3-}$ might be written as $[\mathrm{V}^{5+}(d^0)](\mathrm{BDDT}^{2-})_3$, $[\mathrm{V}^{3+}(d^2)](\mathrm{BDDT}^0)(\mathrm{BDDT}^{2-})_2$ or some intermediate form.

Only four vanadium dithiolene structures of this type have been reported in the literature. The neutral compound, $\mathrm{V(S_2C_2Ph_2)_3}$, has a slightly distorted trigonal-prismatic coordination, while the dianions $\mathrm{V(S_2C_2Ph_2)_3}^{2-}$ and $\mathrm{V(dmit)_3}^{2-}$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) have distorted octahedral $\mathrm{VS_6}$ cores.[4,16,17] The crystal structure of $[\mathrm{(C_4H_9)_4N}][\mathrm{V(DDDT)_3}]$[13], where the anion has a trigonal-prismatic (TP) geometry, is the first example in which the complex anion is mononegative.

The BDDT^{2-} ligand (Figure 1) has an extended cyclic system compared to PDDT^{2-} and DDDT^{2-}.[18] We have now prepared a tris-vanadium complex as a monoanion. The complex has been characterized including an X-ray structural analysis. In addition, in order to more fully understand the electronic structure of both DDDT^{2-} and BDDT^{2-} and their vanadium complexes in terms of the oxidation state of the central vanadium ion, we have carried out a molecular orbital (MO) study based upon extended Hückel calculations[19] on both $\mathrm{V(BDDT)_3}^-$ and $\mathrm{V(DDDT)_3}^-$.

EXPERIMENTAL

Reagents

2,7,9,11-Tetrathiabicyclo[6.3.0]undec-1(8)-en-10-thione (TTUET) and its derivative, 2,7,9,11-tetrathiabicyclo[6.3.0]undec-1(8)-en-10-one (TTUEO), were prepared by literature methods[20] with some modifications, and characterized by IR, NMR, elemental analysis and melting point (mp.). Vanadium chloride was purchased from Fisher Chemical Company. Tetraethylammonium bromide and potassium metal were obtained from Aldrich Chemical Company, Inc. Argon was purchased from

Air Products, Inc. All chemicals were used without further purification. THF was obtained from Fisher and freshly distilled from Na/benzophenone prior to use. Methyl alcohol and acetonitrile were purchased from Fisher Chemical Company and stored over 4Å sieves for more than 24 h before use. Ethyl alcohol was purchased from Aaper Alcohol and Chemical Company. Ethyl alcohol and water, used in the syntheses of complexes, were deoxygenated with argon for 30 min prior to use.

General Procedure

All reactions were carried out under a static atmosphere of argon using standard Schlenk techniques unless otherwise stated. Transfers of liquid solvents and/or reagents were made using argon purged ground glass syringes with Luer-lock type stainless steel needles.

Syntheses

[$C_7H_8S_5$ (TTUET)]

To a stirred solution (0°C) of 200 mL CS_2 in 400 mL of DMF, 10 g of sliced potassium metal was added very slowly and carefully. After stirring for 1 h, 10 g of sliced potassium metal and 30 mL of CS_2 were added to the solution. This same addition was again repeated 1 h later. An additional 50 mL of CS_2 was added and stirred for 3–4 h. To the reaction mixture, 100 mL of DMF was added and then 1,4-dibromobutane (46 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. To destroy any unreacted potassium metal, approximately 20 mL of MeOH, followed by H_2O (200 mL) was added. To remove any by-product, the solution was filtered, extracted with chloroform and washed with H_2O. The organic extracts were combined, dried over K_2CO_3 and concentrated to give an orange-brown solid. The crude product was recrystallized from ethanol to give orange crystals: mp. 107–108°C; ^1H NMR ($CDCl_3$) δ 3.05 (t, 4H), 2.04 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 212.2, 140.2, 38.4, 27.4; IR (KBr) 2920(m), 2900(s), 1440(s), 1400(s), 1288(s), 1055(vs), 1020(s), 880(m), 855(s), 800(m), 765(m), 505(m), 445(m), cm^{-1}; *Anal.* Calcd. for $C_7H_8S_5$: C, 33.31; H, 3.19; S, 63.50. Found: C, 33.45; H, 3.13; S, 63.26.

[$C_7H_8S_4O$ (TTUEO)]

To a solution of 2.50 g (1.0×10^{-2} mol) of TTUET in 30 mL $CHCl_3$, 3.2 g of $Hg(OAc)_2$ in 50 mL HOAc was added. The solution was refluxed for approximately 6 h and the solution turned black. Approximately 8 g of anhydrous Na_2SO_4 was added and the reaction mixture was filtered to remove any by-product. To the filtrate, a saturated Na_2CO_3 aqueous solution was added slowly. Extraction with CH_2Cl_2, drying over $MgSO_4$ and concentration gave a yellow solid. The crude product was recrystallized from ethanol to yield light yellow crystals: mp. 78–80°C; ^1H NMR ($CDCl_3$) δ 3.00 (t, 4H), 2.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 189.7, 131.6, 38.6, 27.5; IR (KBr) 2950(m), 2930(m), 2910(s), 1755(m), 1750(vs), 1600(vs), 1440(m), 1420(s), 1408(s), 1295(s), 1275(m), 1170(m), 1005(m), 900(s), 880(vs), 805(s), 765(s), 730(s), 550(m), 455(m), 380(m) cm^{-1}; *Anal.* Calcd. for $C_7H_8S_4O$: C, 35.57; H, 3.41; S, 54.25. Found: C, 35.52; H, 3.37; S, 54.13.

[K_2(BDDT)]

Potassium ethoxide was prepared by adding 3.2 g (8×10^{-2} mol) of sliced potassium metal to 8 mL (excess) of absolute ethanol under argon. Then approximately 200 mL of freshly distilled THF was added to this solution, followed by 4.73 g (2×10^{-2} mol) of TTUEO. A light cream-colored precipitate formed after a few minutes. The mixture was stirred for about 15 h, filtered, washed with diethyl ether, dried and stored in a Schlenk tube for further use.

[$(C_2H_5)_4N$][$V(C_6H_8S_4)_3$]

A solution of 0.26 g (1.7×10^{-3} mol) of VCl_3 in 10 mL of THF was added dropwise to 1.20 g (4.2×10^{-3} mol) of K_2BDDT in 20 mL of THF solution. The solution was stirred for 3 h at room temperature and then filtered through a frit to remove any by-product. A solution of 1.20 g of tetraethylammonium bromide in 30 mL of EtOH was added to the filtrate, and stirred for 20 min. A dark blue precipitate was formed and filtered (crude yield was not determined). Recrystallization from acetonitrile gave 0.183 g (16%) of dark blue shiny crystals: mp. 189°C (decomposed); ^{1}H NMR (DMSO-d^6) δ 3.20 (q, 8H), 3.15 (br. s, 12H), 1.70 (br. s, 12H), 1.15(dt, 12H); IR (KBr) 2990(w), 2920(m), 2860(w), 1480(s), 1435(s), 1420(s), 1390(s), 1355(vs), 1285(vs), 1240(m), 1225(m), 1170(s), 1130(w), 1035(w), 1005(m), 980(s), 965(m), 870(m), 840(m), 815(s), 785(s), 745(s), 450(m), 395(m) cm^{-1}; *Anal.* Calcd. for $VC_{26}H_{44}NS_{12}$: C, 38.73; H, 5.50; N, 1.74. Found: C, 38.47; H, 5.45; N, 1.85.

Physical Measurements

Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer over the range 4000–350 cm^{-1}. UV-vis spectra were obtained on a Hewlett Packard 8452A Diode Array Spectrophotometer. Electrochemical data were obtained with a BAS CV-27 potentiostat. A platinum wire was used for both the working and auxiliary electrode and a Ag/AgCl electrode was used as the reference electrode. The solution contained 0.10 M tetraethylammonium perchlorate as the supporting electrolyte in DMF with the metal complex concentration of 10^{-3} M. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Nuclear magnetic resonance spectra were obtained with a G.E. GN 300 (300MHz) spectrometer. Chemical shifts are in δ units (ppm) with TMS (0.0ppm) used as an internal standard for ^{1}H NMR.

Single-crystal X-ray Analysis

Unit cell dimensions were determined by rotation photographs and obtained from 15 reflections. A data set was collected on a Nicolet R3m/μ diffractometer equipped with a graphite monochrometer and using molybdenum radiation (λ = 0.71069 Å). All diffractometer data were collected at room temperature. No corrections for absorption were applied due to the small absorption coefficients. Unit cell dimensions were determined by a least-squares refinement of the setting angles of 15 reflections with 2θ values between 10 and 20°. Table 1 contains all relevant crystallographic parameters for the structure reported.

$[(C_2H_5)_4N][V(C_6H_8S_4)_3]$

Dark blue crystals suitable for X-ray analysis were grown by the slow evaporation of a saturated anhydrous acetonitrile solution. Axial photographs and unit cell constants demonstrated that the crystal possessed orthorhombic symmetry. Systematic absences were consistent with the space group P2$_1$/c. Two check reflections collected after every 48 reflections revealed no unexpected variation in intensity. Atomic scattering factors for all atoms were taken from the International Tables for X-ray Crystallography.[21] Relevant crystallographic information is given in Table 1. The vanadium and sulfur atoms were located by the direct methods program SOLV of the crystallographic software package SHELXTL.[22] The remaining non-hydrogen

Table 1 X-ray crystallographic parameters of $[(C_2H_5)_4N][V(BDDT)_3]$

	Crystal parameters
formula	$VC_{26}H_{44}NS_{12}$
formular weight	806.30
crystal size, mm	0.3 × 0.3 × 0.6
crystal color	dark blue
crystal habit	orthorhombic
cell dimensions	a = 10.798(11) Å
	b = 19.244(48) Å
	c = 36.37(4) Å
volume	7551.83 Å^3
space group	$P2_1/c$
molecules/unit cell	8
density calc., g/cm^3	1.42
F(000)	3376
	Data collection parameters
radiation(MoKα)	λ = 0.71069 Å
temperature	ambient
2Θ range	36°–46°
scan type	ω
no. of refl	9757
no. of refl used ($I>3\sigma_{(I)}$)	3610
linear absorption coefficient	9.32 cm^{-1}
	Refinement parameters[a]
final R index	R = 0.1106
	Rw = 0.1504
goodness of fit	1.121
largest Δ/σ	0.05
data/parameter ratio	5.6

[a] The data fit criteria were

$$R = \frac{\Sigma\|F_o| - |F_c\|}{\Sigma|F_o|},\quad R_\omega = \sqrt{\frac{\Sigma\omega(\Delta F)^2}{\Sigma F_0^2}},\quad GOF = \Sigma\sqrt{\frac{\omega(\|F_o| - |F_c\|)^2}{(N_o - N_v)}}.$$

atoms were found by subsequent difference Fourier techniques to give the appropriate trial structure. This trial structure was further refined by the block-diagonal least squares technique using SHELXTL on a Data General Microeclipse computer. The quantity to be minimized was $\Sigma w(\Delta F)^2$, where w is the weight to be assigned to an observation $w = 1/(\sigma^2(F) + 0.01602F^2)$. Non-hydrogen atoms were refined with anisotropic temperature factors except for C9A, C10A, C11A, C15B, and C16B which were refined with isotropic temperature factors. Owing to the disorder present in the -$(CH_2)_4$- regions of the ligand, only some carbons could be refined with anisotropic temperature factors. All hydrogen atoms were placed in calculated positions 0.96 Å away from the attached carbon nuclei and were not refined. A final difference Fourier map revealed no missing or misplaced electron density. Atomic coordinates, anisotropic temperature factors, and calculated and observed structure factors are available in the supplementary material. The drawings of the two anions were plotted using the SHELXTL graphic package and are displayed in Figure 2 and 3. A packing diagram was plotted using the program ORTEP[23] and is shown in Figure 4. Atomic coordinates are presented in Table 2. Bond lengths and bond angles are given in Tables 3 and 4. A complete listing of anisotropic parameters and calculated and observed structure factors may be obtained from the author.

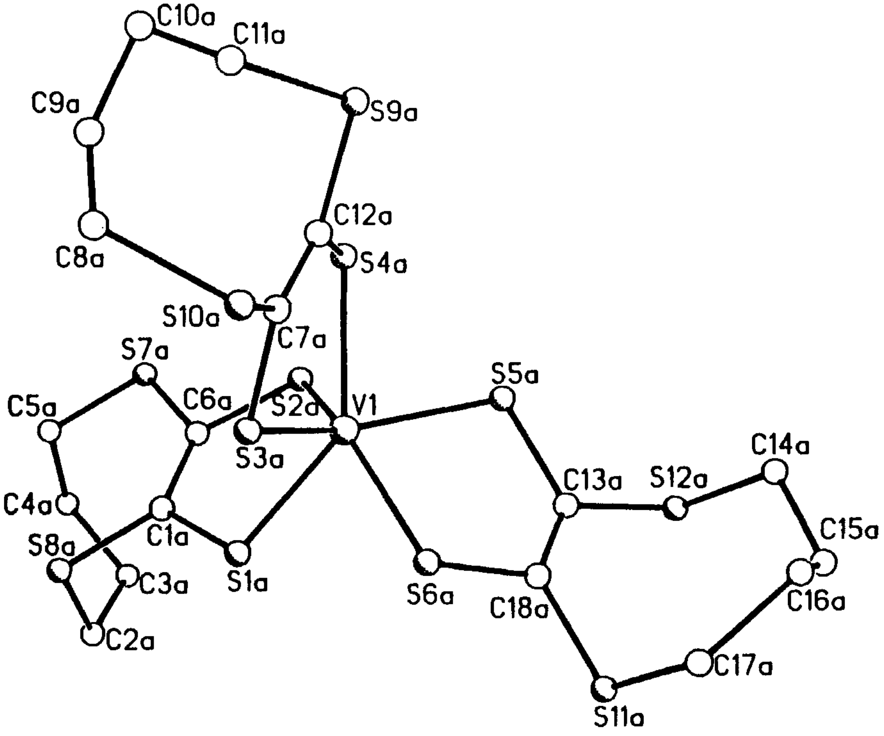


Figure 2 Thermal ellipsoid drawing of $V(BDDT)_3^-$ anion 1.

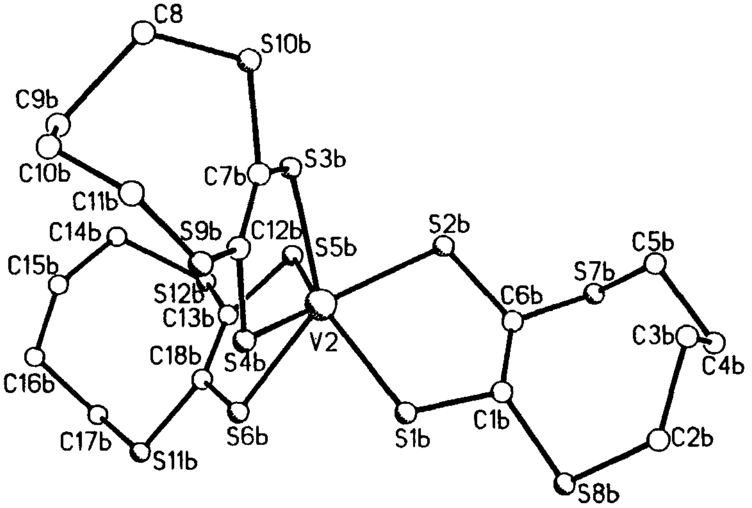


Figure 3 Thermal ellipsoid drawing of $V(BDDT)_3^-$ anion 2.

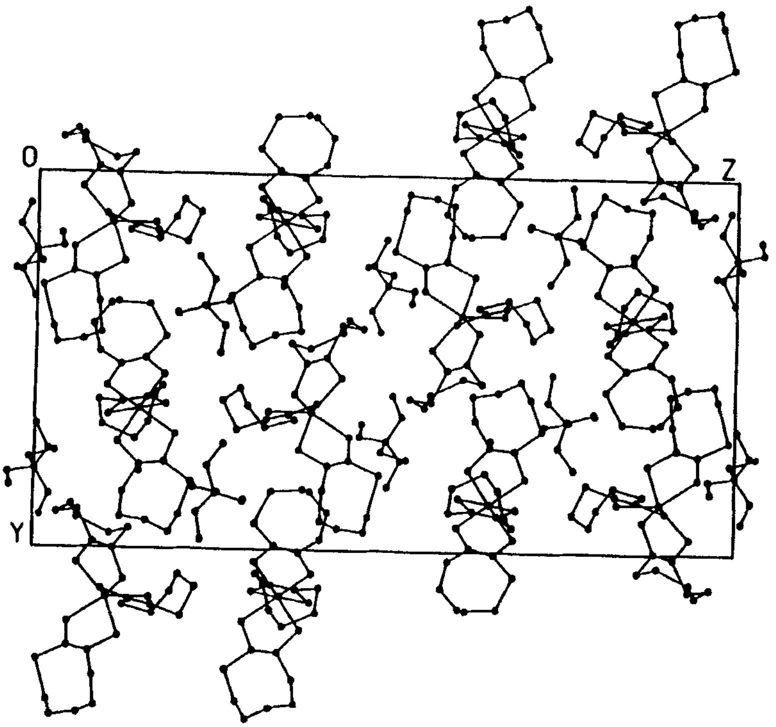


Figure 4 Packing diagram of $[(C_2H_5)_4N][V(BDDT)_3]$.

Table 2 Atomic coordinates (× 10^4) and their standard deviations of the anions in the complex $[(C_2H_5)_4N][V(BDDT)_3]$ (values for $(C_2H_5)_4N^+$ in supplementary material).

	x	*y*	*z*
V	8184(3)	1322(2)	1062(1)
S(1A)	7675(5)	1313(3)	1674(1)
S(2A)	6024(5)	1092(3)	984(1)
S(3A)	9189(7)	2345(3)	1241(2)
S(4A)	7794(6)	1979(4)	521(2)
S(5A)	8403(5)	393(3)	639(2)
S(6A)	10027(5)	847(3)	1310(2)
S(7A)	3376(5)	1529(4)	1308(2)
S(8A)	5650(6)	1805(4)	2125(2)
S(9A)	9082(7)	2997(4)	87(2)
S(10A)	10697(9)	3417(5)	894(2)
S(11A)	11276(7)	-517(4)	1365(2)
S(12A)	9570(7)	-1011(4)	642(2)
C(1A)	6137(22)	1524(12)	1704(5)
C(2A)	4956(23)	1017(14)	2323(5)
C(3A)	3948(22)	694(16)	2079(6)
C(4A)	2800(20)	1162(14)	1970(7)
C(5A)	3045(19)	1741(14)	1727(6)
C(6A)	5416(19)	1382(12)	1390(7)
C(7A)	9466(29)	2766(13)	829(9)
C(8A)	9631(47)	4231(27)	926(13)
C(9)	8136(46)	4215(26)	523(14)
C(9A)	8986(71)	4422(42)	677(22)
C(10)	8200(73)	4049(39)	158(22)
C(10A)	8910(67)	4511(39)	299(20)
C(11)	9537(56)	3813(34)	58(13)
C(11A)	9761(140)	4104(76)	245(38)
C(12A)	8854(25)	2612(12)	525(6)
C(13A)	9497(19)	-151(12)	862(5)
C(14A)	10916(38)	-932(15)	341(8)
C(15)	11965(53)	-424(30)	441(16)
C(15A)	12107(61)	-1156(35)	547(18)
C(16)	12548(44)	-306(25)	728(14)
C(16A)	12475(76)	-809(44)	630(23)
C(17A)	12654(26)	-380(16)	1093(10)
C(18A)	10156(19)	17(12)	1141(6)
V(2)	7572(3)	6269(2)	1488(1)
S(1B)	6949(8)	5340(3)	1842(2)
S(2B)	6545(9)	5659(5)	1022(2)
S(3B)	9036(7)	6426(6)	1041(2)
S(4B)	9349(6)	6131(5)	1870(2)
S(5B)	6552(8)	7160(4)	1180(2)
S(6B)	7033(7)	6941(3)	2002(2)
S(7B)	4484(10)	4739(7)	915(4)
S(8B)	4969(11)	4324(6)	1854(4)
S(9B)	11860(8)	5654(7)	1820(4)
S(10B)	11599(8)	6034(6)	914(3)
S(11B)	6127(7)	8229(4)	2230(2)
S(12B)	5431(6)	8511(4)	1271(2)
C(1B)	5771(21)	4910(13)	1568(10)
C(2B)	5482(52)	3465(22)	1619(13)
C(3B)	5742(51)	3412(30)	1171(14)
C(4B)	4633(62)	3461(33)	1068(18)
C(5)	3641(64)	4231(37)	1029(19)
C(5B)	5308(67)	4013(37)	819(20)
C(6B)	5584(27)	5089(14)	1220(7)
C(7B)	10431(18)	6082(14)	1254(9)
C(8)	12479(52)	6698(30)	961(16)
C(8B)	12575(68)	7146(38)	1097(20)
C(9B)	12651(34)	7078(24)	1424(11)
C(10B)	13461(30)	6633(24)	1615(10)

Table 2 *(Continued)*

	x	*y*	*z*
C(11B)	13042(52)	5930(29)	1709(15)
C(12B)	10571(27)	5956(16)	1600(9)
C(13B)	6207(21)	7778(14)	1489(8)
C(14B)	6656(27)	9162(15)	1238(8)
C(15B)	7359(22)	9267(14)	1600(8)
C(16B)	6704(22)	9566(15)	1924(8)
C(17B)	5667(23)	9093(13)	2069(7)
C(18B)	6441(17)	7698(13)	1842(5)

Table 3 Bond lengths (Å) for the anions in $[(C_2H_5]_4N][V(BDDT)_3]$ (for cation, see supplementary material).

V(1)-S(1A)	2.312(6)	V(1)-S(2A)	2.380(6)
V(1)-S(3A)	2.328(7)	V(1)-S(4A)	2.364(7)
V(1)-S(5A)	2.377(7)	V(1)-S(6A)	2.336(6)
S(1A)-C(1A)	1.717(24)	S(2A)-C(6A)	1.732(24)
S(3A)-C(7A)	1.739(32)	S(4A)-C(12A)	1.671(26)
S(5A)-C(13A)	1.752(22)	S(6A)-C(18A)	1.719(24)
S(7A)-C(5A)	1.792(22)	S(7A)-C(6A)	1.807(21)
S(8A)-C(1A)	1.726(22)	S(8A)-C(2A)	1.849(26)
S(9A)-C(10)	2.255(77)	S(9A)-C(11)	1.649(66)
S(9A)-C(11A)	2.318(144)	S(9A)-C(12A)	1.784(24)
S(10A)-C(7A)	1.834(30)	S(10A)-C(8A)	1.951(53)
S(11A)-C(17A)	1.838(33)	S(11A)-C(18A)	1.762(23)
S(12A)-C(13A)	1.841(24)	S(12A)-C(14A)	1.859(39)
C(1A)-C(6A)	1.382(30)	C(2A)-C(3A)	1.510(34)
C(3A)-C(4A)	1.571(35)	C(4A)-C(5A)	1.453(35)
C(7A)-C(12A)	1.301(39)	C(8A)-C(9A)	1.180(92)
C(9)-C(9A)	1.129(89)	C(9)-C(10)	1.370(93)
C(9)-C(10A)	1.319(90)	C(9A)-C(10A)	1.384(108)
C(9A)-C(11A)	1.907(166)	C(10)-C(10A)	1.270(106)
C(10)-C(11)	1.568(101)	C(10)-C(11A)	1.706(169)
C(10A)-C(11)	1.753(99)	C(10A)-C(11A)	1.228(168)
C(11)-C(11A)	0.906(147)	C(13A)-C(18A)	1.260(29)
C(14A)-C(15)	1.530(67)	C(14A)-C(15A)	1.526(74)
C(14A)-C(16A)	1.965(88)	C(15)-C(15A)	1.467(88)
C(15)-C(16)	1.220(76)	C(15)-C(16A)	1.139(100)
C(16)-C(16A)	1.034(99)	C(16)-C(17A)	1.334(64)
C(16A)-C(17A)	1.879(91)	V(2)-S(1B)	2.318(8)
V(2)-S(2B)	2.309(9)	V(2)-S(3B)	2.331(8)
V(2)-S(4B)	2.338(8)	V(2)-S(5B)	2.305(9)
V(2)-S(6B)	2.365(7)	S(1B)-C(1B)	1.788(28)
S(2B)-C(6B)	1.689(29)	S(3B)-C(7B)	1.793(24)
S(4B)-C(12B)	1.709(32)	S(5B)-C(13B)	1.688(28)
S(6B)-C(18B)	1.686(24)	S(7B)-C(5)	1.408(73)
S(7B)-C(5B)	1.705(73)	S(7B)-C(6B)	1.728(29)
S(8B)-C(1B)	1.782(31)	S(8B)-C(2B)	1.952(44)
S(9B)-C(11B)	1.454(57)	S(9B)-C(12B)	1.683(31)
S(10B)-C(7B)	1.803(29)	S(10B)-C(8)	1.599(58)
S(11B)-C(17B)	1.824(26)	S(11B)-C(18B)	1.784(23)
S(12B)-C(13B)	1.808(27)	S(12B)-C(14B)	1.829(30)
C(1B)-C(6B)	1.320(41)	C(2B)-C(3B)	1.666(70)
C(3B)-C(4B)	1.245(86)	C(3B)-C(5B)	1.772(89)
C(4B)-C(5)	1.831(96)	C(4B)-C(5B)	1.586(98)
C(7B)-C(12B)	1.284(45)	C(8)-C(8B)	0.999(92)
C(8)-C(9B)	1.838(71)	C(8B)-C(9B)	1.195(82)
C(9B)-C(10B)	1.391(56)	C(10B)-C(11B)	1.471(72)
C(13B)-C(18B)	1.309(34)	C(14B)-C(15B)	1.507(41)
C(15B)-C(16B)	1.512(40)	C(16B)-C(17B)	1.551(36)

Table 4 Bond angles (°) for anions of [$(C_2H_5)_4N$][$V(BDDT)_3$] (for cations, see supplementary material).

S(1A)-V(1)-S(2A)	81.1(2)	S(1A)-V(1)-S(3A)	82.1(2)
S(2A)-V(1)-S(3A)	129.4(3)	S(1A)-V(1)-S(4A)	139.8(3)
S(2A)-V(1)-S(4A)	81.8(2)	S(3A)-V(1)-S(4A)	81.1(2)
S(3A)-V(1)-S(5A)	139.4(3)	S(4A)-V(1)-S(5A)	83.2(2)
S(1A)-V(1)-S(6A)	81.8(2)	S(2A)-V(1)-S(6A)	142.1(3)
S(3A)-V(1)-S(6A)	80.9(2)	S(4A)-V(1)-S(6A)	130.6(3)
S(5A)-V(1)-S(6A)	81.4(2)	V(1)-S(1A)-C(1A)	109.0(7)
V(1)-S(2A)-C(6A)	103.9(7)	V(1)-S(3A)-C(7A)	104.3(10)
V(1)-S(4A)-C(12A)	106.5(8)	V(1)-S(5A)-C(13A)	103.4(7)
V(1)-S(6A)-C(18A)	107.8(7)	C(5A)-S(7A)-C(6A)	110.8(10)
C(1A)-S(8A)-C(2A)	103.4(11)	C(10)-S(9A)-C(11)	44.0(30)
C(10)-S(9A)-C(11A)	43.8(43)	C(11)-S(9A)-C(11A)	18.0(42)
C(10)-S(9A)-C(12A)	101.4(22)	C(11)-S(9A)-C(12A)	120.2(24)
C(11A)-S(9A)-C(12A)	102.3(36)	C(7A)-S(10A)-C(8A)	97.5(18)
C(17A)-S(11A)-C(18A)	102.9(13)	C(13A)-S(12A)-C(14A)	103.3(12)
S(1A)-C(1A)-S(8A)	117.3(12)	S(1A)-C(1A)-C(6A)	114.6(16)
S(8A)-C(1A)-C(6A)	127.8(18)	S(8A)-C(2A)-C(3A)	113.7(16)
C(2A)-C(3A)-C(4A)	117.1(23)	C(3A)-C(4A)-C(5A)	115.6(19)
S(7A)-C(5A)-C(4A)	116.0(19)	S(2A)-C(6A)-S(7A)	108.1(12)
S(2A)-C(6A)-C(1A)	123.2(16)	S(7A)-C(6A)-C(1A)	128.5(18)
S(3A)-C(7A)-S(10A)	110.9(17)	S(3A)-C(7A)-C(12A)	121.9(22)
S(10A)-C(7A)-S(12A)	127.2(24)	S(10A)-C(8A)-C(9A)	122.5(52)
C(9A)-C(9)-C(10)	119.5(67)	C(9A)-C(9)-C(10A)	68.3(59)
C(10)-C(9)-C(10A)	56.3(50)	C(8A)-C(9A)-C(9)	135.5(82)
C(8A)-C(9A)-C(10A)	144.2(76)	C(9)-C(9A)-C(10A)	62.4(55)
C(8A)-C(9A)-C(11A)	105.5(70)	C(9)-C(9A)-C(11)	81.5(68)
C(10A)-C(9A)-C(11A)	40.0(57)	C(9A)-C(10)-C(9)	110.9(48)
C(9A)-C(10)-C(10A)	115.1(58)	C(9)-C(10)-C(10A)	59.8(52)
C(9A)-C(10)-C(11)	47.0(32)	C(9)-C(10)-C(11)	111.8(59)
C(10A)-C(10)-C(11)	75.5(57)	S(9A)-C(10)-C(11A)	70.1(56)
C(9)-C(10)-C(11A)	83.7(66)	C(10A)-C(10)-C(11A)	45.9(66)
C(11)-C(10)-C(11A)	31.8(54)	C(9)-C(10A)-C(9A)	49.3(46)
C(9)-C(10A)-C(10)	63.9(54)	C(9A)-C(10A)-C(10)	109.1(71)
C(9)-C(10A)-C(11)	104.0(55)	C(9A)-C(10A)-C(11)	113.1(61)
C(10)-C(10A)-C(11)	60.0(50)	C(9)-C(10A)-C(11A)	108.5(90)
C(9A)-C(10A)-C(11A)	93.6(85)	C(10)-C(10A)-C(11A)	86.1(90)
C(11)-C(10A)-C(11 A)	29.2(68)	S(9A)-C(11)-C(10)	89.0(42)
S(9A)-C(11)-C(10A)	125.2(46)	C(10)-C(11)-C(10A)	44.5(41)
S(9A)-C(11)-C(11A)	127.8(60)	C(10)-C(11)-C(11A)	82.6(60)
C(10A)-C(11)-C(11A)	41.4(60)	S(9A)-C(11A)-C(9A)	110.8(70)
S(9A)-C(11A)-C(10)	66.1(54)	C(9A)-C(11A)-C(10)	73.3(70)
S(9A)-C(11A)-C(10A)	113.2(54)	C(9A)-C(11A)-C(10A)	46.4(64)
C(10)-C(11A)-C(10A)	48.0(60)	S(9A)-C(11A)-C(11)	34.2(85)
C(9A)-C(11A)-C(11)	134.6(80)	C(10)-C(11A)-C(11)	65.7(99)
C(10A)-C(11A)-C(11A)	109.5(99)	S(4A)-C(12A)-C(9A)	114.5(13)
S(4A)-C(12A)-C(7A)	119.8(20)	S(9A)-C(12A)-C(7A)	125.6(22)
S(5A)-C(13A)-C(12A)	112.1(11)	S(5A)-C(13A)-C(18A)	124.7(19)
S(12A)-C(13A)-C(18A)	123.2(18)	S(12A)-C(14A)-C(15)	120.0(29)
S(12A)-C(14A)-C(15A)	110.5(30)	C(15)-C(14A)-C(15A)	57.4(36)
S(12A)-C(14A)-C(16A)	111.6(29)	C(15)-C(14A)-C(16A)	35.3(34)
C(15A)-C(14A)-C(16A)	23.4(36)	C(14A)-C(15)-C(15A)	61.2(36)
C(14A)-C(15)-C(16)	132.4(51)	C(15A)-C(15)-C(16)	84.7(47)
C(14A)-C(15)-C(16A)	93.7(57)	C(15A)-C(15)-C(16A)	34.2(50)
C(16)-C(15)-C(16A)	51.8(20)	C(14A)-C(15A)-C(15)	61.5(35)
C(14A)-C(15A)-C(16)	97.4(39)	C(15)-C(15A)-C(16)	41.9(32)
C(14A)-C(15A)-C(16A)	109.7(83)	C(15)-C(15A)-C(16A)	50.7(71)

Table 4 *(Continued)*

C(16)-C(15A)-C(16A)	13.7(69)	C(15)-C(16)-C(15A)	53.4(38)
C(15)-C(16)-C(16A)	60.0(57)	C(15A)-C(16)-C(16A)	10.9(51)
C(15)-C(16)-C(17A)	148.6(50)	C(15A)-C(16)-C(17A)	106.0(38)
C(16A)-C(16)-C(17A)	104.3(61)	C(14A)-C(16A)-C(15)	51.0(44)
C(14A)-C(16A)-C(15A)	47.0(63)	C(15)-C(16A)-C(15A)	95.2(88)
C(14A)-C(16A)-C(16)	110.5(64)	C(15)-C(16A)-C(16)	68.1(62)
C(15A)-C(16A)-C(16)	155.5(80)	C(14A)-C(16A)-C(17A)	126.1(47)
C(15)-C(16A)-C(17A)	106.6(63)	C(15A)-C(16A)-C(17A)	135.4(89)
C(16)-C(16A)-C(17A)	43.5(44)	S(11A)-C(17A)-C(16)	120.7(28)
S(11A)-C(17A)-C(16A)	111.3(29)	C(16)-C(17A)-C(16A)	32.2(34)
S(6A)-C(18A)-S(11A)	116.2(12)	S(6A)-C(18A)-C(13A)	118.3(18)
S(11A)-C(18A)-S(13A)	125.4(19)	S(1B)-V(2)-S(2B)	82.7(3)
S(1B)-V(2)-S(3B)	134.9(4)	S(2B)-V(2)-S(3B)	82.7(3)
S(1B)-V(2)-S(4B)	80.4(3)	S(2B)-V(2)-S(4B)	137.5(4)
S(3B)-V(2)-S(4B)	82.3(3)	S(1B)-V(2)-S(5B)	134.4(3)
S(2B)-V(2)-S(4B)	79.3(3)	S(3B)-V(2)-S(5B)	83.6(3)
S(4B)-V(2)-S(5B)	137.6(3)	S(1B)-V(2)-S(6B)	84.1(3)
S(2B)-V(2)-S(6B)	137.1(3)	S(3B)-V(2)-S(6B)	132.5(4)
S(4B)-V(2)-S(6B)	79.3(3)	S(5B)-V(2)-S(6B)	81.4(3)
V(2)-S(1B)-C(1B)	105.2(10)	V(2)-S(2B)-C(6B)	107.7(9)
V(2)-S(3B)-C(7B)	103.4(10)	V(2)-S(4B)-C(12B)	108.4(11)
V(2)-S(5B)-C(7B)	108.3(10)	V(2)-S(6B)-C(18B)	107.5(7)
C(5)-S(7B)-C(5B)	80.7(38)	C(5)-S(7B)-C(6B)	121.2(31)
C(5B)-S(7B)-C(6B)	95.8(26)	C(1B)-S(8B)-C(2B)	97.3(18)
C(11B)-S(9B)-C(12B)	117.4(26)	C(7B)-S(10B)-C(8)	108.3(24)
C(17B)-S(11B)-C(18B)	109.1(11)	C(13B)-S(12B)-C(14B)	103.8(12)
S(1B)-C(1B)-S(8B)	108.5(18)	S(1B)-C(1B)-C(6B)	119.5(21)
S(8B)-C(1B)-C(6B)	131.8(21)	S(8B)-C(2B)-C(3B)	122.8(31)
C(2B)-C(3B)-C(4B)	95.4(48)	C(2B)-C(3B)-C(5B)	128.1(43)
C(4B)-C(3B)-C(5B)	60.5(18)	C(3B)-C(4B)-C(5)	129.6(67)
C(3B)-C(4B)-C(5B)	76.4(49)	C(5)-C(4B)-C(5B)	72.4(43)
S(7B)-C(5)-C(4B)	101.6(44)	S(7B)-C(5B)-C(3B)	120.8(45)
S(7B)-C(5B)-C(4B)	100.1(46)	C(3B)-C(5B)-C(4B)	43.1(35)
S(2B)-C(6B)-S(7B)	113.5(15)	S(2B)-C(6B)-C(1B)	120.2(21)
S(7B)-C(6B)-C(1B)	126.1(22)	S(3B)-C(7B)-S(10B)	108.7(17)
S(3B)-C(7B)-C(12B)	123.9(21)	S(10B)-C(7B)-C(12B)	127.1(20)
S(10B)-C(8)-C(8B)	142.5(21)	S(10B)-C(8)-C(9B)	117.0(36)
C(8B)-C(8)-C(9B)	36.6(50)	C(8)-C(8B)-C(9B)	113.6(77)
C(8)-C(9B)-C(8B)	29.9(41)	C(8)-C(9B)-C(10B)	104.7(35)
C(8B)-C(9B)-C(19B)	125.7(50)	C(9B)-C(10B)-C(11B)	119.2(36)
S(9B)-C(11B)-C(10B)	133.0(43)	S(4B)-C(12B)-S(9B)	116.0(19)
S(4B)-C(12B)-C(7B)	117.4(22)	S(9B)-C(12B)-C(7B)	126.6(24)
S(5B)-C(13B)-S(12B)	111.6(16)	S(5B)-C(13B)-C(18B)	122.1(21)
S(12B)-C(13B)-C(18B)	126.2(21)	S(12B)-C(14B)-C(15B)	112.1(20)
C(14B)-C(15B)-C(16B)	119.8(22)	C(15B)-C(16B)-C(17B)	114.1(22)
S(11B)-C(17B)-C(16B)	116.9(17)	S(6B)-C(18B)-S(11B)	107.7(11)
S(6B)-C(18B)-C(13B)	119.8(19)	S(11B)-C(18B)-C(13B)	132.2(20)

RESULTS AND DISCUSSION

The unit cell for the complex $[(C_2H_5)_4N][V(S_4C_6H_8)_3]$ contains eight cations and eight anions. The six sulfurs from the three dithiolenes are coordinated to the vanadium in a trigonal prismatic (TP) array, with an average V–S distance of 2.339(9) Å. Table 5 compares the distances and angles of this vanadium structure

Table 5 Comparison of distances (Å) and angles (°) of vanadium dithiolenes.

		Selected distances of vanadium dithiolenes				
Complex	M–S	S–S (intra)	S–S (inter)	S–C	C=C	Ref.
V(BDDT)$_3$-	2.339 (9)	3.066	2.926	1.788	1.313	This work
V(DDDT)$_3$-	2.340 (4)	3.055	3.074	1.708 (6)	1.378 (21)	24
V(sdt)$_3^{-a}$	2.337 (6)	3.061 (12)	3.07 (13)	1.69 (1)	1.41 (2)	26
V(mnt)$_3^{2-b}$	2.36 (1)	3.14 (4)	3.20 (23)	1.72 (3)	1.33 (3)	26
V(dmt)$_3^{2-c}$	2.375 (3)	3.196 (3)	3.421 (3)	1.723 (8)	1.375 (18)	26
V(S$_2$C$_2$Ph$_2$)$_3$	2.338 (4)	3.058 (6)	3.064	1.69 (1)	1.41 (1)	4

		Selected angles of vanadium dithiolenes	
Complex	S–M–S (bite)	S–M–S (trans)	Coordination
V(BDDT)$_3^-$	81.9 (3)	135.5 (4)	TP
V(DDDT)$_3^-$	81.5 (1)	135.5 (2)	TP
V(sdt)$_3^{-a}$	81.7 (6)	136	TP
V(mnt)$_3^{2-b}$		158.6	Dist. Oh
V(dmt)$_3^{2-e}$	84.6 (1)	164.3 (1)	Dist. Oh

[a] sdt = stilbene dithiolene. [b] mnt = malenitriledithiolate [c] dmt = 1-thioxo-2,3-dithiole-4,5-dithiolate V(S$_2$C$_2$Ph$_2$)$_3$ = tris(cis-1,2-diphenylethene-1,2-dithiolato) vanadium.

with some selected vanadium dithiolenes reported to date. The coordination geometry of the VS$_6$ core of several other dithiolene complexes is also given for comparison. The V–S distances for the three trigonal prismatic structures are quite similar but are distinctly different from those of the two distorted octahedral complexes.

The cyclic voltammogram of V(BDDT)$_3^-$ displays two reversible waves (monoanion to dianion and dianion to trianion) and an irreversible wave in which the monoanion is likely oxidized to the neutral molecule (Figure 5). This is different from that observed for V(DDDT)$_3^-$, where the neutral molecule was apparently stable.[24] These cyclic coltamograms (Table 6) are not 'ideal' but are quite reproducible. While we have identified the oxidation and reduction waves where possible, there also seems to be more complex chemistry which occurs. We know, for example, that the oxidation of Ni(DDDT)$_2^0$ yields not a positive ion but a dimer, [Ni(DDDT)$_2$]$_2^+$, as a solid at the electrode surface.

Optical and infrared absorption spectra were obtained for the complex and some bands are presented in Table 7. The infrared spectrum contains all the common features of 1,2-dithiolene complexes.[5] Tentative assignments for some of the characteristic bands in the infrared spectrum have been made based on their relative intensities and energies. The C=C vibrational frequency near 1480 cm^{-1} is at higher frequency than observed for the DDDT complex of vanadium at 1406 and 1445 cm^{-1}.

In an attempt to more fully understand the electronic structure of these dithiolenes, we undertook an extended Hückel molecular orbital calculation. The atomic orbitals employed in the calculations are as follows: Hii, taken to be the negative of valence orbital ionization potentials, and the exponent ς_i of the Slater-type atomic orbital χ_i are, respectively, -20.0 and 2.122 for S 3s, -13.3 and 1.827 for S 3p, -21.4 and 1.625 for C 2s, -11.4 and 1.625 for C 2p, -13.6 and 1.3 for H 1s, -8.81 and 1.30 for V 4s, and -5.52 and 1.30 for V 4p. The *d* orbitals of V are represented by a linear combination of two Slater-type orbitals of

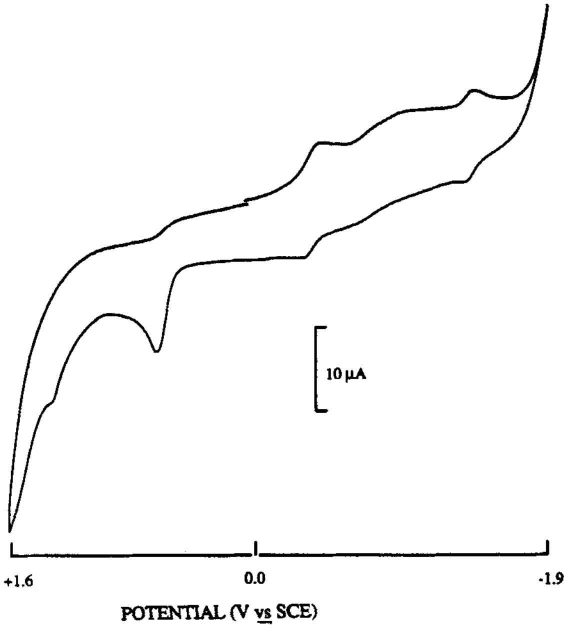


Figure 5 Cyclic voltammogram of $V(BDDT)_3^-$.

exponents ς_i and $\overline{\varsigma_i}$ with weighting factor c_i and $\overline{c_i}$, respectively. The Hii (eV), ς_i, c_i, $\overline{\varsigma_i}$, and $\overline{c_i}$ values are, respectively, −11.00, 4.75, 0.47551, 1.70 and 0.70521 for V 3d. The off-diagonal Hamiltonian matrix elements H_{ij} were obtained by a modified Wolfsberg-Helmholz formula.[25]

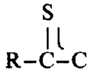
The coefficients for the metal *d* orbital in both the HOMO and LUMO which result from the EH-MO calculation are shown in Table 8. The energy gaps between the HOMO and LUMO are small for both $V(BDDT)_3^-$ and $V(DDDT)_3^-$ (0.3 eV and 0.6 eV, respectively). The HOMO for $V(BDDT)_3^-$ has only a small metal character and immediately below the HOMO level, none of the MO's show any significant metal character. Thus, even a reassignment of the HOMO from one of these later orbitals would still result in a HOMO of essentially ligand character. In contrast however, the HOMO of $V(DDDT)_3^-$ and the next lowest energy level both are MO's having larger metal AO coefficients. Since these orbitals, *which are still quite*

Table 6 Cyclic voltammetry parameters[a] for selected $[VL_3]^{n-}$ dithiolene complexes.

	$E_{1/2}$, V			
Compound	n:2⇌3	n:1⇌2	n:0⇌1	ref.
$[V(BDDT)_3]^-$	- 1.39	- 0.35	+ 0.65[b]	This work
$[V(DDDT)_3]^-$	- 1.44	- 0.51	+ 0.39	24
$[V(mnt)_3]^{2-}$	- 0.49	+ 0.66		26
$[V(sdt)_3]^-$		- 0.71	+ 0.30	26
$[V(tfd)_3]^{-c}$		+ 0.47		26

[a] *vs* SCE. [b] irreversible oxidation. [c] tfd = bis(trifluoromethyl)ethene-1,2-dithiolate.

Table 7 Frequencies (cm^{-1}) and tentative assignments of the bands observed in the infrared and optical spectra of the complex $[(C_2H_5)_4N][V(BDDT)_3]$.

Frequency	Assignments
1480(s)	C=C
1285(vs)	C=S
870(m)	 $R-\overset{\overset{S}{\Vert}}{C}-C$
840(m)	
450(m)	M−S
395(m)	

UV-VIS absorption maxima in DMF

ν (cm^{-1})	ε ($M^{-1}cm^{-1}$)
36200	4.81×10^4
29400	1.21×10^4
24800	5.30×10^3
16600	1.23×10^4

covalent, are also filled, the EH−MO calculation suggests that the vanadium in $V(DDDT)_3^-$ is in a somewhat *lower* oxidation state. From the perspective of the ligands, this would suggest that the DDDT ligands are partially oxidized in this latter complex. This is supported by the results of the single crystal X-ray structure analysis (Table 5). A partially oxidized ligand would have a 'ketone' resonance contribution with shorter C−S bonds and a longer C=C bond as noted above.

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[24] for trigonal prismatic dithiolenes is preferred over that of Schrauzer and Mayweg[26] because of better correlation with optical and ESR spectra.[5,27] This scheme is reproduced in Figure 6. The levels of interest are 4e′, a M−L bonding orbital with *d* metal and π_v

Table 8 MO calculation data for vanadium dithiolenes (metal *d* orbital coefficients).

$V(BDDT)_3^-$	HOMO (− 11.089 eV)	LUMO (− 10.823 eV)
$d_{x^2-y^2}$	− 0.0781	− 0.0639
d_{z2}	− 0.3321	− 0.1655
d_{xy}	− 0.0616	− 0.1982
d_{xz}	− 0.0210	0.0247
d_{yz}	− 0.0612	0.0893

$V(DDDT)_3^-$	HOMO (− 9.909 eV)	LUMO (− 9.365 eV)
$d_{x^2-y^2}$	− 0.1063	− 0.0613
d_{z^2}	− 0.3162	0.0555
d_{xy}	− 0.5727	0.0798
d_{xz}	0.0091	− 0.1997
d_{yz}	0.0731	− 0.1591

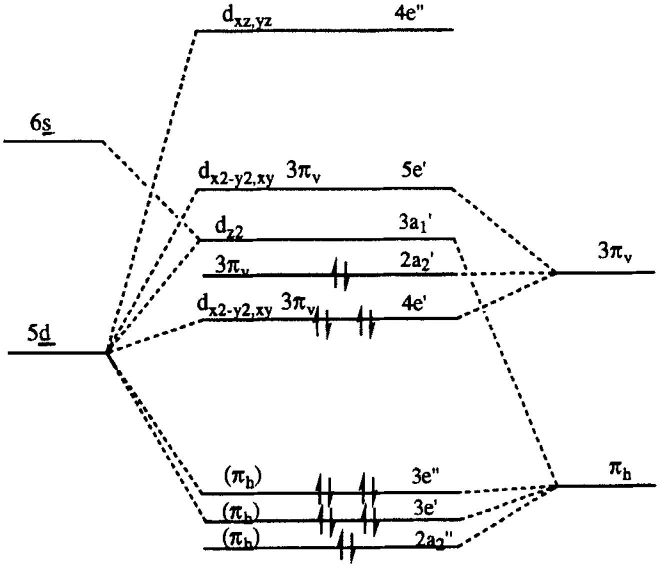


Figure 6 MO diagram for tris(dithiolenes)[24].

(vertical) ligand character, $2a_2'$, a nonbonding orbital localized on the ligand, $3a_1'$, a M–L antibonding orbital with *d* metal and π_h (horizontal) ligand character, and 5e', an antibonding orbital of *d* metal and π_v ligand character. The electron configuration shown is that of $V(DDDT)_3^-$.

It has been shown by Gray[24] however, that the $3a_1'$ and $2a_2'$ levels invert as the charge on a vanadium dithiolene changes from −2 to 0. This inversion results from increased stabilization of the meal orbitals over the ligand orbitals as the positive charge on the complex increases. If this inversion were to occur as the charge changes from −2 to −1, then the HOMO of the monoanion would be $3a_1'$. Since the 4e' level is primarily ligand based, the vanadium in $V(DDDT)_3^-$ would have small *d* electron density. In this case, the ligands must be partially oxidized and would be intermediate between a dithiolate and dithiodiketone structure. As noted above, a comparison of the S–C distances and C=C distances in Table 5 support this conclusion when comparing $V(DDDT)_3^-$ and $V(BDDT)_3^-$.

Referring to Table 5, we can also see that the *structural* parameters for $V(DDDT)_3^-$ and $V(S_2C_2Ph_2)_3$ are very similar. Since an inversion of the electronic levels has been established by Gray for the neutral complex, these data support a similar HOMO for $V(DDDT)_3^-$. Also, based on the EH–MO calculations discussed above, the $V(BDDT)_3^-$ does not show significant metal character in the HOMO, and the 4e' level is considered to be predominantly ligand in character. Using the energy level diagram in Figure 6, the complex has a ligand localized HOMO like $2a_2'$.

Supplementary material available from the authors. (a) Anisotropic thermal parameters. (b) H-atom coordinates and isotropic thermal parameters. (c) Structure factor tables. (58 pages). (d) Atomic Positions, bond lengths, and bond angles for $(C_2H_5)_4N^+$ cation.

Acknowledgement

The authors wish to thank Dr. M.-H. Whangbo, Dr. Anton Schreiner, and Dr. Dennis Wertz for help and discussions concerning the MO calculations and their interpretations.

References

1. R.B. King, *Inorg. Chem.* **2**, 641 (1963).
2. A.E. Smith, G.N. Schrauzer, V.P. Mayweg and W. Heinrich, *J. Am. Chem. Soc.* **87**, 5798 (1965).
3. R. Eisenberg and J.A. Iber, Inorg. Chem. **5**, 411 (1966).
4. R. Eisenberg and H.B. Gray. *Inorg. Chem.* **6**, 1844 (1967).
5. J.A. McCleverty, *Prog. Inorg. Chem.* **10**, 49 (1968).
6. G.N. Schrauzer, *Transition Met. Chem.* **4**, 299 (1968).
7. R. Eisenberg, *Prog. Inorg. Chem.* **12**, 295 (1970).
8. R.P. Burns and C.A. McAuliff, *Adv. Inorg. Chem. Radiochem.* **22**, 303 (1979).
9. C. Mahadevan, *J. Crystallogr. Spectrosc. Res.* **16**, 347 (1986).
10. C.T. Vance, R.D. Bereman, J. Bordner, W. Hatfield and J.H. Helms, *Inorg. Chem.* **24**, 2905 (1985).
11. C.T. Vance and R.D. Bereman, *Inorg. Chim. Acta* **149**, 229 (1988).
12. J. Schultz, H.H. Wang, L.C. Soderholm, T.L. Sifter, J.M. Williams, K. Bechgaard, and M.-H. Whangbo, *Inorg. Chem.* **26**, 3757 (1987).
13. J.H. Welch, R.D. Bereman and P. Singh, *Inorg. Chem.* **27**, 2862 (1988).
14. G.N. Schrauzer, *Acc. Chem. Res.* **2**, 72 (1969).
15. H.B. Gray, R. Eisenberg and E.I. Stiefel, *Adv. Chem. Ser.* **42**, 641 (1967).
16. E.I. Stiefel, Z. Dori and H.B. Gray, *J. Am. Chem. Soc.* **89**, 3353 (1967).
17. R. Olk, W. Dietzsch, R. Kirmse, J. Stach, E. Hoyer and L. Golic, *Inorg. Chim. Acta* **128**, 251 (1987).
18. (a) C.T. Vance and R.D. Bereman, *Inorg. Chim. Acta* **149**, 229 (1988). (b) C.T. Vance, J.H. Welch and R.D. Bereman, *Inorg. Chim. Acta* **164**, 191 (1989). (c) R.D. Bereman, and H. Lu, *Inorg. Chim. Acta* **204**, 53 (1993).
19. R. Hoffmann, *J. Chem. Phys.* **13**, 1397 (1963).
20. R.E.D. Clarke, *Analyst* **60**, 242 (1936).
21. *International Table for X-ray Crystallography* (Kynoch: Birmingham, England; Vol. IV, 1974) pp 71–102.
22. G.M. Sheldrick, 'SHELXTL' (X-Ray Instruments Group, Nicolet Instrument Corp.: Madison, WI 53711, 1985).
23. C.K. Johnson, *ORTEP-II*: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations ORNL-5L38 (National Technical Information Service: Springfield, VA 1976).
24. E.I. Stiefel, R. Eisenberg, R. Rosenberg and H.B. Gray, *J. Am. Chem. Soc.* **88**, 2956 (1966).
25. J.H. Ammeter, H-B., Bürgi, J.C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.* **100**, 3686 (1978).
26. G.N. Schrauzer and V.P. Mayweg, *J. Am. Chem. Soc.* **88**, 3235 (1966).
27. E.J. Wharton and J.A. McCleverty, *J. Chem. Soc. A* 2258 (1969) and references therein.