

LMCT state of $[\text{MoS}_4]^{2-}$ and $[\text{WS}_4]^{2-}$ is not much distorted with regard to the ground state while $[\text{MnO}_4]^-$, which photolyses efficiently upon long-wavelength irradiation,²⁷ is distorted much more strongly.^{25,26} Unfortunately, the excited-state distortions of $[\text{VS}_4]^{3-}$ and $[\text{ReS}_4]^-$ are not known to establish a correlation between the extent of excited state distortion and the efficiency of the photoreaction.

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Registry No. $[\text{MoS}_4]^{2-}$, 16330-92-0; $[\text{WS}_4]^{2-}$, 14916-78-0; $[\text{VS}_4]^{3-}$, 14791-51-6; $[\text{ReS}_4]^-$, 16829-47-3; $[\text{MoO}_2\text{S}_2]^{2-}$, 16608-22-3; $[\text{WO}_2\text{S}_2]^{2-}$, 16450-49-0; $[\text{VO}_2\text{S}_2]^{3-}$, 26815-91-8; $[\text{ReO}_2\text{S}_2]^-$, 112113-55-0; O_2 , 7782-44-7; S_2 , 23550-45-0; S_8 , 10544-50-0.

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Metal/Sulfide/Thiolate Chemistry for an Early 3d Transition Metal: Variation of Product Identity as a Function of V:S Reaction Ratio and Structure and Redox Properties of Discrete V/S/edt Complexes

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A systematic investigation of the $\text{VCl}_3/\text{elemental S}/\text{Na}_2\text{edt}$ reaction system in MeCN is described. Particular emphasis has been placed on determining the influence of the S:V ratio (n) on the identity of the reaction product(s). Values of n in the 0–2.5 range have been employed. In some cases, the influence of the $\text{edt}^{2-}:\text{V}$ ratio on reaction product(s) has also been investigated. These combined variations have led to the synthesis of five discrete complexes, the structures of two of which are described. The $n = 0$ reaction ratio leads to high-yield preparation of $(\text{PPh}_4)_2[\text{V}_2(\text{edt})_4]$ (**1**). The $n = 0.5$ reaction ratio yields a mixture of products, being composed of an approximately 3:1 ratio of $(\text{NEt}_4)_2[\text{V}_2(\text{edt})_4]$ and $(\text{NEt}_4)_3[\text{V}_3\text{S}_4(\text{edt})_3]$ (**2**). Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with the following unit cell dimensions at -154°C : $a = 14.168$ (5) Å, $b = 18.446$ (7) Å, $c = 19.803$ (8) Å, $\beta = 104.91$ (2)°, and $Z = 4$. A total of 3806 unique reflections with $F > 2.33\sigma(F)$ were employed, and the structure solution was refined to values of conventional indices R and R_w of 8.39 and 8.59%, respectively. The structure of the anion of **2** consists of a V_3 triangle with one central capping $\mu_3\text{-S}$ atom and a $\mu\text{-S}$ atom bridging each edge. A terminal edt completes five-coordination at each metal. The V_3S_4 core can be described as a "partial cube" and is isostructural with the more common Mo_3S_4 cores in Mo/S chemistry. Charge considerations necessitate a mixed-valence trivanadium(III,2IV) description, but on the basis of inspection of structural parameters, there is no justification for a trapped-valence assignment, and the anion is best described as electronically delocalized with an average metal oxidation state of $+3^{2/3}$. The $n = 1$ reaction ratio yields $(\text{NEt}_4)\text{Na}[\text{VS}(\text{edt})_2]$ (**3**), the structure of which had been determined in previous work and contains the multiply bonded VS^{2+} unit. The $n = 1.5$ reaction ratio gave differing products depending on the $\text{edt}^{2-}:\text{V}$ ratio employed. When $\text{edt}^{2-}:\text{V} = 3:1$, high yields of **3** were obtained, whereas an $\text{edt}^{2-}:\text{V} = 2:1$ ratio yielded a preparative route to pure **2**. This difference in behavior is attributed to the strongly chelating nature of the edt^{2-} ligand favoring complex **3** when sufficient edt^{2-} is available and preventing aggregation by further incorporation of available S^{2-} . The $n = 2$ ratio also yielded differing products, depending on the $\text{edt}^{2-}:\text{V}$ ratio. When this ratio was 5:1, the product again was **3**. When this ratio was 2.5:1, a mixture of highly crystalline $(\text{NEt}_4)_2\text{Na}[\text{V}_2\text{OS}_4(\text{edt})]$ (**4**) and microcrystalline $(\text{NEt}_4)_2\text{Na}[\text{V}_2\text{S}_5(\text{edt})]$ (**5**) was obtained; the two materials have been satisfactorily separated manually. Complex **4** crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell dimensions at -155°C : $a = 12.955$ (6) Å, $b = 15.963$ (8) Å, $c = 15.338$ (8) Å, $\beta = 109.83$ (2)°, and $Z = 4$. A total of 3112 unique reflections with $F > 3.00\sigma(F)$ were employed, and the structure solution was refined to values of conventional indices R and R_w of 4.34 and 4.37%, respectively. The anion of **4** consists of a five-coordinate vanadium(IV) atom bridged by two $\mu\text{-S}^{2-}$ species to a four-coordinate vanadium(V) atom. The former additionally contains terminal edt^{2-} and O^{2-} groups, while the latter contains two terminal S^{2-} groups. Complex **5** is assigned the same structure but with O^{2-} replaced by S^{2-} . The $n = 2.5$ reaction ratio was found to yield only complex **5**. The cyclic voltammetric properties of these complexes are also described, and the isolated oxidation levels are shown to be members of multicomponent electron-transfer series, with the exception of **3**, which shows no reversible behavior.

Introduction

It is becoming increasingly apparent that the chemistry of vanadium bound to sulfur is of great relevance and/or importance to a wide variety of chemical, industrial, and biological systems. For example, the polymeric group 5 sulfides have exhibited interesting magnetic and electrical properties, and substances such as Li_xVS_2 (and the group 4 sulfide Li_xTiS_2) have been attracting the attention of industrial researchers seeking novel conducting materials for use as electrodes in solid-state batteries.¹ In addition, the large amounts of vanadium impurities in the heavier crude oils result in conversion of the former to insoluble vanadium sulfide deposits, which help to poison the Mo/Co catalyst during hydrodesulfurization (HDS). This has stimulated interest in both the identity of the crude oil impurities and the mechanism of their subsequent conversion to vanadium sulfide.² Finally, the recent identification of a vanadium nitrogenase,³ its subsequent study by the EXAFS technique,⁴ and comparison with the better understood Mo nitrogenase suggest that the vanadium is located in

a complete or partial environment of sulfur.

The combined developments described above have suggested to us that the time had come for a better understanding of the fundamental chemistry and properties of discrete complexes containing vanadium bound to sulfide and/or sulfur-based ligands such as thiolate (RS^-). This belief represents the primary stimulus for the work described herein. In addition, such studies with a 3d metal would provide illuminating comparisons and contrasts with 4d Mo/S and 5d W/S chemistry, both of which have already been extensively developed.⁵

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The area of V/S chemistry is currently poorly explored, except primarily for the work of Rauchfuss and co-workers, who have synthesized a variety of V/S organometallics such as $Cp_2V_2S_5$ and related species.⁶ Our own contribution has avoided the use of organometallic-type ligation.

The most convenient source of vanadium for this work is VCl_3 , and our synthetic strategy has been to react this material with sodium thiolate in the presence of various amounts of elemental sulfur. For consistency, we have used ethane-1,2-dithiol (H_2edt) throughout, a chelating dithiol known to be a versatile ligand capable of supporting the formation of nonpolymeric complexes with a variety of transition metals.⁷ The presence of elemental sulfur allows "oxidative addition" reactions to take place to potentially yield products anywhere in the vanadium(III-V) oxidation-state range. Since there is no basis on which to predict the nature of products in this unexplored area of V/S/SR chemistry, we have systematically varied both the S:V (n) and, in some cases, the $edt^{2-}:V$ ratios. As we shall describe, we have found both these parameters to have a great effect on the clarity of obtained products. This paper will concentrate on the syntheses, structures, and redox properties of V/S/ edt species; detailed variable-temperature magnetic susceptibility studies will be presented in a future report.^{8b}

Experimental Section

Compound Preparation. All manipulations were performed with use of standard inert-atmosphere techniques and a purified dinitrogen atmosphere. Acetonitrile was purified by distillation from CaH_2 , and Et_2O and THF were distilled from Na/benzophenone. Solid Na_2edt was prepared by the reaction of ethane-1,2-dithiol with sodium metal in THF; the white precipitate was collected by filtration, washed well with THF, and dried in vacuo. VCl_3 was used as received (Aldrich).

A. $n = 0$. (PPh_4) $_2[V_2(edt)_4]$ (**1**). A solution of Na_2edt (20 mmol) in $EtOH$ (100 mL) was prepared from the thiol (1.68 mL, 20 mmol) and Na metal (0.92 g, 40 mmol). To this stirred solution was added solid VCl_3 (1.57 g, 10 mmol), which rapidly dissolved to give an intense red coloration and some fine off-white solid (NaCl). Stirring was continued for a further 5 min, and then PPh_4Br (4.19 g, 20 mmol) was added, followed by Et_2O (40 mL). The flask was left undisturbed at ambient temperature for 1 h and the dark red microcrystalline precipitate collected by filtration, washed with Et_2O , and dried in vacuo. The crude product was extracted into DMF/ $MeCN$ (ca. 1:1), the solution filtered, and Et_2O added to the filtrate to initiate crystallization. After overnight storage in a freezer, the resulting black prisms were collected by filtration, washed with Et_2O , and dried in vacuo. Overall yields were typically ca. 60%. Anal. Calcd for $C_{56}H_{56}P_2S_8V_2$: C, 58.52; H, 4.91; S, 22.31; V, 8.86. Found: C, 58.50; H, 4.86; S, 22.17; V, 9.20. The NMe_4^+ and NEt_4^+ salts can be prepared in an analogous manner and recrystallized from DMF/ Et_2O and $MeCN/Et_2O$, respectively. The 1H NMR spectrum of **1** shows the expected resonances due to the cations and two multiplets centered at δ values of ca. 1.90 and 1.77 in CD_3CN . Electronic spectrum (DMF; λ_{max} , nm (ϵ_m/V_2 , $L mol^{-1} cm^{-1}$): 320 sh (13 890), 366 (14 370), 500 sh (544), 543 (627), 616 (401), 884 (314), 1246 (382).

B. $n = 0.5$. (NEt_4) $_2[V_2(edt)_4]$ and (NEt_4) $_3[V_3S_4(edt)_3]$ (**2**). To a slurry of Na_2edt (1.38 g, 10 mmol) in $MeCN$ (80 mL) were added NEt_4Br (1.05 g, 5 mmol) and elemental S (0.08 g, 2.5 mmol), followed by addition of solid VCl_3 (0.785 g, 5 mmol). After the mixture was stirred for ca. 2.5 h, the resulting deep brown solution was filtered. Addition of Et_2O (60 mL) to the filtrate resulted in the formation of a black crystalline precipitate, which was collected by filtration, washed with Et_2O , and dried in vacuo. Recrystallization from $MeCN/Et_2O$ yielded black crystals. Examination under a microscope showed this product to be composed of an approximately 3:1 mixture of block-shaped

and needle-shaped crystals; these were individually identified as (NEt_4) $_2[V_2(edt)_4]$ and (NEt_4) $_3[V_3S_4(edt)_3]$, respectively (see text). The not-too-dissimilar solubility of these two materials has prevented easy purification of the latter from this mixture.

C. $n = 1$. (PPh_4) $Na[VS(edt)_2] \cdot DMF$. To a slurry of Na_2edt (4.15 g, 30 mmol) in $MeCN$ (100 mL) were added elemental S (0.32 g, 10 mmol) and PPh_4Br (4.19 g, 10 mmol), followed by addition of solid VCl_3 (1.57 g, 10 mmol). After the mixture was stirred overnight at ambient temperature, Et_2O (50 mL) was added to the resulting deep brown solution and the flask stored in a freezer for several hours. The solid material thus obtained was collected by filtration, washed with $MeCN/Et_2O$ (1:1), and dried in vacuo. The crude material was extracted into DMF, the solution filtered, and Et_2O added to the filtrate to initiate crystallization. Storage in a freezer yielded dark, orange-brown crystals in ca. 60% overall yield. Anal. Calcd for $C_{31}H_{35}NOPS_5NaV$: C, 52.98; H, 5.02; N, 1.99. Found: C, 52.86; H, 4.99; N, 2.02. The NEt_4^+/Na^+ salt can be prepared in an analogous manner and recrystallized from $MeCN/Et_2O$. IR (Nujol): $\nu(V=S)$ 522 cm^{-1} .

D. (a) $n = 1.5$; $edt^{2-}:V = 3:1$. (NEt_4) $Na[VS(edt)_2]$ (**3**). To a stirred slurry of Na_2edt (2.07 g, 15 mmol), NEt_4Br (2.10 g, 10 mmol), and S (0.24 g, 7.5 mmol) in $MeCN$ (80 mL) was added VCl_3 (0.785 g, 5 mmol). The resulting orange-brown solution was stirred for a further 3–4 hr. and filtered and Et_2O (75 mL) added to the filtrate. Overnight storage of the flask in a refrigerator yielded dark orange-brown crystals, which were collected by filtration, washed with Et_2O , and dried in vacuo. The product had IR and electronic spectra identical with that of authentic complex **3**. The overall yield was 65%.

(b) $n = 1.5$; $edt^{2-}:V = 2:1$. (NEt_4) $_3[V_3S_4(edt)_3] \cdot 2MeCN$ (**2**). To a stirred slurry of Na_2edt (1.38 g, 10 mmol), NEt_4Br (2.10 g, 10 mmol), and S (0.24 g, 7.5 mmol) in $MeCN$ (80 mL) was added solid VCl_3 (0.785 g, 5 mmol). The resulting dark brown solution was stirred for a further 3–4 h and filtered and Et_2O (50 mL) added to the filtrate. Overnight storage of the flask at ambient temperature yielded small black needlelike crystals. These were collected by filtration, washed with Et_2O , and dried in vacuo. The crude product was dissolved in $MeCN$ (80 mL), the solution filtered, and Et_2O (40 mL) added to the filtrate. Storage of the flask at ambient temperature yielded well-formed large black needles of **2** in 20% overall yield. Anal. Calcd for $C_{31}H_{73.5}N_{3.5}S_{10}V_3$: C, 38.4; H, 7.7; N, 5.1; S, 33.0. Found: C, 37.7; H, 7.6; N, 5.1; S, 32.3. Electronic spectrum ($MeCN$; λ_{max} , nm (ϵ_m/V_3 , $L mol^{-1} cm^{-1}$): 335 (sh, 13 136), 400 (sh, 9550), 477 (sh, 6068), 644 (2793). Further addition of Et_2O to the crystallization filtrate yielded more **2**, but it was contaminated with a product with IR bands assignable to complex **5**. Similarly, further addition of Et_2O to the reaction filtrate yielded a small amount of orange-brown crystals with an IR spectrum identical with that of complex **3**.

E. (a) $n = 2$; $edt^{2-}:V = 5:1$. (NEt_4) $Na[VS(edt)_2]$ (**3**). To a stirred slurry of Na_2edt (3.46 g, 25 mmol), NEt_4Br (2.10 g, 10 mmol), and S (0.32 g, 10 mmol) in $MeCN$ (80 mL) was added solid VCl_3 (0.785 g, 5 mmol) and the reaction mixture stirred at room temperature for a further 4 h. A purple solid was removed by filtration and Et_2O (50 mL) added to the orange-brown filtrate. Overnight storage of the flask at ambient temperature yielded orange-brown crystals of complex **3** in $\geq 50\%$ yield; the identity of the product was deduced by IR and electronic spectral comparison with authentic material.

(b) $n = 2$; $edt^{2-}:V = 2.5:1$. (NEt_4) $_2Na[V_2OS_4(edt)]$ (**4**) and (NEt_4) $_2Na[V_2S_5(edt)]$ (**5**). To a stirred slurry of Na_2edt (3.46 g, 25 mmol), NEt_4Br (2.10 g, 10 mmol), and S (0.64 g, 20 mmol) in $MeCN$ (100 mL) was added solid VCl_3 (1.57 g, 10 mmol) and the mixture stirred overnight at room temperature. The resulting red-brown solution was filtered and Et_2O (100 mL) added to the filtrate to yield a black oil; the latter solidified on overnight storage in a freezer. The black solid was collected by filtration, washed with Et_2O , and dried in vacuo. The solid was dissolved in $MeCN$ (80 mL), the solution filtered, and the filtrate layered with Et_2O (60 mL). After several days, extremely long (≤ 3 cm) dark purple needles of **4** and a black microcrystalline precipitate of **5** were obtained. These were carefully collected by filtration, washed with Et_2O , and dried in vacuo. The two products were readily separable manually, and complexes **4** and **5** were obtained in overall yields of 20% and 30%, respectively. Anal. Calcd for **4**, $C_{18}H_{44}N_2OS_6NaV$: C, 34.77; H, 7.13; N, 4.50. Found: C, 34.55; H, 7.15; N, 4.48. Calcd for **5**, $C_{18}H_{44}N_2S_7NaV$: C, 33.89; H, 6.95; N, 4.39. Found: C, 33.68; H, 6.79; N, 4.70. Electronic spectra ($MeCN$; λ_{max} , nm (ϵ_m/V_2 , $L mol^{-1} cm^{-1}$): **4**, 312 (sh, 14 510), 380 (10 155), 528 (6425), 728 (808); **5**, 328 (sh, 11 730), 440 (sh, 4720), 558 (6380), 756 (1125).

F. $n = 2.5$. (NEt_4) $_2Na[V_2S_5(edt)]$ (**5**). To a stirred slurry of Na_2edt (3.11 g, 22.5 mmol), NEt_4Br (2.10 g, 10 mmol), and S (0.80 g, 25 mmol) in $MeCN$ (80 mL) was added solid VCl_3 (1.57 g, 10 mmol) and the reaction mixture stirred overnight at ambient temperature. The resulting dark red solution was filtered and THF (70 mL) added to the filtrate.

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Table I. Crystallographic Data for Complexes 2 and 4

	2	4
formula	C ₃₄ H ₇₈ N ₃ S ₁₀ V ₃	C ₁₈ H ₄₄ N ₂ OS ₆ NaV ₂
molar mass, amu	1030.54	621.85
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /c
temp, °C	-154	-155
a, Å	14.168 (5) ^a	12.955 (6) ^a
b, Å	18.446 (7)	15.963 (8)
c, Å	19.803 (8)	15.338 (8)
β, deg	104.91 (2)	109.83 (2)
Z	4	4
vol, Å ³	5001.52	2983.95
radiation ^b	Mo Kα	Mo Kα
abs coeff, cm ⁻¹	9.633	10.380
cryst size, mm	0.25 × 0.25 × 0.30	0.20 × 0.20 × 0.24
scan spd, deg/min	4.0	4.0
scan width, deg	2.0 ^c	2.0 ^c
scan range, deg	6 ≤ 2θ ≤ 45	6 ≤ 2θ ≤ 45
no. of data collcd	7259	4436
no. of unique data	6567	3909
averaging R	0.066 ^d	0.024 ^d
no. of obsd data	3806 ^e	3112 ^f
R, % ^g	8.39	4.34
R _w , % ^h	8.59	4.37
goodness of fit ⁱ	1.713	0.948

^a 30 reflections. ^b 0.71069 Å. ^c Plus dispersion. ^d 314 and 266 reflections, respectively, measured more than once. ^e $F > 2.33\sigma(F)$. ^f $F > 3.00\sigma(F)$. ^g $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^h $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$. ⁱ Goodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Overnight storage at ambient temperature yielded a black microcrystalline precipitate, which was collected by filtration, washed with THF, and dried in vacuo. Yields of 25–35% have routinely been obtained. The IR and electronic spectra of this material were identical with those obtained for this material isolated in the previous preparation.

X-ray Crystallography and Structure Solution. Data were collected on a Picker four-circle diffractometer using standard low-temperature procedures; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.⁹ Data collection parameters are summarized in Table I. The structures were solved by a combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least squares.

(NEt₄)₃[V₃S₄(edt)₃]₂MeCN (2). A suitable crystal was kept in contact with the mother liquor until mounted to avoid solvent loss problems noticed with earlier crystals, which were found not to diffract. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to the unique space group P2₁/n. The non-hydrogen atoms of the anion and three independent cations were located and refined with anisotropic thermal parameters. There were no serious disorder problems, although one edt ligand of the anion displayed somewhat large thermal parameters. A difference Fourier at this stage revealed six major peaks and several nearby minor peaks assigned to seriously disordered MeCN solvate molecules. Because of this disorder, hydrogen atoms of the anion and cations were placed in calculated positions and included in the final refinement cycles together with the six major solvate peaks, which were refined with isotropic thermal parameters. The final difference Fourier showed only several peaks near the disordered solvate atoms with intensities of 1.1–1.6 e/Å³, but no attempt was made to include them.

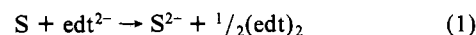
(NEt₄)₂Na[V₂OS₄(edt)] (4). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to the unique space group P2₁/c. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. No disorder problems were encountered. In the latter stages, the hydrogen atoms were located and included in the final refinement cycles with isotropic thermal parameters. A final difference Fourier was essentially featureless.

Other Measurements. Infrared (Nujol mull) and electronic spectra (MeCN solution) were recorded on Perkin-Elmer Model 283 and Hewlett-Packard Model 8450A instruments, respectively. Electrochemical measurements were performed in the cyclic voltammetry (CV) mode by

using an IBM Model EC 225 voltammetric analyzer employing a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and an SCE reference electrode. Potentials are quoted versus the normal hydrogen electrode (NHE) employing ferrocene as an external standard ($E_{1/2} = +0.400$ V vs NHE).¹⁰ No *i*R compensation was employed.¹⁰ Studies were performed at 200 mV/s in MeCN solution containing 0.1 M (N-n-Bu)₄CIO₄ (TBAP) as supporting electrolyte; the concentration of electroactive species was in the 2–4 mM range.

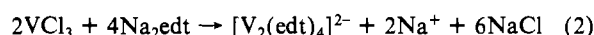
Results and Discussion

Synthesis. We shall describe our synthetic efforts in terms of increasing values of *n*, the S:V ratio. It should be emphasized at the outset that the edt²⁻:V ratio is another parameter that can and will be varied; indeed, increasing amounts of edt²⁻ are necessary as *n* increases to provide the major source of electrons for the reduction of elemental sulfur to sulfide, according to eq 1.¹¹



However, as will become apparent from the discussion to follow, the precise amount of edt²⁻ left in the reaction mixture after the requirements of eq 1 have been satisfied can have a dramatic influence on the identity of the products. It should also be emphasized that all preparations, including separation of mixtures, are perfectly reproducible by using the quantities and other conditions described in the Experimental Section.

A. *n* = 0. This limiting stoichiometry results in good yields of complex 1, which can be obtained in high crystallinity and purity by recrystallization from DMF/MeCN/Et₂O mixtures. Complex 1 was the first example of a homoleptic vanadium thiolate complex and was communicated almost simultaneously by us¹² and others.¹³ Full structural detail is now available elsewhere,^{6c} and the results of our own structural study have, therefore, been included in the supplementary material to this work. The anion of 1 possesses two vanadium(III) centers, indicating no redox reactions to have taken place during its assembly, as is summarized in eq 2.¹⁴ The



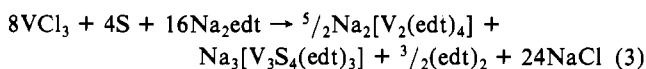
identity of the product is not altered by a greater edt²⁻:V ratio; a 3:1 reaction ratio yielded the same product. An Evans NMR determination of the solution magnetic moment in CD₃CN yielded a value of approximately zero, consistent with a diamagnetic species and supporting retention of the dinuclear structure on dissolution. The ¹H NMR spectrum in rigorously dried and degassed CD₃CN exhibited an extremely sharp and well-resolved multiplet of peaks for the PPh₄⁺ cation and two multiplets in the δ ≈ 2 region assignable to the edt groups. No other features were seen. In less than rigorously purified solvent, the cation peaks are broader and additional peaks appear in the δ 1–4 region. This more complex behavior is most likely due to paramagnetic degradation products of this extremely sensitive material.

B. *n* = 0.5. Addition of ether to the filtered deep brown solution obtained from this reaction stoichiometry yielded a microcrystalline precipitate. Recrystallization yielded black crystals that were obviously a mixture of two products. Microscopic examination showed both needles and approximately cubic crystals to be present in a visual ratio of roughly 1:3, respectively. The unit cell dimensions of a hand-picked crystal of the latter confirmed this product to be (NEt₄)₂[V₂(edt)₄], on the basis of comparison with those of an authentic sample.^{13a} The unit cell dimensions of a hand-picked needle did not correspond to a known compound.

(9) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

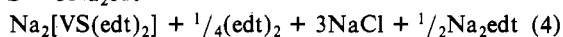
- (10) Gagne, R. G.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.
 (11) In this and following equations, (edt)₂ will be used to represent the disulfide form of the edt²⁻ group, assumed for convenience to be dimeric with an eight-membered ring.
 (12) Wiggins, R. W.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1313.
 (13) (a) Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3179. (b) Szymieski, D.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 885.
 (14) In this and the following equations, reactions will be balanced only by employing Na⁺ cations for convenience; the presence of NR₄⁺ or PPh₄⁺ in the reaction mixture of course leads to precipitation of the corresponding salt on addition of Et₂O.

Since the needles were the minor component and repeated crystallization could not yield a sample free of the cubes for elemental analysis, a full data set was collected and the structure solved. The needles proved to be $(\text{NEt}_4)_3[\text{V}_3\text{S}_4(\text{edt})_3]$ (**2**) as its bis-(acetonitrile) solvate. With the identity of this product established, a synthetic route to pure material was subsequently devised, as will be described below. The formation of both $(\text{NEt}_4)_2[\text{V}_2(\text{edt})_4]$ and **2** from an $n = 0.5$ reaction stoichiometry can be rationalized by eq 3. The predicted 2.5:1 ratio of products is consistent with



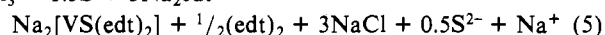
the visually estimated 3:1 ratio from microscopic examination. The oxidation of two vanadium(III) ions to vanadium(IV) and oxidation of three edt^{2-} groups to their disulfides provide the eight electrons necessary for reduction of four S to four S^{2-} groups.

C. $n = 1$. The $n = 1$ reaction stoichiometry yielded an intensely dark orange-brown reaction solution from which the product could be isolated by addition of Et_2O . Recrystallization yielded well-formed orange-brown crystals of $(\text{PPh}_4)\text{Na}[\text{VS}(\text{edt})_2]\cdot\text{DMF}$ (**3**) in good overall yield (60%). The NEt_4^+ salt was prepared similarly and allowed confirmation of the presence of a strong $\text{V}=\text{S}$ stretch in the IR spectrum (522 cm^{-1}) masked in **3** by PPh_4^+ bands. The NMe_4^+ and PPh_4^+ salts had been obtained in previous work by the conversion of $[\text{VO}(\text{edt})_2]^{2-}$ to $[\text{VS}(\text{edt})_2]^{2-}$ with $(\text{Me}_2\text{Si})_2\text{S}$, and the PPh_4^+ salt has been structurally characterized.¹⁵ The formation of **3** by the present route is summarized in eq 4, with



the actual $\text{edt}^{2-}:\text{V}$ ratio employed. The formation of **3** from the $n = 1$ ratio was not, in fact, unexpected since we had already shown in previous work that such reaction stoichiometries with elemental sulfur or selenium lead to direct and high-yield formation of the corresponding $[\text{VS}(\text{SPh})_4]^{2-}$ and $[\text{VSe}(\text{edt})_2]^{2-}$ species and had structurally characterized both $(\text{PhCH}_2\text{NMe}_3)_2[\text{VS}(\text{SPh})_4]$ and $(\text{NEt}_4)_2[\text{VSe}(\text{edt})_2]$.¹⁶ As we describe elsewhere,¹⁶ this is by far the most convenient method of obtaining these VE^{2+} ($\text{E} = \text{S}, \text{Se}$) species, thereby avoiding the need for the prior synthesis of the corresponding VO^{2+} complex.

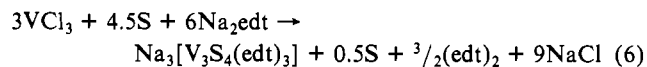
D. (a) $n = 1.5$; $\text{edt}^{2-}:\text{V} = 3:1$. Addition of Et_2O to the reaction filtrate yielded dark brown crystals, which proved to be complex **3** on IR and UV/vis comparison with authentic material. We were surprised that this should be the case, given the presence of excess S in the reaction mixture. The formation of **3** from this reaction stoichiometry is given in eq 5. The fate of the excess



S^{2-} is uncertain. In any event, we suspected that **3** was formed as the major product because sufficient edt^{2-} remained after S reduction (eq 1) to accommodate the $\text{edt}^{2-}:\text{V} = 2:1$ ratio required for formation of **3**. This suggested that strongly chelating edt^{2-} prevents further incorporation of available S^{2-} to yield a higher nuclearity product. If this interpretation was correct, we also reasoned that lowering the $\text{edt}^{2-}:\text{V}$ ratio might preclude formation of **3** and allow aggregation to occur. As we shall describe below, this did indeed turn out to be the case.

(b) $n = 1.5$; $\text{edt}^{2-}:\text{V} = 2:1$. Not only did this reaction stoichiometry confirm our suspicions about the importance of the $\text{edt}^{2-}:\text{V}$ ratio in determining the reaction product but it also yielded an added bonus in allowing a satisfactory route to complex **2**. Addition of Et_2O to the dark brown reaction filtrate yielded a crystalline precipitate. Recrystallization from $\text{MeCN}/\text{Et}_2\text{O}$ gave **2**, which, when it was dried, was analyzed as the hemisolvate. Additional crops of **2** could be obtained from both the remaining reaction filtrate and the recrystallization filtrate, but these were

contaminated with complexes **3** and **5**, respectively, further emphasizing the complexity of these $\text{V}/\text{S}/\text{edt}^{2-}$ reactions. We were thus happy to settle for lowered, but nevertheless adequate, yields of pure **2**. The formation of **2** from this stoichiometry can be summarized in eq 6, if we ignore for convenience the small



amounts of additional products. We also repeated this preparation with an $n = 1.33$ ratio to see if this might also yield complex **2**, as suggested by its formulation. This proved to be the case, and isolated yields of pure material were in the ca. 30% range. More material could again be obtained from the recrystallization filtrate, but this was again contaminated with what appeared to be complex **5**.

E. (a) $n = 2$; $\text{edt}^{2-}:\text{V} = 5:1$. Addition of Et_2O to the orange-brown reaction filtrate yielded dark orange-brown crystals of what proved to be complex **3** on IR and electronic spectral comparison with an authentic sample. This observation further emphasizes that when there is sufficient edt^{2-} in the reaction mixture to form **3**, it precludes further incorporation of available S^{2-} to yield a higher nuclearity species. An intractable dark purple solid was obtained when the reaction solution was filtered, and we believe this represents the fate¹⁷ of the excess S^{2-} . Pursuing the reasoning outlined for the $n = 1.5$ reactions, we repeated the $n = 2$ reaction with a lowered $\text{edt}^{2-}:\text{V}$ ratio and found that formation of **3** was suppressed and a higher nuclearity product was now obtained.

(b) $n = 2$; $\text{edt}^{2-}:\text{V} = 2.5:1$. Addition of Et_2O to the filtered red-brown reaction solution yielded a black oil, which solidified on storage in a freezer. Recrystallization from $\text{MeCN}/\text{Et}_2\text{O}$ gave what was obviously a mixture of products; long purple needles and a black microcrystalline solid were obtained, and these proved to be complexes **4** and **5**, respectively. The extreme difference in crystallinity was fortuitous and allowed ready manual separation of the two materials. Complex **4** was structurally characterized and shown to be $(\text{NEt}_4)_2\text{Na}[\text{V}_2\text{OS}_4(\text{edt})]$. With the identity of **4** established, complex **5** is believed to be $(\text{NEt}_4)_2\text{Na}[\text{V}_2\text{S}_5(\text{edt})]$, a conclusion consistent with analytical and spectral data. The two complexes have virtually identical IR spectra except for the presence of a strong band at 915 cm^{-1} in **4**, assignable to a $\text{V}=\text{O}$ stretch.¹⁸ Further support for the structural assignment of **5** derives from the electronic spectra; the spectra of **4** and **5** in MeCN solution are very similar except for a red shift in the bands of **5** compared to those of **4**. This is consistent with conversion of a $\text{V}=\text{O}^{2+}$ unit in **4** to a $\text{V}=\text{S}^{2+}$ unit in **5**. Parallel behavior has been seen in the spectra of the $[\text{VE}(\text{edt})_2]^{2-}$ ($\text{E} = \text{O}, \text{S}$) pair.¹⁵ The formation of **4** and **5** from the $n = 2$ reaction ratio is difficult to rationalize with a balanced equation. Yields must obviously be sacrificial since the $\text{S}:\text{V}$ ratio is not 2.5:1, and this is the most likely reason for the incorporation of adventitious O (from O_2 , H_2O) to also yield significant quantities of **4**. As we shall describe below, a more convenient route to pure complex **5** has been devised, but the $n = 2$ reaction ratio remains our only route to **4** at the present time. Fortunately, its extreme crystallinity provides reproducible access to relatively low, but nevertheless adequate, yields (20%).

F. $n = 2.5$. To complete our description of the influence of n on reaction product, the $n = 2.5$ reaction was explored as a potentially more convenient route to pure complex **5**, and this has proven to be the case. Addition of THF to the dark red reaction filtrate yielded black microcrystals of pure complex **5** as the sole product. Its IR and electronic spectra are identical with those of the manually separated material from the previous preparation. We have not yet been able to obtain this material in a form suitable for structural studies, however. In addition, complex **5** seems very

(15) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297.

(16) Nicholson, J. R.; Huffman, J. C.; Ho, D.; Christou, G. *Inorg. Chem.* **1987**, *26*, 3030.

(17) This residue from the filtration also contains NaCl. Washing with water to remove the NaCl and allow analysis of the purple solid was thwarted by the decomposition of the purple solid, no doubt due to hydrolysis.

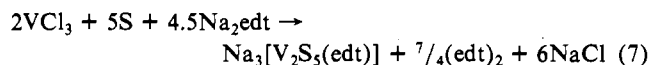
(18) The $\text{V}=\text{S}$ stretch in **5** is not resolved from the other $\text{V}=\text{S}$ stretches present.

Table II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10$) for Complex 2

atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
V(1)	8695 (2)	2160 (1)	8526 (1)	15
V(2)	10329 (2)	3029 (1)	8396 (1)	14
V(3)	10201 (2)	1516 (1)	7957 (1)	15
S(4)	9124 (3)	2482 (2)	7513 (2)	17
S(5)	9602 (3)	2944 (2)	9289 (2)	18
S(6)	11500 (2)	2195 (2)	8483 (2)	19
S(7)	9333 (3)	1049 (2)	8681 (2)	17
S(8)	7162 (3)	2348 (3)	7772 (2)	40
C(9)	6245 (11)	2234 (12)	8238 (9)	46
C(10)	6677 (14)	1796 (17)	8955 (10)	91
S(11)	7789 (3)	2045 (4)	9365 (3)	64
S(12)	11263 (3)	3935 (2)	9120 (2)	18
C(13)	11796 (10)	4437 (8)	8528 (7)	21
C(14)	10994 (11)	4661 (8)	7894 (8)	25
S(15)	10242 (3)	3883 (2)	7510 (2)	25
S(16)	9997 (3)	1307 (2)	6781 (2)	24
C(17)	10778 (13)	525 (10)	6712 (9)	39
C(18)	11576 (12)	433 (10)	7363 (9)	36
S(19)	11089 (3)	397 (2)	8122 (2)	25
N(20)	1981 (8)	1287 (6)	591 (6)	21
C(21) ^a	3034 (10)	1264 (8)	1035 (7)	22
C(22)	3758 (13)	1513 (12)	660 (9)	47
C(23) ^a	1809 (11)	792 (9)	-21 (7)	26
C(24)	2064 (12)	-6 (9)	168 (8)	32
C(25) ^a	1696 (12)	2030 (8)	292 (8)	29
C(26)	1808 (14)	2637 (10)	824 (10)	48
C(27) ^a	1369 (11)	1069 (10)	1107 (8)	29
C(28)	271 (12)	1044 (12)	761 (9)	45
N(29)	7694 (9)	2096 (7)	1567 (7)	30
C(30) ^a	8462 (13)	2556 (10)	1350 (10)	43
C(31)	8637 (19)	3280 (10)	1674 (16)	83
C(32) ^a	6724 (12)	2502 (10)	1424 (9)	35
C(33)	6266 (17)	2696 (14)	649 (10)	73
C(34) ^a	7973 (11)	1938 (9)	2330 (8)	29
C(35)	8930 (15)	1563 (10)	2608 (11)	57
C(36) ^a	7594 (11)	1417 (10)	1136 (8)	32
C(37)	6820 (13)	882 (11)	1209 (10)	45
N(38)	2863 (8)	67 (6)	3573 (6)	18
C(39) ^a	2486 (15)	786 (11)	3243 (10)	49
C(40)	1332 (12)	761 (12)	2930 (8)	48
C(41) ^a	2358 (14)	-124 (11)	4145 (11)	51
C(42)	2447 (12)	472 (8)	4690 (8)	28
C(43) ^a	3908 (16)	181 (12)	3882 (10)	55
C(44)	4479 (11)	-536 (9)	4193 (8)	27
C(45) ^a	2630 (16)	-528 (10)	3038 (10)	53
C(46)	3226 (15)	-377 (11)	2442 (9)	51
C(47) ^b	4006 (26)	3844 (21)	-135 (19)	119 (10)
C(48) ^b	3949 (26)	3299 (21)	-341 (19)	106 (10)
C(49) ^b	4318 (27)	2730 (22)	-805 (20)	137 (11)
C(50) ^b	5981 (25)	-1348 (20)	1308 (18)	132 (9)
C(51) ^b	5544 (31)	-803 (23)	1054 (22)	197 (12)
C(52) ^b	4913 (27)	-337 (20)	540 (19)	119 (10)

^aNitrogen-bound carbon atoms. ^bDisordered solvate atoms.

sensitive to oxygen sources and contamination with complex 4 will be obtained in less than rigorously dried solvents. The formation of 5 is summarized in eq 7.



Reactions with higher values of n are currently under investigation and will form the contents of a future report. We can, however, state at this time that the $n = 3$ reaction with a $\text{edt}^{2-}:\text{V}$ ratio of 6:1 yields copious amounts of the intractable dark purple solid in the reaction solution. From the filtered orange-brown solution, addition of Et_2O yields complex 3 in $\sim 60\%$ yield. Its identity was confirmed by IR and electronic spectral comparisons. Again, lowering the $\text{edt}^{2-}:\text{V}$ ratio suppresses the formation of 3, and the identity of the product(s) is under investigation.

Description of Structures. The structure of 1 has been described in detail elsewhere^{6c,12,13} and is only briefly outlined here. The anion contains two vanadium(III) atoms quadruply bridged by four μ -S atoms from two edt groups. The V...V distance (2.600

Table III. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10$) for Complex 4

atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
V(1)	7936 (1)	383 (1)	8830 (1)	15
V(2)	8492 (1)	371 (1)	7099 (1)	19
O(3)	9077 (3)	717 (2)	9583 (2)	16
S(4)	6525 (1)	1090 (1)	9163 (1)	25
C(5)	6670 (5)	611 (4)	10268 (4)	30
C(6)	6555 (5)	-322 (4)	10180 (4)	31
S(7)	7445 (1)	-779 (1)	9595 (1)	21
S(8)	7476 (1)	1283 (1)	7532 (1)	21
S(9)	8532 (1)	-692 (1)	8028 (1)	19
S(10)	10125 (1)	805 (1)	7383 (1)	23
S(11)	7745 (1)	50 (1)	5693 (1)	27
N(12)	9815 (3)	3185 (3)	-484 (3)	20
C(13) ^a	10324 (5)	2459 (4)	-809 (4)	25
C(14)	11227 (5)	2703 (4)	-1173 (4)	29
C(15) ^a	8820 (5)	2879 (4)	-246 (4)	29
C(16)	9039 (5)	2411 (4)	642 (4)	34
C(17) ^a	9401 (5)	3845 (4)	-1240 (4)	26
C(18)	8636 (5)	3535 (4)	-2162 (4)	36
C(19) ^a	10630 (5)	3637 (4)	340 (4)	27
C(20)	11471 (5)	3106 (4)	1046 (4)	34
N(21)	4900 (3)	1494 (3)	3360 (3)	22
C(22) ^a	4656 (5)	581 (4)	3054 (4)	27
C(23)	5633 (5)	34 (4)	3134 (4)	35
C(24) ^a	5529 (5)	1544 (4)	4396 (4)	26
C(25)	4934 (6)	1269 (4)	5020 (4)	36
C(26) ^a	5616 (4)	1912 (4)	2874 (4)	27
C(27)	5134 (5)	1947 (5)	1837 (4)	39
C(28) ^a	3793 (4)	1929 (4)	3117 (4)	24
C(29)	3860 (5)	2829 (4)	3401 (5)	32
Na(30)	10526 (1)	187 (1)	9141 (1)	21

^aNitrogen-bound carbon atoms.

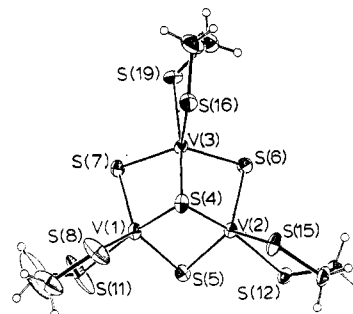


Figure 1. ORTEP projection of the anion of complex 2 at the 50% probability level. The large thermal parameters evident in one edt ligand may be due to positional disorder; however, no resolution was possible.

(1 \AA) is indicative of direct metal-metal bonding. A similar quadruply bridged $[\text{V}_2(\text{edt})_2]^{2+}$ core is also found in $\text{Cp}_2\text{V}_2(\text{edt})_2$, which has a V...V distance of 2.542 (1) \AA .¹⁹ The vanadium atoms in the anion of 1 each possess a terminal edt group completing six-coordination at each metal. The geometry has been alternately described as trigonal prismatic with an edge rotated by 45° and as square prismatic with two diagonally opposite sites of a face vacant. We prefer the latter description, which allows ready extension, for example, to the quadruply bridged dinuclear niobium species $\text{Nb}_2\text{Cl}_8(\text{PME}_2\text{Ph})_4$, where the Nb atoms are eight-coordinate with four terminal ligands and a square-antiprismatic coordination geometry.²⁰

Complex 2 crystallizes in monoclinic space group $P2_1/n$ and contains well-separated cations, anions, and MeCN solvate molecules. Fractional coordinates and selected bond distances and angles are collected in Tables II and IV, respectively. An ORTEP projection is shown in Figure 1. The anion of 2 contains three vanadium atoms disposed in a triangular fashion and bridged by μ_3 -sulfur atom S(4). The V...V distances are in the narrow

(19) Rajan, O. A.; McKenna, M.; Noordik, J.; Haltiwanger, R. C.; Rakowski-DuBois, M. *Organometallics* 1984, 3, 831.

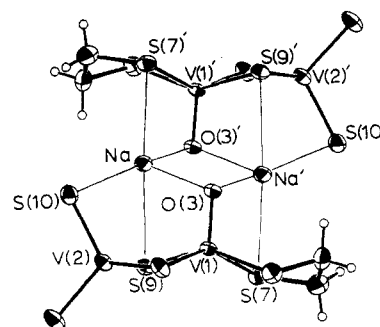
(20) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* 1984, 23, 945.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex 2

a. Bonds			
V(1)···V(2)	2.881 (2)	V(1)–S(5)	2.241 (4)
V(1)···V(3)	2.911 (2)	V(1)–S(7)	2.229 (5)
V(2)···V(3)	2.915 (2)	V(2)–S(5)	2.270 (4)
		V(2)–S(6)	2.236 (4)
V(1)–S(4)	2.318 (4)	V(3)–S(6)	2.249 (4)
V(2)–S(4)	2.335 (4)	V(3)–S(7)	2.284 (4)
V(3)–S(4)	2.363 (4)	mean	2.252
mean	2.339		
V(1)–S(8)	2.324 (5)	V(1)–S(11)	2.356 (5)
V(2)–S(15)	2.337 (4)	V(2)–S(12)	2.371 (4)
V(3)–S(16)	2.305 (4)	V(3)–S(19)	2.395 (5)
mean	2.322	mean	2.374
b. Angles			
S(8)–V(1)–S(11)	82.97 (18)	S(4)–V(1)–S(11)	160.91 (18)
S(12)–V(2)–S(15)	83.82 (15)	S(4)–V(2)–S(12)	160.72 (17)
S(16)–V(3)–S(19)	85.33 (16)	S(4)–V(3)–S(19)	165.14 (17)
mean	84.04	mean	162.26
S(4)–V(1)–S(8)	79.35 (15)	S(5)–V(1)–S(7)	111.02 (16)
S(4)–V(2)–S(15)	80.92 (15)	S(5)–V(2)–S(6)	111.66 (16)
S(4)–V(3)–S(16)	81.34 (15)	S(6)–V(3)–S(7)	115.34 (6)
mean	80.54	mean	112.67
S(4)–V(1)–S(5)	100.73 (16)	S(5)–V(1)–S(8)	128.06 (20)
S(4)–V(1)–S(7)	99.62 (16)	S(7)–V(1)–S(8)	120.24 (20)
S(4)–V(2)–S(5)	99.34 (15)	S(5)–V(2)–S(15)	133.21 (18)
S(4)–V(2)–S(6)	98.39 (16)	S(6)–V(2)–S(15)	114.58 (17)
S(4)–V(3)–S(6)	97.20 (16)	S(6)–V(3)–S(16)	115.86 (17)
S(4)–V(3)–S(7)	96.72 (15)	S(7)–V(3)–S(16)	128.59 (17)
mean	98.67	mean	123.42
S(5)–V(1)–S(11)	84.57 (22)	V(1)–S(4)–V(2)	76.50 (13)
S(7)–V(1)–S(11)	95.44 (21)	V(1)–S(4)–V(3)	76.89 (13)
S(5)–V(2)–S(12)	82.66 (15)	V(2)–S(4)–V(3)	76.68 (13)
S(6)–V(2)–S(12)	98.65 (15)	mean	76.69
S(6)–V(3)–S(19)	94.49 (16)	V(1)···V(2)···V(3)	60.29 (6)
S(7)–V(3)–S(19)	86.47 (16)	V(2)···V(1)···V(3)	60.44 (6)
mean	90.38	V(1)···V(3)···V(2)	59.27 (6)

range 2.881–2.915 Å. Each edge of the triangle is bridged by a sulfide atom, and a terminal edt group on each vanadium completes five-coordination at each metal center. The edge-bridging sulfides lie below the V_3 plane, and the μ_3 -sulfide lies above this plane (by 1.632 Å). This arrangement lends the V_3S_4 core a structure akin to a “partial cube”. The anion has idealized C_{3v} symmetry, but no elements are crystallographically imposed. The coordination geometry around the V atoms is closest to trigonal bipyramidal with S(4)–V(1–3)–S(11,12,19) (160.91–165.14°) representing the axes. The trianionic nature of the complex necessitates a mixed-valence trivanadium(III,2IV) description. However, inspection of the structural parameters in Table IV shows no trend that would justify a trapped-valence assignment, and the complex is best described as electronically delocalized with an average metal oxidation state of $+3\frac{2}{3}$.

There are many examples in inorganic chemistry of triangles of metal atoms capped by one or two μ_3 -sulfide atoms. These include recently reported complexes such as $Cr_3(\mu_3-S)_2(\mu-S)_3$ -(dmpe)₃²¹ (dmpe = 1,2-bis(dimethylphosphino)ethane) and $Pd_3(\mu_3-S)_2(S_2C_2O_2)(PMe_3)_4$.²² In M/S/SR chemistry, examples can be found for M = Fe,²³ Co,²³ Ni,²⁴ and Zr.²⁵ In Mo chemistry, several examples are known of species containing $[Mo_3S_4]^{4+}$ cores,^{26–30} including $[Mo_3S_4(edt)_3]^{2-}$, which is isostructural but

**Figure 2.** ORTEP projection showing the discrete centrosymmetric structure adopted by two Na^+ ions and two anions of complex 4. Only sulfur atoms bound to Na^+ centers are labeled. Primed and unprimed atoms are related by the center of symmetry. $Na-O(3,3') = 2.359$ (3), 2.345 (3) Å; $Na-S(7',9,10) = 2.846$ (2), 2.927 (2), 2.749 (2) Å.**Table V.** Selected Bond Distances (Å) and Angles (deg) for Complex 4

a. Bonds			
V(1)–O(3)	1.626 (3)	V(1)···V(2)	2.977 (1)
V(1)–S(4)	2.3470 (18)	V(2)–S(8)	2.2102 (18)
V(1)–S(7)	2.3927 (18)	V(2)–S(9)	2.2039 (18)
V(1)–S(8)	2.3620 (18)	V(2)–S(10)	2.1265 (19)
V(1)–S(9)	2.3870 (17)	V(2)–S(11)	2.1060 (19)
b. Angles			
O(3)–V(1)–S(4)	105.98 (13)	S(4)–V(1)–S(9)	150.40 (6)
O(3)–V(1)–S(7)	103.60 (12)	S(7)–V(1)–S(8)	148.38 (6)
O(3)–V(1)–S(8)	107.92 (13)	S(8)–V(2)–S(9)	101.47 (7)
O(3)–V(1)–S(9)	103.13 (13)	S(8)–V(2)–S(10)	112.12 (7)
S(4)–V(1)–S(7)	84.81 (7)	S(8)–V(2)–S(11)	110.75 (7)
S(4)–V(1)–S(8)	84.15 (6)	S(9)–V(2)–S(10)	108.34 (6)
S(7)–V(1)–S(9)	83.26 (7)	S(9)–V(2)–S(11)	112.12 (7)
S(8)–V(1)–S(9)	92.04 (7)	S(10)–V(2)–S(11)	111.63 (7)

not isoelectronic with the anion of **2**.²⁹ Interestingly, the “partial cube” structure of the $[Mo_3S_4]^{4+}$ core is complemented by the existence of the cubane $[Mo_4S_4]$ cores.^{26,31–33} The cubane complex corresponding to the anion of **2** would be of formula $[V_4S_4(edt)_4]^{2-}$, but we have yet to detect this as a product of our reaction systems. Attempts to prepare such a species are continuing, however, and we note that the V_4S_4 core has been reported in $(MeCp)_4V_4S_4$.³⁴

Complex 4 crystallizes in monoclinic space group $P2_1/c$ and contains well-separated NEt_4^+ and anion molecules; the Na^+ atoms are bound to the anions as described below and shown in Figure 2. An ORTEP projection of an individual anion unit is available in ref 8a. Fractional coordinates and selected bond distances and angles are listed in Tables III and V, respectively. The anion of **4** contains two vanadium atoms, which are 2.977 (1) Å apart and are bridged by two $\mu-S^{2-}$ atoms to yield a nonplanar $[V_2S_2]^{5+}$ core. A terminal edt²⁻ ligand and multiply bonded O(3), S(10), and S(11) atoms complete coordination to the metals to yield idealized C_s symmetry. The trianionic nature of the anion necessitates a mixed-valence divanadium(IV,V) description. V(1) and V(2) are formally assigned as the vanadium(IV) and vanadium(V) centers,

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Table VI. Redox Potentials in MeCN Solution^a

complex	process	nature ^b	E/V ^c
1	2-/1-	rev	-0.63
	1-/0	irrev	-0.16
2	3-/4-	rev	-1.51
	2-/3-	rev	-0.63
3	1-/2-	irrev	-0.00
	2-/1-	irrev	-0.46
4	3-/4-	rev	-1.23
5	3-/4-	rev	-1.23

^aVs NHE. ^bProcesses designated as reversible have $i_a/i_c \approx 1$. ^cQuoted values are $(E_f - E_r)/2$ for reversible and E_f for irreversible processes; estimated error ± 10 mV.

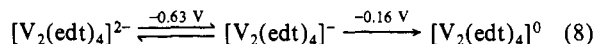
respectively, on the basis of (i) the square-pyramidal geometry at V(1) characteristic of VO^{2+} species, (ii) the $\text{V}=\text{O}$ bond length (1.626 (3) Å) identical with that in $[\text{VO}(\text{edt})_2]^{2-}$ (1.625 (3) Å),¹⁵ and (iii) the approximately tetrahedral geometry at V(2) as seen³⁵ in VS_4^{3-} . The V(2)-S(10,11) bond lengths (2.126 (2) and 2.106 (2) Å, respectively) are slightly shorter than those in VS_4^{3-} (2.135–2.175 (1) Å), consistent with increased π -bonding in the former to compensate for the major loss of π -donation from the other two S atoms (S(8) and S(9)), which now bridge to V(1). The fact that the V(2)-S(10) distance is longer than V(2)-S(11) can be rationalized by noting that S(10) is interacting with the Na^+ ion (vide infra).

In our report of the structures of $(\text{PPh}_4)\text{Na}[\text{VE}(\text{edt})_2]$ (E = O, S),¹⁵ we described how anion/ Na^+ interactions lead to assembly of discrete $\text{Na}_2[\text{VE}(\text{edt})_2]_2$ structures in the solid state. This is also the case for complex 4. Discrete units of formula $\text{Na}_2[\text{V}_2\text{OS}_4(\text{edt})_2]$ are present, as shown in Figure 2. The dimeric assembly is centrosymmetric and is held together by Na-O and Na-S interactions; each Na^+ is five-coordinate and possesses an S_2O_2 coordination environment. Na-O and Na-S distances are included in the caption to Figure 2 and are similar to those found in the $\text{Na}_2[\text{VE}(\text{edt})_2]_2$ assemblies. The coordination geometry at the Na^+ is severely distorted from both the square-pyramidal and trigonal-bipyramidal extremes.

The overall structure of complex 4 has no known counterpart in Mo or W chemistry with the edt^{2-} ligand. However, other Mo/S and W/S complexes are known with a structure similar to that of 4. Examples include $[(\text{MS}_4)\text{MO}(\text{MS}_4)]^{2-}$ (M = Mo, W),⁵ $[(\text{MoS}_4)\text{MoO}(\text{S}_2\text{MoO}(\text{S}_2))]^{2-}$,⁵ $[(\text{S}_4)\text{MoS}(\text{MoS}_4)]^{2-}$,³⁶ and $[(\text{S}_2)\text{MoS}(\text{MoS}_4)]^{2-}$.³⁶ All these complexes possess $[\text{MoE}(\text{MoS}_4)]$ units akin to the $[\text{VE}(\text{VS}_4)]$ (E = O, S) units of complexes 4 and 5.

Redox Properties. We have undertaken a study of the redox properties of complexes 1–5 using the cyclic voltammetric (CV) technique. The results are summarized in Table VI. Couples designated as reversible (rev) have $i_a/i_c \approx 1$. Peak separations are reproducibly in the 80–110 mV range and are similar to those of the ferrocene/ferrocenium couple (80–100 mV) under our experimental conditions, defining the observed couples as one-electron processes.

Complex 1 displays two oxidation processes at -0.63 and -0.16 V, the first reversible. The more positive process has a well-formed forward wave, with i_a approximately equal to the i_a value of the reversible process, but no feature on the reverse scan. These results indicate complex 1 to be a terminal member of the three-component electron-transfer series shown in eq 8. A controlled-po-



tential coulometry experiment gave a value of $n = 1.00 \pm 0.05$ for the first couple, confirming the one-electron nature of this process, but attempts to obtain the monoanion on a bulk scale by using chemical oxidants such as ferrocenium or I_2 have proven unsuccessful. In contrast, $[\text{Cp}_2\text{V}_2(\text{edt})_2]^+$ has been successfully

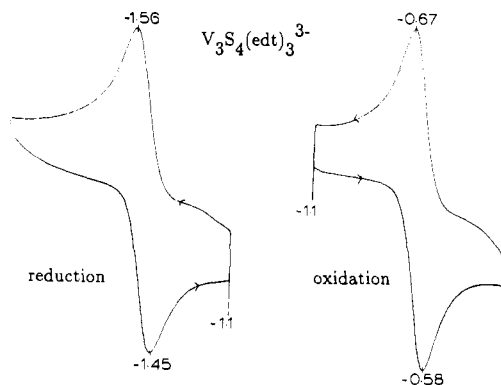


Figure 3. Cyclic voltammogram of complex 2 in MeCN at 200 mV/s.

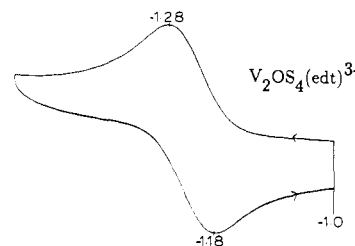
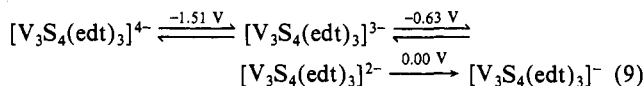


Figure 4. Cyclic voltammogram of complex 4 in MeCN at 200 mV/s.

isolated following chemical oxidation of $\text{Cp}_2\text{V}_2(\text{edt})_2$.¹⁹

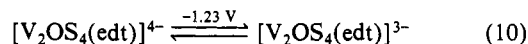
Complex 2 displays rich redox behavior with three one-electron processes observable, two of which are reversible. The irreversible process shows a well-formed forward wave with an i_a value approximately equal to those of the reversible processes but with no reversible feature. The reversible processes are reproduced in Figure 3. These results show complex 2 to be a member of the four-component electron-transfer series of eq 9. The iso-



structural $[\text{Mo}_3\text{S}_4]$ cores of $[\text{Mo}_3\text{S}_4(\text{ida})_3]^{2-}$ (H_2ida = iminodiacetic acid) and $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ have been reported as possessing similarly rich redox chemistry and being components of four-²⁸ and three-membered²⁶ electron-transfer series, respectively.

Complex 3 displays no reversible redox processes, a result consistent with our previous electrochemical investigation of the $[\text{VS}(\text{edt})_2]^{2-}$ complex.¹⁵ Only a grossly irreversible oxidation process at $E_a = -0.46$ V is observed.

Complex 4 displays only a single redox process at -1.23 V, and this is reversible. This process, reproduced in Figure 4, corresponds to a reduction of the trianion and defines the two-component electron-transfer series of eq 10. We were initially somewhat



surprised at the reversibility of this couple since the site of reduction is presumably the vanadium(V) center and this would yield a species with formally a four-coordinate vanadium(IV). Obviously, the dinuclear ($\mu\text{-S}$)₂-bridged nature of 4 makes the identity of the acceptor orbital less clear and precludes a simplistic and formal assignment of oxidation-state changes. We are unaware, for instance, of any reports describing a reversible reduction of the isolated VS_4^{3-} anion. Finally, complex 5 displays a reversible reduction essentially identical in appearance and potential with that of 4, supporting the structural similarity between these two complexes and suggesting that the identity of the multiply bonded atom (O or S) has a negligible effect on the energy of the acceptor orbital.

Summary and Conclusions

Our systematic investigation of the V/S/ edt^{2-} reaction system has confirmed our belief that a variety of discrete V/S complexes are capable of existence and that this area may yet prove to be as extensive as that developed for Mo/S and W/S chemistry.

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Suitable synthetic procedures have now been developed, and the precise identity of the products has been shown to be very dependent on both the S:V and $\text{edt}^2\text{:V}$ reaction ratios. Such considerations will be important as this work is extended to other thiolate groups. Further studies in this rich new area of early-transition-metal sulfide chemistry are in progress.³⁷

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Supplementary Material Available: Tables S1-S12, giving fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for complexes **1**, **2**, and **4** (27 pages); complete listings of observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (No. 83073, 86154, and 85160 for **1**, **2**, and **4**, respectively) are available on request from the Indiana University Chemistry Library.

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Redox Properties of Aqua Complexes of Ruthenium(II) Containing the Tridentate Ligands 2,2':6',2''-Terpyridine and Tris(1-pyrazolyl)methane

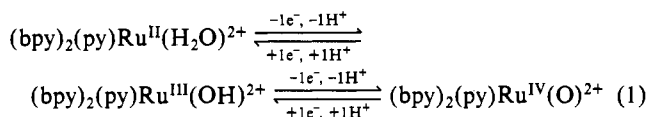
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A series of complexes containing either the facial tridentate ligand tris(1-pyrazolyl)methane (tpm) ($[(\text{tpm})(\text{b})\text{RuX}]^{n+}$ (b = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (4,4'-(CH_3)₂-bpy), 1,10-phenanthroline (phen); X = Cl^- , H_2O , O^{2-}) or the meridional tridentate ligand 2,2':6',2''-terpyridine (trpy) (*cis*- and *trans*- $[(\text{trpy})(\text{pic})\text{RuX}]^{m+}$ (pic = picolinate anion; X = Cl^- , H_2O , O^{2-}) and the μ -oxo ions *cis*- and *trans*- $[(\text{trpy})(\text{pic})\text{Ru}(\text{H}_2\text{O})_2]^{2+}$ have all been prepared and their redox properties investigated. As observed in related complexes, *cis*- and *trans*- $[(\text{trpy})(\text{pic})\text{Ru}(\text{H}_2\text{O})]^{2+}$ and the series $[(\text{tpm})(\text{b})\text{Ru}(\text{H}_2\text{O})]^{2+}$ undergo two pH-dependent, chemically reversible one-electron oxidations corresponding to the associated Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples. In acetonitrile, the μ -oxo ions *cis*- and *trans*- $[(\text{trpy})(\text{pic})\text{Ru}(\text{H}_2\text{O})_2]^{2+}$ undergo reversible one-electron oxidations and reductions while in water a two-electron, pH-dependent, chemically reversible reduction occurs for which the resulting II,II ion appears to be stabilized by formation of a μ -hydroxo bridge.

Introduction

There is by now an extensive higher oxidation state chemistry of Os and Ru based on polypyridyl containing complexes.² The higher oxidation states can be reached from the corresponding aqua complexes of Ru(II) or Os(II) by sequential oxidation and proton loss, e.g., eq 1,^{2a,b} where bpy is 2,2'-bipyridine and py is



pyridine. The higher oxidation states have an extensive stoichiometric and catalytic chemistry as oxidants.³ One of the

features of interest in this chemistry for us has been that in contrast to more conventional oxidants like MnO_4^- or CrO_3 , it is possible, at least in principle, to create a family of related oxidants where the redox characteristics can be varied systematically by changing the ligands.

Progress has been made in the design of new oxidatively stable ligand systems that are capable of supporting the higher oxidation states of Ru and Os, most notably by Che and co-workers.⁴ We report here on the redox properties of a series of polypyridyl

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