inspection of Table VI reveals that ΔE_Q values increase steadily as the precentage of $S = {}^3/_2$ character increases. We have noted previously the correlation of large ΔE_Q with small spin-orbit coupling (ζ) and small hyperfine field ($P\kappa/g_N\beta_N$).[5,7] The results suggest that the carborane ligand is a stronger field ligand than hexafluoroantimonate since they analyze for 92 and 98% $S = {}^3/_2$, respectively. This is interesting because viewing their structures solely in the context of spin state would lead to the opposite conclusion. The Fe-N bond lengths and the Fe out-of-plane displacements[11] are smaller for the carborane than for the hexafluoroantimonate, as expected for a *lower* $S = {}^5/_2$ contribution. An explanation lies in the interplay of field strengths and binding strength and reminds us that these factors are not synonymous nor necessarily correlated. The p_π donor capability of the fluoride donor apparently makes SbF_6^- a weaker field ligand than $B_{11}CH_{12}^-$ despite the stronger binding indicated in the structural comparison. The carborane is not capable of p_π donation. If the two anions were hypothetically assumed to have equal σ-donor interactions, then the SbF_6^- coordination parameters would be expected to be the same as or *smaller than* $B_{11}CH_{12}^-$. That they are larger indicates that the σ-donor interaction of SbF_6^- is considerably greater than that of $B_{11}CH_{12}^-$. This further supports the hypothesis[11] that $B_{11}CH_{12}^-$ is the lesser coordinating of these two anions.

In summary, a combination of susceptibility and Mössbauer studies and a knowledge of structure lead to a good quantitative description of the magnetic properties of intermediate-spin iron(III) porphyrins. Previously unrecognized intermolecular antiferromagnetic coupling of moderate magnitude seems to be the rule rather than the exception in five-coordinate complexes, particularly when association into dimers occurs in the crystal lattice. The question of spin coupling among six-coordinate porphyrin complexes remains open since coupling involving more than a pair of lattice sites does not provide an easily identified signature in the Mössbauer spectrum.

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Registry No. $[Fe(TPP)(B_{11}CH_{12})]\cdot C_7H_8$, 102149-51-9; Fe(TPP)Br, 25482-27-3.

Supplementary Material Available: For $[Fe(TPP)(B_{11}CH_{12})]\cdot C_7H_8$, Table IS (magnetic measurements), Tables IIS and IIIS (fixed atomic coordinates), and Table IVS (anisotropic temperature factors) (5 pages); a listing of observed and calculated structure amplitudes (×10) (25 pages). Ordering information is given on any current masthead page.

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Direct Synthesis of VE^{2+} (E = S, Se) Complexes Using Elemental Chalcogens. Preparation, Structure, and Properties of $[VS(SPh)_4]^{2-}$ and $[VSe(edt)_2]^{2-}$ (edt^{2-} = Ethane-1,2-dithiolate)

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The reaction of elemental sulfur or selenium with VCl_3/sodium thiolate reaction mixtures in MeCN provides a convenient and direct route to mononuclear complexes containing the VE^{2+} (E = S, Se) moiety. The preparation of complexes containing the $[VS(SPh)_4]^{2-}$, $[VSe(SPh)_4]^{2-}$, or $[VSe(edt)_2]^{2-}$ dianion is described. $[PhCH_2NMe_3]_2[VS(SPh)_4]$ (**1**) crystallizes in monoclinic space group $P2_1$ with unit cell dimensions (at −156 °C) of a = 10.312 (4) Å, b = 16.293 (6) Å, c = 13.930 (6) Å, β = 117.57 (2)°, and Z = 2. The anion contains a vanadium(IV) center in its characteristic square-pyramidal geometry with a multiply bonded S atom in the apical position and four benzenethiolate S atoms in the basal positions. The V═S bond length is 2.078 (2) Å. $(NEt_4)_2[VSe(edt)_2]$ (**3**) crystallizes in orthorhombic space group $P2_1ab$ with unit cell dimensions (at −155 °C) of a = 15.005 (4) Å, b = 12.769 (3) Å, c = 14.248 (3) Å, and Z = 4. Again, the vanadium(IV) center has square-pyramidal geometry with a multiply bonded Se atom in the apical position and four thiolate S atoms from two chelating edt^{2-} groups occupying the basal positions. Complex **3** is the first structurally characterized example of a VSe^{2+} species. The V═Se bond length is 2.196 (3) Å. Complex **1** is only the third example of a structurally characterized VS^{2+} species. A linear relationship has been found to exist between the bond length and the IR stretching frequency of the the V═S unit.

Introduction

Research in this group is directed toward the development of discrete metal-sulfide-thiolate chemistry for an early 3d transition metal, namely vanadium. Preliminary progress has been the subject of several recent reports,[2-7] and we now have V/S/SR species spanning the oxidation level range III-V and nuclearities of 1-4. In one of these reports[2] we described how the oxovanadium(IV) complex $[VO(edt)_2]^{2-}$ could be converted to the sulfur analogue $[VS(edt)_2]^{2-}$ by treatment with $(Me_3Si)_2S$. While pure product was obtained, its yield was relatively low (34%) and, of course, this procedure required prior preparation of the oxo complex. As we continued to extend our studies of V/S/SR chemistry, it was recognized that a direct synthetic route to thiovanadium(IV) complexes could make available large quantities and allow future reactivity studies of these highly reactive materials to be more conveniently performed. We thus decided to seek such a direct synthetic procedure and herein report the results of this search. As we describe below, this objective has been realized. We have also extended it and developed a direct route to complexes containing the extremely rare $[V{=}Se]^{2+}$ unit, and describe the first structural characterization of such a species.

Experimental Section

Syntheses. All manipulations were performed by using standard inert-atmosphere techniques and a purified dinitrogen atmosphere. MeCN (CaH_2) and Et_2O (Na/benzophenone) were purified by distillation and thoroughly degassed before use. Dry NaSPh and Na_2edt were prepared

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from the thiol and Na metal in THF; the resulting white powder was collected by filtration, washed well with THF, and dried in vacuo. VCl_3 was used as received.

$(PhCH_2NMe_3)_2[VS(SPh)_4]$ (1). A stirred slurry of NaSPh (6.60 g, 50 mmol) and $(PhCH_2NMe_3)Cl$ (3.70 g, 20 mmol) in MeCN (70 mL) was treated with solid VCl_3 (1.57 g, 10 mmol). Initially, a dark brown coloration was observed, but this converted to an orange powder after ca. 2 min, presumably a polymeric V/SPh species. Addition of sulfur (0.32 g, 10 mmol) caused the rapid formation of an intense orange-brown solution and dissolution of the majority of the solid material. After being stirred a further 2 h, the solution was filtered and Et_2O (35 mL) added to yield a dark brown oil that crystallized on agitation. After storage in a freezer overnight, the solid was collected by filtration, washed with $MeCN/Et_2O$ (1:2), and dried in vacuo. The filtrate was left undisturbed at ambient temperature for several days, and a second crop of well-formed crystals was isolated as above. The majority product, the first crop, was repeatedly found by IR spectroscopy to be contaminated with relatively small, but nevertheless significant, amounts of an unidentified component, and attempted purification by recrystallization was unsuccessful due to the instability of **1** on redissolution. The second crop, representing an overall yield of ~10%, was found to be analytically pure and suitable for structural studies and was used for product characterization. Anal. Calcd for $C_{44}H_{52}N_2S_5V$: C, 64.4; H, 6.4; N, 3.4. Found: C, 64.5; H, 6.4; N, 3.4. $\nu(VS) = 521\ cm^{-1}$.

$(PhCH_2NMe_3)_2[VSe(SPh)_4]$ (2). The previous procedure, employing NaSPh (3.96 g, 30 mmol), $(PhCH_2NMe_3)Cl$ (1.86 g, 10 mmol), and VCl_3 (0.79 g, 5 mmol), was followed until the orange slurry was obtained. At this point, elemental selenium (gray; 0.40 g, 5 mmol) was added, rapidly yielding an intense orange-brown solution and some brown precipitate. After the reaction mixture was stirred for a further 1.5 h, the brown solid was removed by filtration and Et_2O (14 mL) slowly added to the stirred filtrate. After overnight storage at room temperature, the resulting well-formed brown crystals were collected by filtration, washed with $MeCN/Et_2O$ (2:1) and Et_2O, and dried in vacuo. This material was found to be analytically pure, and no second crop was sought. The yield was 2.17 g (50%). Anal. Calcd for $C_{44}H_{52}N_2S_4SeV$: C, 60.9; H, 6.0; N, 3.2; S, 14.8; V, 5.9. Found: C, 60.8; H, 6.1; N, 3.5; S, 14.9; V, 6.2. The material was again found to be too unstable on redissolution to allow recrystallization. The NMe_4^+ salt can be prepared analogously.

$(NEt_4)_2[VSe(edt)_2]$ (3). To a slurry of Na_2edt (1.24 g, 9 mmol) in MeCN (30 mL) were added NEt_4Br (1.26 g, 6 mmol) and elemental Se (0.24 g, 3 mmol). After the mixture was stirred for a few minutes, solid VCl_3 (0.47 g, 3 mmol) was added, and this reacted rapidly to yield an intense orange-brown solution and some off-white solid (NaCl). After a further 3-h reaction time, the solution was filtered and Et_2O (20 mL) added to the filtrate. Precipitation of a microcrystalline solid began almost immediately. The flask was left undisturbed at room temperature overnight and the product collected by filtration, washed with $MeCN/Et_2O$ (1:1), and dried in vacuo. Additional Et_2O (5 mL) was added to the filtrate (without washings) and the flask stored at −20 °C for 3 days. An additional crop of dark brown crystals, which were found suitable for structural studies, was collected as above. The combined yields were ~50–55%. Anal. Calcd for $C_{20}H_{48}N_2S_4SeV$: C, 41.8; H, 8.4; N, 4.9; V, 8.9. Found: C, 41.9; H, 8.7; N, 5.1; V, 8.5. Electronic spectrum in MeCN λ_{max}, nm (ϵ_M, L mol^{-1} cm^{-1}): 436 (3275), 500 (sh, 1724).

X-ray Studies. Data were collected at approximately −155 °C on a Picker four-circle diffractometer. Details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[8] The structures were solved by the usual combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least squares. Full details of the data collection and structure refinement are listed in Table I.

For complex **1**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with systematic absences of $0k0$ for $k = 2n + 1$ and monoclinic symmetry, indicating either $P2_1$ or $P2_1/m$ as the space group. Subsequent solution and refinement confirmed the noncentrosymmetric choice. All non-hydrogen atoms were readily located with no disorder problems; these atoms were refined with anisotropic thermal parameters. In the latter stages, all hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen parameters and were included in the final refinement cycles with isotropic thermal parameters. A final difference Fourier was essentially featureless, with the largest peak being 0.25 e/Å^3. Final values of discrepancy indices R and R_w are included in Table I.

Table I. Crystallographic Data for Complexes **1** and **3**

param	**1**	**3**
formula	$C_{44}H_{52}N_2S_5V$	$C_{20}H_{48}N_2S_4SeV$
M_r	820.18	574.79
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$P2_1ab$
temp, °C	−156	−155
a, Å	10.312 (4)[a]	15.005 (4)[b]
b, Å	16.293 (6)	11.769 (3)
c, Å	13.930 (6)	14.248 (3)
β, deg	177.57 (2)	...
Z	2	4
vol, Å^3	2074.76	2729.94
λ(Mo Kα),[c] Å	0.710 69	0.710 69
abs coeff	5.072	19.764
cryst size, mm	0.18 × 0.18 × 0.25	0.13 × 0.15 × 0.20
scan speed, deg/min	4.0	4.0
scan width, deg	1.6 + dispersion	2.0 + dispersion
scan range, deg	$6 \leq 2\theta \leq 45$	$6 \leq 2\theta \leq 45$
tot. no. of data	4104	2107
no. of unique data	2836	1882
av R	0.025[d]	*e*
no. of obsd data	2556, $F > 2.33\sigma(F)$	1681, $F > 3.00\sigma(F)$
R,[f] %	3.33	5.78
R_w,[g] %	3.38	5.84
goodness of fit[h]	0.736	1.368

[a] 30 reflections at −156 °C. [b] 36 reflections at −155 °C. [c] Graphite monochromator. [d] 1201 reflections measured more than once. [e] Zero reflections measured more than once. [f] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [g] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$. [h] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsns} - N_{params})]^{1/2}$.

For complex **3**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to either of the orthorhombic space groups $Pmab$ and $P2_1ab$. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric choice $P2_1ab$. The non-hydrogen atoms were readily located, and one NEt_4^+ cation was found to contain a disorder problem. The methylene carbons were disordered between two distinct sites with occupancies that refined to 60 and 40%. All non-hydrogen atoms were refined with anisotropic thermal parameters, and because of the disorder, no attempt was made to include the hydrogen atoms in the refinement except as fixed atom contributors. No hydrogen atoms were placed on the disordered cation. A final difference Fourier was essentially featureless with the largest peak being 0.63 e/Å^3. Final values of discrepancy indices R and R_w are included in Table I.

Since both complexes **1** and **3** crystallize in noncentrosymmetric space groups, the solutions of opposite hand were also investigated. In both cases, the alternative solutions gave higher values of discrepancy index R.

Other Measurements. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 238 spectrophotometer. Electronic spectra were recorded in MeCN solution on a Hewlett Packard Model 8450A spectrophotometer.

Results and Discussion

Syntheses. After it was decided that a direct synthesis of complexes containing the VS^{2+} moiety would be beneficial, the question arose as to how to effect this synthesis. Obviously, a procedure employing elemental sulfur would be the most desirable, and one such example had, in fact, already been reported. The reaction of vanadium(II) porphyrins with S_8 had been shown to yield the corresponding thiovanadium(IV) porphyrins.[9] We naturally desired to avoid the need for prior synthesis of vanadium(II) thiolates and we, therefore, decided to investigate the reactions of S_8 with commercially available VCl_3, the most convenient source of low-oxidation-state vanadium, in the presence of excess thiolate. This strategy has proven successful. The procedure essentially entails oxidative addition of sulfur to vanadium, but with electrons from both vanadium(III) *and* thiolate groups effecting the reduction of sulfur to sulfide, as summarized in eq 1. The presence of quaternary ammonium cations in the

$$VCl_3 + S + 5NaSR \xrightarrow{MeCN} Na_2[VS(SR)_4] + {}^1/_2RSSR + 3NaCl \quad (1)$$

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Table II. Fractional Coordinates and Isotropic Thermal Parameters for **1**[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
V(1)	5022 (1)	2296	7415 (1)	14
S(2)	4643 (2)	1520 (1)	8442 (1)	20
S(3)	3766 (1)	1809 (1)	5604 (1)	18
C(4)	1867 (5)	1711 (3)	5160 (4)	15
C(5)	1279 (6)	1495 (4)	5843 (5)	20
C(6)	−192 (6)	1338 (4)	5457 (5)	21
C(7)	−1143 (6)	1375 (4)	4356 (5)	22
C(8)	−580 (6)	1594 (4)	3668 (5)	25
C(9)	908 (6)	1757 (4)	4053 (4)	24
S(10)	7128 (1)	1807 (1)	7300 (1)	20
C(11)	6821 (5)	805 (3)	6727 (4)	17
C(12)	6798 (6)	685 (4)	5718 (5)	23
C(13)	6716 (7)	−105 (4)	5313 (5)	26
C(14)	6644 (6)	−777 (4)	5882 (5)	24
C(15)	6611 (7)	−653 (4)	6856 (5)	27
C(16)	6690 (6)	118 (4)	7262 (5)	22
S(17)	6635 (1)	3397 (1)	8418 (1)	21
C(18)	8248 (6)	3038 (4)	9533 (5)	21
C(19)	8263 (6)	2376 (4)	10175 (5)	23
C(20)	9536 (6)	2180 (4)	11099 (5)	24
C(21)	10790 (7)	2624 (5)	11398 (5)	33
C(22)	10807 (6)	3269 (5)	10767 (5)	29
C(23)	9566 (6)	3458 (4)	9841 (5)	22
S(24)	3236 (1)	3369 (1)	6779 (1)	19
C(25)	3297 (5)	3950 (4)	7883 (4)	19
C(26)	3388 (6)	3573 (4)	8805 (5)	22
C(27)	3312 (7)	4035 (4)	9615 (5)	25
C(28)	3160 (7)	4867 (4)	9532 (5)	28
C(29)	3113 (6)	5259 (4)	8643 (5)	25
C(30)	3178 (6)	4795 (4)	7814 (5)	20
N(31)	−1306 (5)	5857 (3)	761 (4)	21
C(32)	−801 (7)	5350 (4)	1768 (5)	30
C(33)	−250 (7)	5739 (5)	310 (5)	28
C(34)	−1286 (7)	6738 (4)	1059 (5)	28
C(35)	−2864 (7)	5595 (4)	−60 (5)	24
C(36)	−3487 (6)	6043 (4)	−1111 (5)	23
C(37)	−3348 (6)	5726 (4)	−1994 (5)	21
C(38)	−3944 (7)	6145 (4)	−2975 (5)	25
C(39)	−4662 (6)	6880 (4)	−3082 (5)	27
C(40)	−4846 (6)	7193 (4)	−2230 (5)	26
C(41)	−4247 (6)	6789 (4)	−1249 (5)	23
N(42)	8559 (5)	4016 (3)	6000 (4)	25
C(43)	6945 (7)	4036 (5)	5568 (6)	30
C(44)	9015 (7)	3147 (4)	6020 (6)	30
C(45)	9046 (7)	4538 (4)	5309 (5)	23
C(46)	9281 (7)	4346 (5)	7129 (5)	34
C(47)	8397 (6)	4288 (4)	4140 (5)	21
C(48)	9133 (7)	3749 (4)	3786 (5)	26
C(49)	8519 (7)	3528 (4)	2716 (5)	31
C(50)	7170 (8)	3829 (4)	1977 (5)	29
C(51)	6446 (7)	4374 (4)	2303 (5)	22
C(52)	7076 (7)	4617 (4)	3398 (5)	23

[a] Fractional coordinates are ×10^4; B_{iso} values are ×10.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for **3**[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
V(1)	2655	406 (2)	7313 (1)	12
Se(2)	2522 (2)	463 (1)	5779 (1)	31
S(3)	1287 (3)	−331 (3)	7816 (3)	18
C(4)	605 (9)	830 (13)	7553 (11)	22
C(5)	908 (10)	1751 (12)	8129 (12)	26
S(6)	2114 (3)	1978 (3)	7966 (3)	18
S(7)	3281 (3)	−1226 (3)	7788 (3)	20
C(8)	4460 (9)	−964 (11)	7986 (10)	16
C(9)	4771 (8)	10 (11)	7430 (10)	15
S(10)	4071 (3)	1127 (3)	7692 (3)	16
N(11)	2734 (7)	407 (8)	759 (7)	13
C(12)	3172 (9)	−456 (11)	1343 (9)	14
C(13)	3737 (10)	−1220 (10)	800 (11)	19
C(14)	3437 (10)	986 (10)	182 (10)	16
C(15)	4149 (10)	1513 (10)	746 (11)	20
C(16)	2269 (9)	1133 (10)	1421 (9)	16
C(17)	1715 (10)	1957 (12)	975 (10)	23
C(18)	2089 (10)	−52 (11)	35 (11)	15
C(19)	1305 (10)	−651 (10)	469 (10)	16
N(20)	10266 (8)	7909 (9)	5263 (8)	17
C(21)	9706 (20)	6916 (23)	5378 (20	30 (6)
C(22)	8906 (12)	6844 (13)	4642 (11)	31 (3)
C(23)	10920 (17)	7966 (19)	6028 (17)	21 (5)
C(24)	11567 (11)	7052 (13)	6127 (12)	30 (3)
C(25)	10705 (14)	7859 (16)	4323 (15)	11 (4)
C(26)	11391 (11)	8678 (13)	4139 (11)	27 (3)
C(27)	9692 (15)	8910 (18)	5260 (16)	16 (4)
C(28)	9104 (11)	8976 (12)	6187 (11)	28 (3)
C(29A)[b]	10806 (28)	8835 (34)	5098 (29)	31 (8)
C(30A)[b]	10809 (26)	6867 (29)	5402 (27)	24 (7)
C(31A)[b]	9611 (36)	7767 (41)	4438 (35)	48 (11)
C(32A)[b]	9735 (28)	8035 (32)	6263 (28)	29 (8)

[a] Fractional coordinates are ×10^4; B_{iso} values are ×10. [b] The A suffix refers to the disorder positions of the cation methylene groups.

reaction mixture allows for isolation of the corresponding salt of the product.

Initial reactions employed NaSPh and led to isolation of complexes containing the $[VS(SPh)_4]^{2-}$ anion, as confirmed by crystallography. Unfortunately, this anion has only limited stability on redissolution in MeCN; an initially orange-brown solution turns purple within a few minutes and colorless on prolonged standing. This instability precluded recrystallization, for example, and would obviously be detrimental to future use of this complex as a synthetic reagent. Thus, although these preliminary experiments had been invaluable in establishing the feasibility of our synthetic approach, it was evident that more stable products should be sought (vide infra).

The now-established access to VS^{2+} species via S_8 and VCl_3 suggested that the corresponding reaction system employing elemental selenium might allow synthesis of the extremely rare VSe^{2+} unit. The synthesis of VSe(porph) (porph = a porphyrin ligand) by the reaction of V^{II}(porph) with $Cp_2Ti(Se_5)$ (Cp = cyclopentadienyl) had been reported;[9] but this represents somewhat of an inconvenient procedure, and no structural data are avilable. The procedure described above with VCl_3 was, therefore, investigated and found to successfully yield a VSe^{2+} species. Again, NaSPh was used initially, and salts containing the $[VSe(SPh)_4]^{2-}$ anion were obtained in good yields. Although extremely well-formed crystals were repeatedly obtained from multiple preparations, they were found to be poor diffractors of X-rays. In addition, the $[VSe(SPh)_4]^{2-}$ anion was found to be unstable on redissolution, and again, as for the $[VS(SPh)_4]^{2-}$ complexes, it was evident that more stable products were needed.

The ligand edt^{2-} (ethane-1,2-dithiolate) had been previously shown by us to yield stable, recrystallizable salts containing the $[VS(edt)_2]^{2-}$ anion.[2] We thus turned to the use of this dithiolate in the direct synthesis procedure. It was subsequently established that high yields (≥60%) of salts containing $[VS(edt)_2]^{2-}$ could be directly obtained. We refrain from further discussion here because the synthesis of these salts will be described as part of a full report on the synthesis of various-nuclearity V/S/edt complexes as a function of varying the S:V ratio.[7]

Similarly, use of Na_2edt in the reaction of Se with VCl_3 gave good yields of the $[VSe(edt)_2]^{2-}$ anion, which was isolated in analytical purity as its $NEt_4{}^+$ salt. This complex is much more stable than the PhS$^-$ complex, although instability on redissolution in MeCN was again evident on standing. Nevertheless, crystals were found to be good diffractors of X-rays, allowing the first structural characterization of the VSe^{2+} moiety.

Description of Structures. Fractional coordinates for the nonhydrogen atoms of complexes **1** and **3** are listed in Tables II and III, respectively.

The structure of the anion of **1** is depicted in Figure 1. The vanadium has square-pyramidal geometry with multiply bonded S(2) in the apex and four S atoms from PhS$^-$ groups occupying the basal positions. The vanadium atom is 0.807 Å above the S(3, 10, 17, 24) least-squares plane. The VS_5 core closely approaches C_{4v} symmetry, as emphasized by the narrow range of the S(2)–V–S and S–V–S angles, 110.73–108.07 (7) and 82.96–84.42

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

V(1)-S(2)	2.078 (2)	V(1)-S(3)	2.377 (2)
		V(1)-S(10)	2.388 (2)
S(3)-V(1)-S(17)	139.15 (6)	V(1)-S(17)	2.405 (2)
S(10)-V(1)-S(24)	141.93 (6)	V(1)-S(24)	2.392 (2)
mean	140.54	mean	2.391
S(2)-V(1)-S(3)	110.10 (7)	S(3)-V(1)-S(10)	83.26 (6)
S(2)-V(1)-S(10)	108.07 (7)	S(3)-V(1)-S(24)	84.42 (6)
S(2)-V(1)-S(17)	110.73 (7)	S(10)-V(1)-S(17)	83.22 (6)
S(2)-V(1)-S(24)	110.00 (7)	S(17)-V(1)-S(24)	82.96 (6)
mean	109.73	mean	83.47

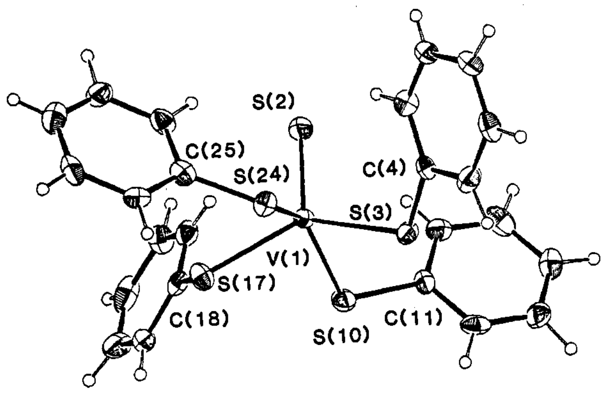

Figure 1. ORTEP projection of the anion of complex **1** at the 50% probability level, showing the atom-numbering scheme. Phenyl carbons are numbered consecutively around the ring.

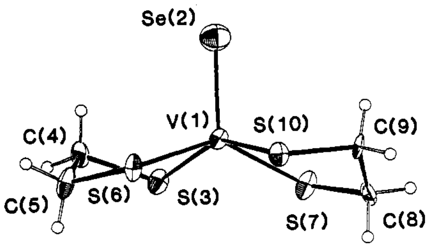

Figure 2. ORTEP projection of the anion of complex **3** at the 50% probability level, showing the atom-numbering scheme.

(6)°, respectively. The V–S–C angles are in the range 110.96 (18)–112.36 (21)°, and the Ph rings are folded up toward the apical sulfur, presumably due to packing effects since both cations lie below the S_4 basal plane. The four Ph rings are arranged in a four-blade propeller fashion imparting near-C_4 symmetry to the whole anion.

A comparison between the anion of **1** and the $[VS(edt)_2]^{2-}$ anion[2] shows that in the former the V═S bond is shorter (2.078 (2) vs. 2.087 (1) Å) and the V–SR bonds are on average longer (2.391 vs. 2.364 Å). This is consistent with the fact that PhS^- is less basic than edt^{2-}, leading to a compensatory increase in axial V–S π-bonding and a resulting shorter and stronger multiple bond. This difference is also reflected in the IR spectra (vide infra).

The structure of the anion of **3** is depicted in Figure 2. The coordination geometry of the vanadium atom is again square pyramidal with multiply bonded Se(2) occupying the apical position and four dithiolate S atoms in the basal positions. The V═Se bond length is 2.196 (3) Å, a value longer than in the corresponding $[VS(edt)_2]^{2-}$ anion (2.087 (1) Å), as expected for the greater size of Se. The $VSeS_4$ core closely approaches C_{4v} symmetry, as evidenced by the structural parameters in Table V, and the overall anion has near-C_{2v} symmetry.

Complex **3** extends to 3 the number of structurally characterized members of the $[VE(edt)_2]^{2-}$ series (E = O, S, Se). The influence of the nature of the axial ligand on the structural parameters of this series can now be better examined, and pertinent details are collected in Table VI. As can be seen, mean basal V–S bond lengths and E–V–S angles are very similar between the three complexes, differences being almost insignificant within the 3σ criterion. As might be expected, the only major differences are in the apical V═E bond lengths and their associated IR stretching frequencies. The band for V═Se was found at 397 cm^{-1}; the corresponding frequencies in a series of selenovanadium(IV) porphyrins were found to be in the 434–447 cm^{-1} range,[9] consistent with greater electron donation from thiolate vs. porphyrin ligation. We have repeatedly observed that thiolate ligation leads to a decrease in the V═E stretching frequency when compared with O- or N-based ligation.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

V(1)-Se(2)	2.196 (3)	V(1)-S(3)	2.370 (4)
		V(1)-S(6)	2.357 (4)
S(3)-V(1)-S(10)	149.22 (15)	V(1)-S(7)	2.384 (4)
S(6)-V(1)-S(7)	140.18 (16)	V(1)-S(10)	2.378 (4)
mean	144.70	mean	2.372
Se(2)-V(1)-S(3)	103.63 (14)	S(3)-V(1)-S(6)	85.42 (15)
Se(2)-V(1)-S(6)	109.47 (14)	S(3)-V(1)-S(7)	84.72 (14)
Se(2)-V(1)-S(7)	110.34 (14)	S(6)-V(1)-S(10)	83.58 (14)
Se(2)-V(1)-S(10)	107.14 (13)	S(7)-V(1)-S(10)	85.54 (14)
mean	107.65	mean	84.82

Table VI. Comparison of Selected Structural Parameters and IR Stretching Frequencies of $[VE(edt)_2]^{2-}$ Complexes (E = O, S, Se)

param	E = O	E = S	E = Se
V–E, Å	1.625 (2)	2.087 (1)	2.196 (3)
V–S,[a] Å	2.378	2.364	2.372
E–V–S,[a] deg	106.34	109.41	107.65
S–V–S,[a] deg	85.56	83.76	84.82
$V-S_4$,[b] Å	0.668	0.784	0.719
ν(V═E), cm^{-1}	930[c]	502[c]	397[d]

[a] Mean of four values. [b] Vanadium to S_4 least-squares plane. [c] NMe_4^+ salt. [d] NEt_4^+ salt.

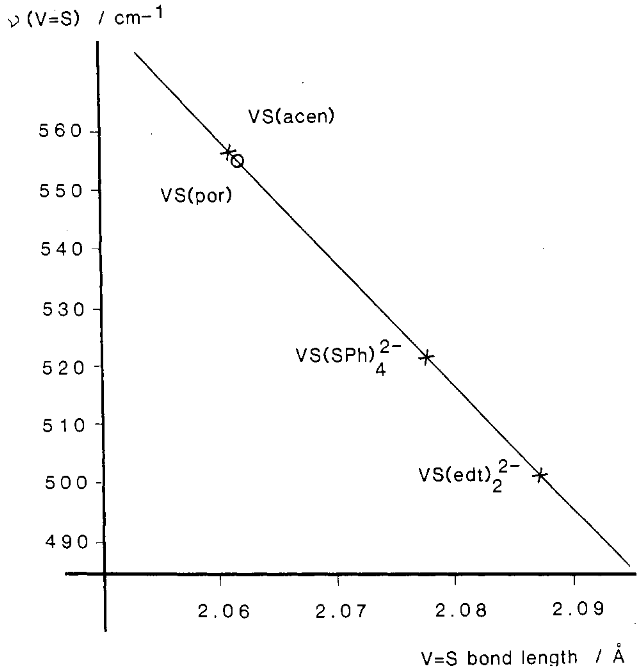

Figure 3. Plot of $V═S^{2+}$ stretching frequency as a function of $V═S^{2+}$ bond length in structurally characterized thiovanadyl complexes (acen = *N*,*N'*-ethylenebis(acetylacetonylideneaminato)).[12]

The electronic spectrum of complex **3** in MeCN solution displays a maximum at 436 nm and a prominent shoulder at ~500 nm. The positions of these absorption peaks follow the trend expected for the $[VE(edt)_2]^{2-}$ series; i.e., the transitions are shifted to lower energy in the order E = O, S, Se.[2,3]

Correlation of V═S Bond Length with IR Stretching Frequency. The structural characterization of complex **1** brings to 3 the number of $[VS]^{2+}$ complexes for which crystal structures have been obtained. This number represents the absolute minimum required to attempt a correlation between the V═S bond length and its associated IR stretching frequency. Note that it is important to compare structural data with solid (Nujol mull) IR data so that any solid-state effects on these parameters are present in *both* measurements.

In Figure 3 is presented a plot of bond length vs. IR stretching frequency. As is evident in this figure, a linear dependence is observed. The edt^{2-} ligated complex leads to the longest V═S bond length and lowest stretching frequency. Of the several parameters probably influencing the observed data, no doubt the total electron-donating ability of the basal ligands and the overall charge of the complex are of paramount importance. It should be said that we have not observed such a linear dependence on comparing V═O bond lengths in the literature with their associated stretching frequencies. This is probably due to the stronger nature of the $V{=}O^{2+}$ bond vs. the $V{=}S^{2+}$ bond, making the former less responsive to differences in complex charge and the electron-donating abilities of the basal ligands, and possibly to other factors being of equal or even greater importance such as axial–basal ligand–ligand repulsions, which would be attenuated with the longer $V{=}S^{2+}$ bond.

The plot of Figure 3 is somewhat preliminary and must obviously stand the test of time as more data points become available, at which time more general conclusions may be possible. Nevertheless, we present this plot at such an early stage because it can already be put to some interesting use. Poncet et al. have studied the VS(por) (por = octaethylporphyrin) complex by the EXAFS technique and obtained a value of 2.06 ± 0.01 Å for the V═S bond length.[9] Using their reported value of 555 cm^{-1} for ν(V═S) in this complex, we predict from Figure 3 a value of 2.062 Å for the V═S bond length, in excellent agreement with the EXAFS conclusion. This agreement both supports the accuracy of the EXAFS technique for obtaining such bond lengths and supports the validity of the correlation of Figure 3. This plot may thus have some value in the future should, for instance, an EXAFS study be carried out on thiovanadyl species formed on the surface of HDS catalysts during refining of vanadium-rich, heavier crudes.[10,11] A knowledge of the V═S bond length could allow conclusions to be reached about the identity of other ligands bound to the metal by reference to Figure 3 in its future version containing more data points.

In summary, a direct-synthesis procedure has now been developed for mononuclear vanadium thiolate species containing the $V{=}E^{2+}$ (E = S, Se) moiety and thus avoiding the need for prior synthesis of the $V{=}O^{2+}$ analogue. This development should make future reactivity studies of these species much more convenient to perform. This is particularly true for the E = Se species for which no facile synthetic route has been available to date. Further studies in vanadium/sulfur (selenium) chemistry are in progress.

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Supplementary Material Available: Complete listings of atom coordinates, thermal parameters, and bond distances and angles (18 pages); listings of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (Nos. 86022 and 86115 for **1** and **3**, respectively) are available on request from the Indiana University Chemistry Library.

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Oxidation of Thiolate Ligands in Cyclopentadienyltungsten Carbonyl Complexes

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The reaction between MCPBA (*m*-chloroperoxybenzoic acid) and a wide variety of $CpW(CO)_3SR$ compounds [SR = SCH_3, SC_6H_5, S(*p*-$C_6H_4CH_3$), S(*p*-C_6H_4Cl), S(*p*-$C_6H_4NO_2$), S(*p*-$C_6H_4NH_2$), S(*o*-$C_6H_4NH_2$), Me_2dtc, S(2-py), and S(2-btz) where substituent abbreviations are 2-py = 2-pyridyl, 2-btz = 2-benzothiazolyl, Me_2dtc = dimethyldithiocarbamato; others are substituted phenyl] is a superior synthetic method for preparation of sulfinato-*S* ($-S(O)_2R$) compounds of tungsten. Yields of these compounds are excellent, and preparation of a pure product from the original tricarbonyl thiolate complex generally requires less than 3 h. In addition, the reaction of MCPBA and $CpW(CO)_2(PPh_3)STol$ (Tol = *p*-$C_6H_4CH_3$) is an efficient method for synthesis of the triphenylphosphine-substituted sulfinato-*S* compound $CpW(CO)_2(PPh_3)SO_2Tol$. Photolyses of $CpW(CO)_3SO_2R$, both by itself (R = Ph) and in the presence of triphenylphosphine (R = Ph, Tol), indicate that carbonyl loss is an important photochemical reaction of these sulfinato-*S* compounds, although the latter reaction unexpectedly yields $CpW(CO)_2(PPh_3)SR$ instead of the simple substitution product $CpW(CO)_2(PPh_3)SO_2R$. The results of unsuccessful attempts to prepare tungsten sulfenato-*S* ($-S(O)R$) compounds by the reactions of $[CpW(CO)_3]^-$ with methanesulfinyl chloride and of $CpW(CO)_3SPh$ with SeO_2 are also detailed.

Organic peracids such as MCPBA (*m*-chloroperoxybenzoic acid) and peroxyacetic acid have been shown to be useful reagents for the oxidation of elemental sulfur[1] and organic sulfides.[2] Recently, it has been reported that organic peroxyacids will rapidly and selectively oxidize inorganic sulfur, selenium, and tellurium in μ_3-E (E = S, Se, Te) and η^2-E_2 (E = S, Se) ligands.[3] Other work[4] has demonstrated the oxidation of the bridging sulfide ligand in $Pt_2(dpm)_2(\mu\text{-}S)Cl_2$ [dpm = bis(diphenylphosphino)methane].

The original impetus for our work was to synthesize new examples of compounds containing coordinated sulfur monoxide. The recent findings[3] that MCPBA reacts with $[Ir(S)_2(dppe)_2]^+$ to give $[Ir(S_2O)(dppe)_2]^+$ and with $Fe_2Pt(S)_2(CO)_6(PPh_3)_2$ to yield $Fe_2Pt(SO)(S)(CO)_6(PPh_3)_2$ prompted our further investigation of MCPBA oxidations. Few SO compounds are presently known,

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