A New Vanadium(V) Persulfide Complex: (NEt4)[VO(S2)2(bpy)]

Stephanie L. Castro, James D. Martin, and
George Christou*

Department of Chemistry and the Molecular Structure
Center, Indiana University, Bloomington, Indiana 47405

Introduction

Over the last several years, we have been investigating nonorganometallic vanadium/sulfide chemistry, concentrating on the higher metal oxidation states (III–V). We have found this area to be rich in structural types and reactivity characteristics.[1] Together with related efforts by others,[2–6] an impressive pool of complexes has now been made available spanning a variety of nuclearities and oxidation levels, including mixed valency. Our interest in this area stems from the conversion of crude oil vanadyl impurities to polymeric vanadium sulfides under the sulfur-rich conditions present during catalytic hydrodesulfurization and hydrodemetalation processes.[7] A variety of discrete V/S species are probably forming as intermediates, and the characterization of V/S species thus becomes of relevance to the understanding of these transformations.

The area of impact of the present work is vanadium persulfide chemistry. A number of V complexes of various metal nuclearities are now known that contain S_2^{2-} groups, in either terminal or bridging modes.[1c,i,4–6,8–10] With very few exceptions, these involve V^{III} or V^{IV}. Persulfido complexes containing V^V are extremely rare, presumably due to the redox instability of this highest V oxidation state in the presence of moderate reducing agents; in fact, to our knowledge, the only characterized example is $(Me_3NCH_2Ph)_2[VS_2(S_2)(SPh)]$.[1i] However, we herein report a convenient, high-yield procedure to a second V^V persulfide complex

(1) (a) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297. (b) Money, J. K.; Folting, K.; Huffman, J. C.; Collison, D.; Temperly, J.; Mabbs, F. E.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4583. (c) Money, J. K.; Nicholson, J. R.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4072. (d) Money, J. K.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 2210. (e) Money, J. K.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1987**, *26*, 944. (f) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1988**, *27*, 507. (g) Christou, G.; Heinrich, D. D.; Money, J. K.; Rambo, J. R.; Huffman, J. C.; Folting, K. *Polyhedron* **1989**, *8*, 1723. (h) Heinrich, D. D.; Folting, K.; Huffman, J. C.; Reynolds, J. G.; Christou, G. *Inorg. Chem.* **1991**, *30*, 300. (i) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204.

(2) (a) Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.

(3) Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.

(4) Al-Ani, F. T.; Hughes, D. L.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1705.

(5) Duraj, S. A.; Andras, M. T.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 1232.

(6) (a) Yang, Y.; Huang, L.; Liu, Q.; Kang, B. *Acta Crystallogr.* **1991**, *C47*, 2085. (b) Yang, Y.; Liu, Q.; Huang, L.; Kang, B.; Lu, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1512.

(7) (a) Silbernagel, B. G. *J. Catal.* **1979**, *56*, 315. (b) Rosa-Brussin, M.; Moranta, D. *Appl. Catal.* **1984**, *11*, 85. (c) Silbernagel, B. G.; Mohan, R. R.; Singhal, G. H. *ACS Symp. Ser.* **1984**, *248*, 91. (d) Mitchell, P. C. H.; Scott, C. E.; Bonnelle, J.-P.; Grimblot, J. G. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1047. (e) Asaoka, S.; Nakata, S.; Takeuchi, C. *ACS Symp. Ser.* **1987**, *344*, 275.

(8) (a) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551. (b) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321. (c) Bolinger, C. M.; Weatherill, T. D.; Rauchfuss, T. B.; Rheingold, A. L.; Day, C. S.; Wilson, S. R. *Inorg. Chem.* **1986**, *25*, 634.

(9) Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.

(10) Floriani, C.; Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2099.

Table I. Crystallographic Data for (NEt4)[VO(S2)2(bpy)]·MeCN (1·MeCN)

$C_{20}H_{31}N_4OS_4V$	fw = 522.67
monoclinic	$P2_1$ (No. 4)
$a = 6.948(1)$ Å	$T = -154$ °C
$b = 13.547(1)$ Å	$\lambda = 0.710\ 69$ Å
$c = 12.930(1)$ Å	$\rho_{calcd} = 1.428$ g cm^{-3}
$\beta = 92.45(1)°$	$\mu = 7.436$ cm^{-1}
$V = 1216.01$ Å^3	$R^a = 0.0209$
$Z = 2$	$R_w^b = 0.0242$

$^a R = \sum\|F_o\| - \|F_c\|/\sum\|F_o\|$. $R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$, where $w = 1/\sigma^2(\|F_o\|)$.

together with its characterization by single-crystal X-ray diffractometry and spectroscopy.

Experimental Section

All manipulations were carried out using standard Schlenk-line techniques or an inert-atmosphere glovebox. Solvents were distilled before use from CaH₂ (MeCN) or Na/benzophenone (Et₂O), except anhydrous EtOH which was used as received in Sure-Seal bottles (Aldrich). Anhydrous Li₂S and elemental S and bpy were used as received. (NEt4)₂[VOCl4] was prepared as described elsewhere.[11]

Preparation of (NEt4)[VO(S2)2(bpy)]·MeCN (1). In an inert-atmosphere glovebox, (NEt4)₂[VOCl4] (0.48 g, 1.0 mmol), sulfur (0.080 g, 2.5 mmol), Li₂S (0.115 g, 2.50 mmol), and bpy (0.803 g, 5.15 mmol) were placed in a flask. The flask was brought into the laboratory and attached to a Schlenk line, and a 1:1 mixture of MeCN/EtOH (80 mL) was added by syringe; the reaction mixture was then stirred overnight at ambient temperature. The resulting deep red solution was filtered, Et₂O (40 mL) added to the filtrate, and the flask stored in a freezer for 1 week. Red/black needles of complex 1·MeCN were collected by filtration, washed with Et₂O, and dried briefly *in vacuo*. The yield was 0.287 g (55%). The same reaction with a V:bpy ratio of 1:1 gave yields of *ca.* 25%. The presence of one interstitial MeCN molecule was demonstrated by the crystallographic studies, but analytical data for a sample vacuum-dried for a more extended period (*ca.* 2 h) indicated loss of the MeCN groups. Anal. Calcd (found) for C₁₈H₂₈N₃OS₄V: C, 44.89 (44.90); H, 5.86 (5.73); N, 8.72 (8.69). Electronic spectrum in MeCN (~5 mM), λ_{max}/nm (ϵ_M/L mol^{-1} cm^{-1}): 336 (7600), 384 (4270), 520 (874).

X-ray Crystallography. Data were collected 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.[12] The crystal employed was a fragment cleaved from a larger crystal and affixed to a glass fiber using silicone grease. It was then transferred to the goniostat where it was cooled to −154 °C for characterization and data collection (Table I). A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections exhibiting monoclinic symmetry. The systematic extinction of 0k0, k = 2n + 1, and subsequent refinement confirmed the space group P2₁. Following the usual data reduction and averaging of equivalent reflections, a unique set of 1682 reflections was obtained. Plots of the four standard reflections measured every 300 reflections showed no significant variation. The structure was solved using a combination of direct methods (SHELXS-86)[13] and standard Fourier techniques. After unsuccessful refinement in the centric space group P2₁/m, the acentric space group P2₁ was considered. The vanadium, sulfur, and oxygen atoms as well as two-thirds of the bpy atoms were located in the initial E map from SHELXS. All the remaining atoms, including the hydrogen atoms, were located in successive difference Fourier maps. The full-matrix, least-squares refinement was completed using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogens. All unique reflections were used for the refinement. An absorption correction was deemed unnecessary and was not performed. Since P2₁ is an acentric space group, the absolute structure for the crystal employed was determined by refinement of both possibilities. The final difference

(11) Rambo, J. R.; Christou, G. Manuscript in preparation.

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

(13) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; pp 175–189.

map was essentially featureless with the largest peaks being ≤ 0.33 e/Å³ in the immediate vicinity of the vanadium atom. Final values of conventional discrepancy indices R and R_W are listed in Table I.

Other Measurements. Infrared (Nujol mull) and electronic absorption solution spectra were recorded on Nicolet Model 510P and Hewlett-Packard Model 8452A spectrophotometers, respectively. [51]V NMR spectra (94.95 MHz) were obtained on a Nicolet NT360 instrument using a sample concentration of *ca.* 50 mM in CD₃CN and 5-mm tubes. Chemical shifts are quoted *versus* VOCl₃ in CDCl₃ as an external reference.

Results

Synthesis of Complex 1. The procedure described in the Experimental Section employs an equimolar mixture of Li₂S and elemental S as a potential source of S₂²⁻. In fact, since the V[IV] is oxidized to V[V], the sulfur reagents must also be involved in additional redox chemistry. The half-reactions describing the various redox changes are shown in eqs 1–3. The overall formation

$$V^{4+} - e^- \rightarrow V^{5+} \tag{1}$$

$$2.5S + 2.5S^{2-} \rightarrow 2.5S_2^{2-} \tag{2}$$

$$0.5S_2^{2-} + e^- \rightarrow S^{2-} \tag{3}$$
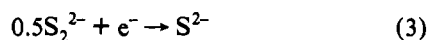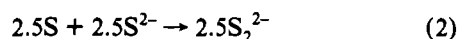
of complex 1 can now be summarized in eq 4; this equation predicts

$$VOCl_4{}^{2-} + 2.5S + 2.5S^{2-} + bpy \rightarrow$$

$$[VO(S_2)_2(bpy)]^- + S^{2-} + 4Cl^- \tag{4}$$
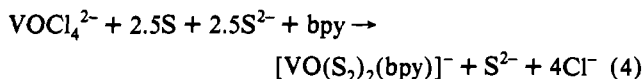
that a S:Li₂S ratio of 2.5:1.5 should suffice for the formation of 1, and we have indeed found that comparable yields are obtained from the 2.5:1.5 reaction system. Note also that the bpy:V ratio employed is larger than the 1:1 suggested by eq 4. In this case, we have found that the presence of excess bpy results in higher yields (approximately double) than for V:bpy = 1:1 reactions. The reason for this is unclear, but we note that the yield of MoO(S₂)₂(bpy) is also improved in the presence of a 100% excess of bpy.[14]

Description of Structure. Fractional coordinates and selected bond distances and angles are collected in Tables II and III, respectively. An ORTEP representation of the anion of 1 is presented in Figure 1. The V atom is seven-coordinate and possesses distorted pentagonal bipyramidal geometry. The multiply-bonded oxygen atom O(18) and bpy nitrogen atom N(17) occupy the axial sites (O(18)–V(1)–N(17) = 165.26(13)°). The anion has idealized C_s symmetry. The five equatorial ligating atoms are approximately in a plane; the maximum deviation from the S(2), S(3), S(4), S(5), N(6) least-squares plane is 0.033 Å for S(4), and V(1) lies 0.324 Å out of this plane toward O(18). The sum of the equatorial angles at V is 355.86°. As expected, there is a significant *trans* influence of O(18) on the V(1)–N(17) distance (2.302(3) Å), which is noticeably longer than equatorial V(1)–N(6) (2.139(3) Å). An alternative description of the metal coordination geometry as trigonal bipyramidal can be presented if the S₂²⁻ ligands are considered to be occupying a single site. If S(2/3) and S(4/5) are used to represent the midpoints of the S(2)–S(3) and S(4)–S(5) bonds, respectively, then the equatorial angles become N(6)–V(1)–S(2/3) = 111.4°, S(2/3)–V(1)–S(4/5) = 135.1°, and S(4/5)–V(1)–N(6) = 109.3°.

It is instructive to compare the structure of the anion of 1 with those of the anions of (NH₄)[VO(O₂)₂(bpy)] (2),[15] MoO(S₂)₂(bpy) (3),[14] and MoO(O₂)₂(bpy) (4);[16] complexes 2 and 4 contain peroxide (O₂²⁻) groups in place of the persulfides

(14) Chakrabarty, P. K.; Bhattacharya, S.; Pierpont, C. G.; Bhattacharyya, R. *Inorg. Chem.* **1992**, *31*, 3573.
(15) Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1983**, *37*, 553.
(16) Schlemper, E. O.; Schrauzer, G. N.; Hughes, C. A. *Polyhedron* **1984**, *3*, 377.

Table II. Selected Atomic Coordinates (×10⁴)[a] and Isotropic Thermal Parameters (×10) for 1·MeCN

atom	x	y	z	B_{eq},[b] Å²
V(1)	4094(1)	964*	7552.1(4)	9
S(2)	6852(1)	862(1)	6576(1)	14
S(3)	5904(1)	−485(1)	7074(1)	13
S(4)	2595(1)	2280(1)	8524(1)	13
S(5)	4726(1)	2682(1)	7553(1)	12
N(6)	2713(5)	15(3)	8614(3)	11
C(7)	962(5)	−366(3)	8351(3)	12
C(8)	52(6)	−1009(3)	8989(3)	16
C(9)	918(6)	−1278(3)	9928(4)	16
C(10)	2698(6)	−882(3)	10199(3)	15
C(11)	3569(5)	−237(3)	9527(3)	11
C(12)	5464(5)	224(3)	9771(3)	12
C(13)	6568(6)	48(3)	10674(3)	14
C(14)	8311(6)	537(3)	10827(3)	14
C(15)	8922(6)	1162(3)	10074(3)	15
C(16)	7776(5)	1302(3)	9180(3)	12
N(17)	6063(4)	844(3)	9025(2)	10
O(18)	2389(4)	852(2)	6684(2)	13
N(19)	9617(5)	3513(3)	5168(3)	13
C(20)	10804(6)	4461(4)	5333(3)	20
C(21)	11296(8)	4708(4)	6453(4)	25
C(22)	10806(6)	2614(4)	5493(3)	17
C(23)	12505(7)	2415(4)	4833(4)	18
C(24)	7853(6)	3532(4)	5813(4)	19
C(25)	6574(7)	4438(4)	5652(4)	19
C(26)	9069(7)	3490(4)	4024(4)	21
C(27)	8006(9)	2565(5)	3669(5)	31

[a] Parameter marked with an asterisk was not varied. [b] Equivalent isotropic values for atoms refined anisotropically were calculated using the published procedure.[22]

Table III. Selected Bond Distances (Å) and Angles (deg) for 1·MeCN

(a) Bonds			
V(1)–O(18)	1.6039(26)	V(1)–N(6)	2.139(3)
V(1)–S(3)	2.4251(12)	V(1)–N(17)	2.302(3)
V(1)–S(2)	2.3437(11)	S(2)–S(3)	2.0531(15)
V(1)–S(5)	2.3686(13)	S(4)–S(5)	2.0549(13)
V(1)–S(4)	2.4403(13)		

(b) Angles			
O(18)–V(1)–S(3)	96.92(10)	S(3)–V(1)–S(2)	50.97(4)
O(18)–V(1)–S(2)	102.35(10)	S(3)–V(1)–S(5)	134.19(4)
O(18)–V(1)–S(5)	103.00(11)	S(3)–V(1)–S(4)	163.72(4)
O(18)–V(1)–S(4)	96.38(10)	S(3)–V(1)–N(17)	81.80(9)
O(18)–V(1)–N(17)	165.26(13)	S(2)–V(1)–S(5)	84.38(4)
O(18)–V(1)–N(6)	93.11(13)	S(2)–V(1)–S(4)	134.19(5)
N(6)–V(1)–S(3)	85.92(9)	S(2)–V(1)–N(17)	88.32(8)
N(6)–V(1)–S(2)	135.26(9)	S(5)–V(1)–S(4)	50.57(4)
N(6)–V(1)–S(5)	132.75(9)	S(5)–V(1)–N(17)	88.00(9)
N(6)–V(1)–S(4)	84.02(9)	S(4)–V(1)–N(17)	82.95(9)
N(6)–V(1)–N(17)	72.15(12)		

(S₂²⁻) of 1 and 3. Pertinent structural parameters are listed in Table IV. It is readily apparent that the four species are extremely similar, both in overall structure and in metric parameters. There are the expected differences due to the S *vs* O variation (for example, the M–E bond lengths) and the expected slight variation in analogous parameters due to the size difference between V⁵⁺ and Mo⁶⁺, but otherwise the complexes are almost indistinguishable within the 3σ criterion. Complex 1 is also related to the V[IV] complex V(S₂)₂(terpy) (terpy = 2,2′:6′,2″-terpyridine),[4] which similarly has distorted pentagonal bipyramidal geometry but with the third pyridyl ring occupying the axial position occupied by the oxo group in 1. The S–S distances in V(S₂)₂(terpy) are 2.043(1) and 2.025(1) Å.

Spectroscopic Studies. The ^{1}H NMR spectrum in CD₃CN displayed NEt₄⁺ resonances and eight bpy resonances, as expected from the solid-state structure of 1 and the C_s symmetry of the anion. To probe with better certainty whether more than one V species is formed on dissolution of 1, [51]V NMR spectroscopy was employed. A single sharp resonance was observed at $\delta = -402$
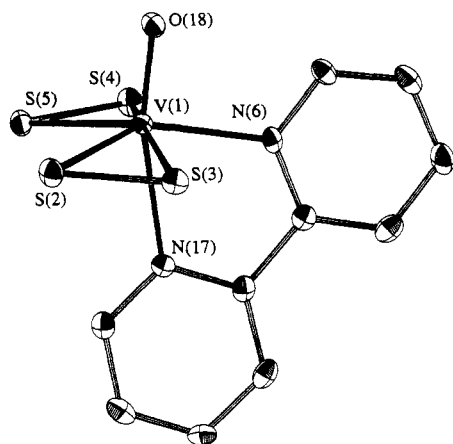
Figure 1. ORTEP representation of the anion of **1** at the 50% probability level. Carbon atoms are numbered sequentially around the rings.

Table IV. Comparative Structural Data[a] for Complexes **1–4**

| param	[VO(S₂)₂-(bpy)]⁻	[VO(O₂)₂-(bpy)]⁻	MoO(S₂)₂-(bpy)	MoO(O₂)₂-(bpy)
M–E$_a$	2.4403(13)	1.909(3)	2.425(4)	1.948(4)
M–E$_b$	2.3686(13)	1.880(3)	2.378(5)	1.908(4)
M–E$_c$	2.3437(11)	1.883(3)	2.364(4)	1.912(5)
M–E$_d$	2.4251(12)	1.911(3)	2.437(4)	1.953(4)
E$_a$–E$_b$	2.0549(13)	1.471(4)	2.055(6)	1.465(6)
E$_c$–E$_d$	2.0531(15)	1.465(4)	2.038(6)	1.459(6)
M–O	1.6039(26)	1.619(3)	1.690(10)	1.682(4)
M–N′	2.139(3)	2.149(4)	2.207(12)	2.199(5)
M–N	2.302(3)	2.288(3)	2.351(12)	2.312(5)
O–M–E$_a$	96.38(10)	99.1(2)	97.9(4)	101.7(2)
O–M–E$_b$	103.00(11)	103.3(2)	103.4(4)	105.6(2)
O–M–E$_c$	102.35(10)	104.0(2)	103.3(3)	105.4(2)
O–M–E$_d$	96.92(10)	100.2(2)	99.3(4)	101.1(2)
O–M–N′	93.11(13)	92.4(2)	91.3(5)	92.4(2)
E$_a$–M–E$_b$	50.57(4)	45.7(1)	50.5(1)	44.6(2)
E$_c$–M–E$_d$	50.97(4)	45.4(1)	50.4(1)	44.4(2)

[a] Tabulated using the labeling scheme
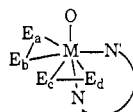
ppm *vs* VOCl₃. The combined NMR results thus support retention of the solid-state structure on dissolution in MeCN. The $\delta(^{51}V)$ value lies between the ranges found for V complexes with exclusively O/N ligation (–537 to –672 ppm)[17] and exclusively S ligation (+101 to +1457 ppm);[1i,18] the complex VO(OH)(S₂CNEt₂)₂, which possesses both O and S ligation, has $\delta(^{51}V) = -468$ ppm.[19] The $\delta(^{51}V)$ value for **1** is comparable with but upfield (more shielded) *vis-à-vis* those for the complexes [V₂(μ-S₂)₂(CS₃)₄]⁴⁻ and V₂(μ-S₂)₂(S₂CX)₄ (X = SMe, NEt, NBuⁿ), which have δ values in the +101 to +173 ppm range and which similarly contain V centers bound to two S₂²⁻ groups.[1i] The relative shielding of **1** compared to these exclusively S-ligated species is as expected given the presence of O and bpy N ligands,

because d⁰ Vⱽ exhibits the so-called inverse polarizability (electronegativity) dependence of metal shielding; i.e., the shielding increases with the more electronegative (or less polarizable) O/N ligands.[19,20]

The IR spectrum of **1** displays the VO multiple-bond stretch at 940 cm⁻¹ and the S–S stretch at 535 cm⁻¹. These values are consistent with expectation and similar to those for isostructural MO(S₂)₂(bpy) (M = Mo, 930 and 540 cm⁻¹; M = W, 940 and 525 cm⁻¹).[14] The electronic spectrum in MeCN displays three distinct and intense features at 336, 384, and 520 nm assignable to ligand (S₂²⁻, bpy)-to-metal charge transfer.

Discussion

Complex **1** represents only the second structurally confirmed example of a vanadium(V) persulfide complex; as mentioned earlier, persulfide complexes of V are primarily found at the Vᴵᴵᴵ and Vᴵⱽ oxidation levels. The other Vⱽ example is (Me₃NCH₂Ph)₂[VS₂(S₂)(SPh)], whose structure is shown as follows. Also shown is the anion [VS₄]³⁻, a tetrahedral ion

[VO(S₂)₂(bpy)]⁻   [VS₂(S₂)(SPh)]²⁻   [VS₄]³⁻
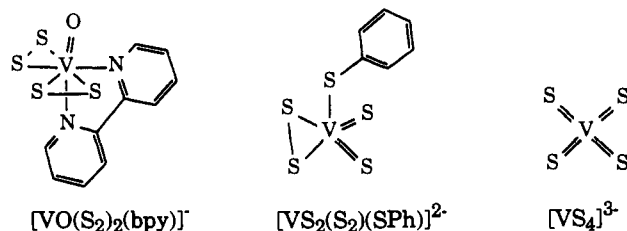
possessing four S²⁻ ligands.[2b,21] It is interesting to note that these species form a trio related by the fact that they each possess four "inorganic" S atoms either as 4S²⁻ in [VS₄]³⁻, as 2S²⁻, S₂²⁻ in [VS₂(S₂)(SPh)]²⁻, or as 2S₂²⁻ in the anion of **1**. Additional ligation is required along this series (from right to left) to compensate for decreasing electron donation from S₂²⁻ *vs* S²⁻ ligands. The S–S bond length in [VS₂(S₂)(SPh)]²⁻ (2.013(3) Å) is noticeably shorter than those in [VO(S₂)₂(bpy)]⁻ (2.0549(13), 2.0531(15) Å), indicating greater electron donation in the former from occupied S₂²⁻ π* orbitals into empty V d orbitals; this would be consistent with the significantly greater coordination number in [VO-(S₂)₂(bpy)]⁻ (7) *vs* [VS₂(S₂)(SPh)]²⁻ (5).

The convenient and high-yield nature of the preparation of **1** suggests that this complex should be an excellent starting point for synthesis of other V/S species. Preliminary observations are supporting this belief. In this regard, **1** appears to be superior to (Me₃NCH₂Ph)₂[VS₂(S₂)(SPh)], which is extremely reactive but suffers from being sparingly soluble and metastable in solution, although it has nevertheless been successfully employed for the synthesis of (Me₃NCH₂Ph)₄[V₂(S₂)₂(CS₃)₄].[1i]

(17) (a) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1173. (b) Rehder, D.; Wieghardt, K. *Z. Naturforsch., B* **1981**, *36*, 1251.

(18) (a) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1986**, 1405. (b) Preuss, F.; Noichl, A. *Z. Naturforsch., B* **1987**, *42*, 121.

(19) Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Inorg. Chem.* **1988**, *27*, 584.

(20) (a) Rehder, D. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; p 1. (b) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 488–493 and references therein.

(21) Krüss, G.; Ohnmais, K. *Chem. Ber.* **1890**, *23*, 2547; *Justus Liebigs Ann. Chem.* **1891**, *263*, 39.

(22) Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.