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Formation of the $\{MO(S_2)_2\}$ (M = Mo, W) Moiety by a MO_4^{2-}–Polysulfide Reaction: Synthesis and Structure of $MO(S_2)_2(bpy)$

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MoO_4^{2-} and WO^{3+} react separately with aqueous S_x^{2-} in the presence of 2,2′-bipyridine (bpy) to give discrete mononuclear complexes $MO(S_2)_2(bpy)$ (M = Mo, W). Both complexes have been characterized crystallographically and have been found to be isostructural. Results of the structure determination on $MoO(S_2)_2(bpy)$ [monoclinic, space group $C2/c$, $a = 25.801$ (7) Å, $b = 8.507$ (2) Å, $c = 12.527$ (2) Å, $\beta = 106.31$ (2)°, $V = 2638.9$ (10) Å^3, $Z = 8$] have shown that the complex molecule is pentagonal bipyramidal with four sulfur atoms and one nitrogen atom defining the equatorial plane and the remaining bpy nitrogen and an oxo ligand in axial positions. The tungsten analog shows two quasireversible one-electron reductions at the metal center, which appear as irreversible reductions for $MoO(S_2)_2(bpy)$.

Introduction

The disulfide ligand, like its dioxygen analog, may exhibit terminal or bridged bonding with metals, usually with a charge of −2.[2-4] A significant difference between the sulfur and oxygen ligand lies in the tendency for formation of polysulfide complexes containing S_x^{2-} units. Dioxygen commonly bonds diatomically as either superoxide or peroxide.

Metal–sulfur compounds containing S_x^{2-} ligands have received continued interest for their prevalence in naturally occurring materials, often in the form of aggregates and clusters.[5] Molybdenum–sulfur and, to a lesser extent, tungsten–sulfur compounds are becoming important as components in electron-transfer enzymes,[6,7] for their role as heterogeneous catalysts in the desulfurization of oil and coal,[8] and as homogeneous photocatalysts in water-splitting reactions.[9] Ammonium polysulfide is a major source of S_x^{2-} species, and binuclear and trinuclear Mo–S clusters have been formed by reactions between MoO_4^{2-} and S_x^{2-} species.[10,11] Recently, a detailed investigation of reactions leading to the formation of complexes containing the $\{M_2O_2S_2\}^{2+}$ (M = Mo, W) core coordinated by η^2-S_x (x = 2, 4) has been described.[12] However, compared to the ubiquity of polynuclear M–S_x (M = Mo, W) aggregates and clusters,[13-21] where one or more or even all metal centers have oxidation states less than 6, mononuclear M–S_x complexes containing Mo(VI) or W(VI) remain rather rare.[4,13,22] Besides the simpler species like tetrathiometalates and their mixed oxo analogs,[23,24] examples of compounds in this class include $Cs_2[MoO(S_2)_2(C_2O_3S)]$,[25,26] $MOS_2(dtc)_2$ (M = Mo, W),[27] and $WSS_2(dtc)_2$.[28]

The present work shows that addition of 2,2′-bipyridine (bpy) to a reaction mixture containing MoO_4^{2-} or WO^{3+} and S_x^{2-} results in formation of the discrete mononuclear complexes $MO(S_2)_2(bpy)$ (M = Mo, W). The complexes containing both metals have been characterized crystallographically and have been found to be isostructural. The results of the structure determination on $MoO(S_2)_2(bpy)$ (**1**) are described herein. This represents the first observation of the $WO(S_2)_2$ moiety, and both complexes

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(1) (a) Jadavpur University. (b) University of Colorado.

(2) The S–S distances in a variety of disulfur compounds prepared by using either S_8, S_x^{2-}, S^{2-}, or S_2Cl_2 fall in the same range, but O–O distances in dioxygen compounds differ substantially according to the charge state of the O_2 ligand.

(3) The name disulfur is used without implying any charge distribution or the formal oxidation state of the ligand.[4]

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may be viewed as persulfide analogs of corresponding peroxo complexes reported earlier.[29]

Experimental Section

Materials. Ammonium molybdate and sodium tungstate (AR grade) were obtained from E. Merck. All other chemicals used were of GR (E. Merck) grade unless specified. All solvents (AR or extrapure grade) used for spectroscopic and other physical methods of characterization were further purified by available literature methods.[30] Commercial tetraethylammonium chloride was converted to pure tetraethylammonium perchlorate (TEAP) by a literature procedure.[31] Dionitrogen gas (Indian Oxygen Ltd.) was purified by successively bubbling it through alkaline dithionite solution and concentrated sulfuric acid. H_2S gas was generated in the laboratory in a Kipp apparatus using FeS (pure, BDH) and sulfuric acid (AR, BDH). Triply distilled water was used throughout the work. Aqueous ammonium polysulfide solution was prepared as described earlier.[32]

Preparation of Complexes. $MoO(S_2)_2(bpy)$ (1). $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2.5 g, 14 mmol of Mo) was dissolved in aqueous ammonia (1:1, 20 mL), and to the solution was added an aqueous $(NH_4)_2S_x$ solution (75 mL). The resulting solution was heated on a boiling water bath for 3–4 h to give a red-brown solution. The solution was filtered, and the filtrate was added to a hot aqueous (50 mL) solution of bpy (1 g, 6 mmol) with constant stirring. After 3–4 h of constant stirring, a red compound separated from solution. The crude product (2.0 g) was isolated by filtration, washed with water, ethanol, CS_2, and diethyl ether, and dried in vacuum. Further purification was carried out by dissolving this material in DMF (100 mL) by heating the mixture for 10 h on a boiling water bath. The dark red solution was filtered to remove undissolved complex, 2-propanol (50 mL) was added to promote crystallization, and the mixture was cooled at 0 °C. After 3–4 days, black crystals of $MoO(S_2)_2(bpy)$ had formed with a small amount of a orange-yellow crystalline product. The black crystals were isolated and recrystallized from a DMF/2-propanol solution a second time to give 1.1 g of purified product in 20% yield.

$WO(S_2)_2(bpy)$ (2). $Na_2WO_4\cdot 2H_2O$ (3 g, 9 mmol) and NH_4SCN (7 g, 90 mmol) were dissolved in 6 M HCl (80 mL). The solution was stirred until a deep green color developed, and then it was filtered. $(NH_4)_2S_x$ solution (90 mL) was added to the filtrate with stirring until the violent exothermic reaction ceased. The resulting orange-red solution was filtered, and the filtrate was added to a 50% aqueous ethanol solution (50 mL) containing bpy (2 g, 13 mmol) with constant stirring. After 2–3 h of stirring, an orange-red compound had separated from solution. The crude product was isolated by filtration, washed with water, ethanol, CS_2, and diethyl ether, and dried in vacuum to give 1.8 g of crude product. Purification was carried out as with 1 to give 1.2 g of $WO(S_2)_2(bpy)$ as red-brown needles in 28% yield.

Physical Measurements. Spectroscopic data were obtained by using the following instruments: IR (CsI or polyethylene disk, 4000–200 cm^{-1}), Perkin-Elmer 597 spectrophotometer; electronic spectra (2600–200 nm), Hitachi Model U-3400 UV–vis–near-IR spectrophotometer. A Phillips Model PW 1730/1710C XRD system powder diffractometer (Cu Kα radiation) was used for measuring *d* spacings. Solution electrical conductance was measured by using a Systronics Model 304 digital conductivity bridge. A Knauer vapor pressure osmometer was used for molecular weight determination using benzil as a calibrant. Magnetic susceptibility was measured by the Guoy method. Electrochemical measurements were made using a PAR Model 378-1 electrochemistry system incorporating the following components: 174A polarographic analyzer; 175 universal programmer; Re 0074 X-Y recorder; 173 potentiostat; 377 cell system. All experiments were performed under a dinitrogen atmosphere. A stout platinum-wire electrode, a platinum foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in the three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. Coulometry was performed on a 273 potentiostat/galvanostat using a 377 cell system equipped with a Pt-wire-gauze working electrode. Microanalyses for C, H, and N were carried out using a Perkin-Elmer 240C elemental analyzer; Mo, W, and S analyses were performed using conventional gravimetric methods (Mo as MoO_2(8-quinolinolate)$_2$, W as WO_3, and S as $BaSO_4$).[33]

Table I. Crystallographic Data for $MoO(S_2)_2(bpy)$

MW	396.4	Z	8
color	black	D_{calcd}, g cm^{-3}	1.995
space group	C2/c	D_{exptl}, g cm^{-3}	2.015
a, Å	25.801 (7)	μ, mm^{-1}	1.566
b, Å	8.507 (2)	λ, Å	0.710 73 (Mo Kα)
c, Å	12.527 (2)	T, K	296
β, deg	106.31 (2)	R, R_w (obsd data)[a]	6.24%, 7.45%
V, Å^3	2638.9 (10)	GOF	1.72

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

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $MoO(S_2)_2(bpy)$

	x/a	y/b	z/c	U(eq)[a]
Mo	3578 (1)	2884 (1)	1221 (1)	32 (1)
S1	4276 (2)	1594 (5)	2568 (4)	47 (2)
S2	3902 (2)	3309 (5)	3213 (3)	40 (1)
S3	3390 (2)	3386 (5)	−767 (3)	45 (2)
S4	3948 (2)	1668 (5)	−109 (4)	49 (2)
O	3028 (4)	1778 (10)	1175 (8)	39 (4)
N1	3121 (5)	5071 (14)	1245 (9)	33 (5)
N2	4149 (5)	5042 (13)	1235 (9)	28 (4)
C1	2599 (6)	5003 (20)	1261 (12)	44 (6)
C2	2301 (7)	6303 (23)	1341 (13)	51 (7)
C3	2549 (8)	7725 (23)	1421 (12)	52 (7)
C4	3087 (7)	7869 (20)	1409 (11)	47 (7)
C5	3357 (7)	6494 (18)	1288 (11)	38 (6)
C6	3932 (6)	6482 (17)	1239 (10)	27 (5)
C7	4203 (8)	7843 (19)	1155 (12)	48 (7)
C8	4722 (7)	7760 (23)	1063 (14)	54 (7)
C9	4961 (7)	6267 (19)	1106 (12)	43 (7)
C10	4648 (7)	4979 (17)	1174 (11)	37 (6)

[a] The equivalent isotropic U is defined as one-third of the trace of the orthongalized U_{ij} tensor.

Crystallographic Structure Determination of $MoO(S_2)_2(bpy)$ (1). Black crystals of 1 were obtained from a DMF/2-propanol solution. A crystal of the complex was mounted and aligned on a Siemens P3/F automated diffractometer. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections in the 2θ range between 23.9 and 39.5° gave the unit cell dimensions listed in Table I. Data were collected by θ–2θ scans within the angular range 3.0–45°. The position of the Mo atom was determined from a Patterson map, and the locations of lighter atoms were determined using the phases of the metal position. Final cycles of least-squares refinement[34-36] converged with discrepancy indices of $R = 0.062$ and $R_w = 0.074$. Final positional parameters for atoms of the complex molecule are listed in Table II.

The structure determination of $WO(S_2)_2(bpy)$ was also carried out, giving results that were not significantly different from those of $MoO(S_2)_2(bpy)$. Information and tables describing this molecule are available as supplementary material.

Results and Discussion

Complexes 1 and 2 are nonelectrolytes in DMF and are diamagnetic. Analytical data for both complexes are listed in Table III. Infrared spectra and X-ray powder diffractograms are identical for 1 and 2, indicating that the Mo and W forms of the complex are isostructural. This has been confirmed by

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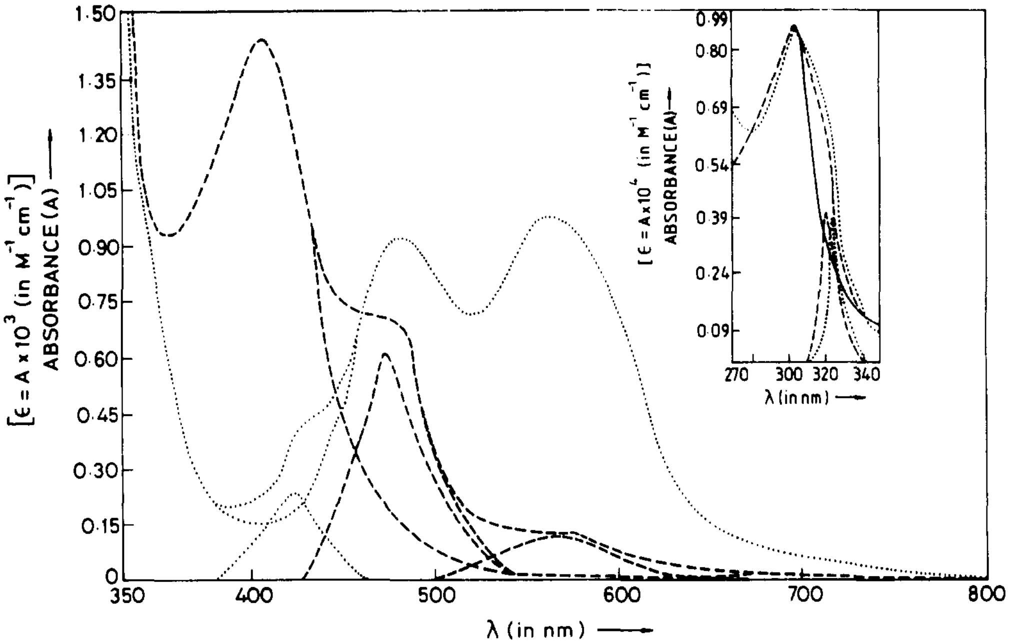

Figure 1. Electronic spectra of MoO(S$_2$)$_2$(bpy) (···) and WO(S$_2$)$_2$(bpy) (- - -) in DMF solutions.

Table III. Analytical Data

Elemental Analytical Data

	found (calcd)					
	% C	% H	% N	% M	% S	MW
1	31.0	2.2	7.0	25.0	32.9	405
	(30.3)	(2.0)	(7.1)	(24.3)	(32.3)	(396)
2	24.3	1.8	5.6	39.1	27.2	480
	(24.8)	(1.7)	(5.8)	(38.0)	(26.5)	(484)

Infrared Spectral Data, cm^{-1}

1 3080 (w), 1615 (s), 1500 (m), 1480 (m), 1450 (s), 1320 (s), 1230 (vw), 1160 (m), 1110 (w), 1080 (w), 1070 (w), 1035 (m), 930 (s), 775 (s), 730 (m), 650 (w), 640 (w), 540 (s), 480 (vw), 420 (vw), 370 (m), 340 (m)

2 3120 (w), 1610 (s), 1500 (m), 1480 (m), 1440 (s), 1320 (s), 1230 (vw), 1160 (m), 1105 (w), 1080 (w), 1070 (w), 1030 (m), 940 (s), 770 (s), 725 (m), 650 (vw), 525 (s), 360 (m), 320 (m)

Electronic Spectral Data in DMF: λ_{max}, nm (ϵ, M^{-1} cm^{-1})

1 305 (9500), 330 (3900), 418 (250), 483 (1000), 565 (1000)

2 305 (9400), 320[a] (4500), 406 (1400), 470 (600), 550 (150)

Powder Diffraction Data: *d* Spacings, Å (I/I_0)

1 8.04 (0.37), 6.97 (1.00), 6.15 (0.95), 4.93 (0.35), 4.38 (0.98), 4.27 (0.35), 3.51 (0.37), 3.36 (0.09), 3.26 (0.09), 3.00 (0.14), 2.90 (0.09), 2.67 (0.09), 2.56 (0.14), 2.48 (0.05), 2.47 (0.09), 2.41 (0.07), 2.36 (0.07), 2.00 (0.07)

2 8.04 (0.47), 6.91 (0.60), 6.15 (0.33), 4.93 (0.25), 4.38 (0.25), 4.25 (1.00), 3.49 (0.44), 3.41 (0.06), 3.00 (0.07), 2.94 (0.05), 2.75 (0.13), 2.67 (0.16), 2.56 (0.10), 2.47 (0.06), 2.38 (0.04), 2.00 (0.12)

[a] Shoulder.

Table IV. Cyclic Voltammetric Data[a]

	scan rate, mV/s	irreversible wave		reversible wave
		E_{pa}, V	E_{pc}, V	$E°_{298}$ (ΔE_p), V (mV)
MoO(S$_2$)$_2$(bpy)	50	1.28	−0.52	−1.07 (60)
	100	1.34	−0.52	−1.07 (60)
	200	1.40	−0.54, −1.26	−1.07 (80)
	500	1.44	−0.56, −1.28	−1.06 (100)
WO(S$_2$)$_2$(bpy)	50	1.32	−0.50	−1.10 (80), −1.27 (60)
	100	1.36	−0.50	−1.10 (80), −1.28 (80)
	200	1.40	−0.52	−1.08 (80), −1.28 (80)
	500	1.44	−0.52	−1.07 (60), −1.29 (100)

[a] Solvent DMF; supporting electrolyte TEAP; potential V vs SCE; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential; $E°_{298}$ = 0.5 (E_{pa} + E_{pc}); ΔE_p = (E_{pa} − E_{pc}).

single-crystal structure determinations on both complexes. The IR spectra of **1** and **2** show a pronounced ν_{S-S} vibration at 540 and 525 cm^{-1}, respectively, and a single sharp and symmetrical $\nu_{M=O}$ vibration at 930 and 940 cm^{-1}, respectively. No bands are observed that might be assigned as ν_{M-S-M} bridging vibrations, indicating that the common S,S-bridged binuclear moiety is not present in either case. Molecular weight data further verify the monomeric nature of the two complexes in DMF.

Five electronic transitions are observed in the electronic spectra of **1** and **2** (Table III); however, the band profiles of the two complexes appear quite different. Gaussian analysis shown in Figure 1 indicates that band positions show the expected hypsochromic shift on substituting Mo by W, but in general, bands appear at similar positions for the two complexes with significant differences in intensity. Maxima at ca. 483 nm (Mo) and 470 nm (W) may be assigned as $\pi^*_v(S_2) \rightarrow \sigma^*$[d(metal)] LMCT transitions.[4,37] The high-energy component of the band for the M(S$_2$) core (i.e., $\pi^*_h(S_2) \rightarrow \sigma^*$[d(metal)][37]) is not observed owing to its possible occlusion within the high-intensity intraligand bpy absorption. The highest wavelength band at ca. 550 nm may be due to a bpy → M LMCT transition, but there is a marked intensity difference with the two different metals. The band at ca. 410 nm may be assigned as the (S$_2$)$_{bonding}$ → [M=O] transition, occurring at lower energy than is typically observed for M(V) cases.[12] The weak shoulder (Gaussian-analyzed) at ca. 320 nm may be a bpy → M=O transition, and the 305-nm band is assigned as an intraligand transition centered on bpy[38] bathochromically shifted in **1** and **2** due to the lowering of the LUMO of bpy upon metal coordination.

Cyclic voltammograms of complexes **1** and **2** have been recorded in DMF/TEAP solution at a solute concentration of 1.0 × 10^{-3} M. The results are summarized in Table IV and shown in Figure 2. In the potential range 0.00 to −2.00 V vs SCE, irreversible or nearly reversible[39] metal-centered cyclic voltammetric responses

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(40) This property of greater reversibility at higher scan rate is characteristic of Mo and W electrochemistry when the metals are linked with more than one S center. See also ref 12.

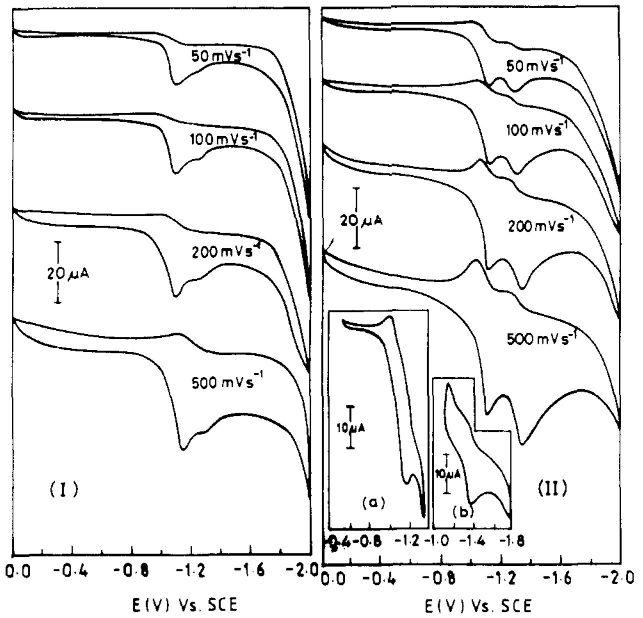

Figure 2. Cyclic voltammograms of (I) $MoO(S_2)_2(bpy)$ and (II) $WO(S_2)_2(bpy)$ in DMF (0.1 M in TEAP) at scan rates of 50–500 mV s^{-1}. Segmented CV's of individual redox responses of $WO(S_2)_2(bpy)$ are shown in (a) and (b) in (II).

are exhibited. The Mo complex **1**, at scan rates of 50 and 100 mV/s, shows only one reductive response at −1.10 V with little development in the coupled oxidation wave on the reverse scan. However, at scan rates of 200 and 500 mV/s the onset of another low-current reduction wave is observed with an increase in current for the oxidation at −1.04 V coupled with the first reduction. It appears that $MoO(S_2)_2(bpy)$ may undergo reduction in two one-electron steps. However, the product of the first reduction is subject to depletion on the time scale of the slower scan rates, possibly due to dimerization, inhibiting development of the wave associated with the second reduction and resulting in little current for the coupled oxidation. Constant-potential coulometry carried out at a potential of −1.5 V provides more information on the nature of these processes. The coulomb count becomes quite slow after one-electron absorption. After the period of 15 min, the solution rapidly absorbs a quantity of charge commensurate with a second one-electron reduction.

In the case of $WO(S_2)_2(bpy)$, two sequential one-electron reduction steps are observed and their reversibility is more pronounced[40] than with $MoO(S_2)_2(bpy)$ (Figure 2). These couples can be assigned to the two metal-based stepwise reduction processes

$$W^{VI}O(S_2)_2(bpy) + e^- \rightleftarrows W^{V}O(S_2)_2(bpy)^- \qquad (1)$$

$$W^{V}O(S_2)_2(bpy)^- + e^- \rightleftarrows W^{IV}O(S_2)_2(bpy)^{2-} \qquad (2)$$

Coulometric reduction at −1.5 V shows smooth absorption of two units of charge with formation of a new species that shows electronic spectral bands at 280, 308, 325, 344, 480, and 615 nm. Bands associated with free bpy are contained in this spectrum, indicating that the complex ultimately decomposes on the Coulombic (but not voltammetric) time scale.

A survey of the literature[28,41–44] reveals that the potential range of the reductions of $MoO(S_2)_2(bpy)$ and $WO(S_2)_2(bpy)$ is typical of the redox behavior of Mo(VI) and W(VI). The MS_4^{2-} (M = Mo, W) ions show broad multistep irreversible reductions within the potential range −0.8 to −1.4 V vs SCE.[42] In CH_3CN/TEAP $Mo^{VI}O(S_2)(Et_2dtc)_2$ undergoes a single-step irreversible two-electron reduction at ca. −1.00 V (vs Ag/AgCl) at the metal center, presumably producing $Mo^{IV}O(Et_2dtc)_2$.[28,43] The tungsten analog behaves similarly, but with a shift of 0.4 V in potential that would be expected for the metal-centered reduction.[28,44] Interestingly, $WS(S_2)(R_2dtc)_2$ is also reduced to a W(IV) complex at a similar potential, but via a W(V) intermediate.[28]

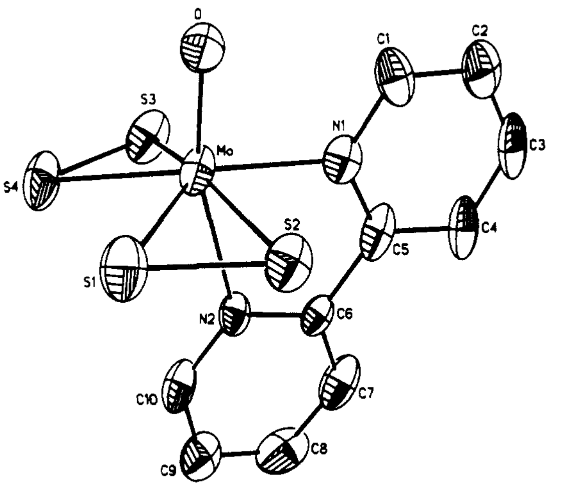

Figure 3. View of the $MoO(S_2)_2(bpy)$ molecule showing the atom-numbering scheme.

Table V. Selected Bond Distances and Angles for $MoO(S_2)_2(bpy)$

	Bond Distances (Å)		
Mo–S1	2.364 (4)	Mo–S3	2.425 (4)
Mo–S2	2.437 (4)	Mo–S4	2.378 (5)
Mo–O	1.690 (10)	Mo–N1	2.207 (12)
Mo–N2	2.351 (12)	S1–S2	2.038 (6)
S3–S4	2.055 (6)		
	Bond Angles (deg)		
S1–Mo–S2	50.4 (2)	S3–Mo–S4	50.5 (1)
N1–Mo–N2	71.2 (4)	N2–Mo–O	162.5 (4)
S1–Mo–O	103.3 (3)	S2–Mo–O	99.3 (4)
S3–Mo–O	97.9 (4)	S4–Mo–O	103.4 (4)
N1–Mo–O	91.3 (5)		

An oxidation wave is observed at ca. 1.30 V for both **1** and **2** which is coupled with a reduction that appears at −0.52 V. This may be attributed to the S_2^{2-} ligand, but the nature of the process is not yet understood.[28]

Molecular Structure of $MoO(S_2)_2(bpy)$. Structure determinations have been carried out on both $MoO(S_2)_2(bpy)$ and $WO(S_2)_2(bpy)$. Both complex molecules are, within error, identical in structure. Consequently, only the results of the determination on $MoO(S_2)_2(bpy)$ will be described in detail, a description of the structure of the tungsten analog is available with the supplementary material. A view of $MoO(S_2)_2(bpy)$ is shown in Figure 3, and selected bond distances and angles are listed in Table V. Viewing the S_2^{2-} ligands as occupying two coordination sites, the complex molecule is heptacoordinated, pentagonal bipyramidal in structure, with the two persulfide ligands occupying four equatorial bonding positions and the chelated bpy ligand bridging the axial and the remaining equatorial sites. The Mo–N lengths involving the bpy nitrogen atoms show the expected trans influence of the axial oxo ligand, with the axial Mo–N2 length 0.14 Å longer than the equatorial Mo–N1 length. The Mo–S lengths involving the persulfide ligands also show significant asymmetry.[12,25–27] This can also be ascribed to environmental differences resulting from a trans effect. Sulfur atoms S1 and S4 bond at sites that are opposite bpy nitrogen N1 and have Mo–S lengths that are 0.06 Å shorter than values to

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S2 and S3 which are more nearly trans to one another with a S2–Mo–S3 angle of 159.6 (1)°. The average value for the Mo–S lengths of $MoO(S_2)_2(bpy)$ compare well with values reported for the persulfide ligand of the $[Mo_2O_2S_2(S_2)(S_4)]^{2-}$ ion, where the Mo(V) centers are five-coordinate. They are longer than the bonds of 2.445 (2) and 2.418 (2) Å to the Mo(V) center of $Mo(S_2)(Et_2dtc)_3$.[27] General features of the $MoO(S_2)_2(bpy)$ molecule resemble those of the $MoO(S_2)_2(C_2O_3S)^{2-}$ dianion,[25,26] although metrical values have been obtained with higher precision in the present case.

Note Added in Proof. Preparation of Complexes. The yield of both **1** and **2** becomes ca. 50% by employing twice the mole proportion of bpy with respect to that of metal ions.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen atom locations for $WO(S_2)_2(bpy)$ (7 pages); listings of observed and calculated structure factors for $MoO(S_2)_2(bpy)$ and $WO(S_2)_2(bpy)$ (10 pages). Ordering information is given on any current masthead page.