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X-ray Structure of (Bu$^n_4$N)[Mo(1,2-Benzenedithiolate)$_3$]. Trigonal-Prismatic versus Octahedral Coordination in Tris(1,2-Benzenedithiolate) Complexes

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Introduction

Early molecular orbital schemes for tris(dithiolene) complexes of transition metals indicated that 12-electron compounds (d^0) are the optimal situation for trigonal-prismatic (TP) geometry, while an increase in the number of electrons is expected to destabilize TP structure, favoring a distortion toward octahedral geometry.[1] Thus, while the structures of the complexes $[Mo^{VI}(S_2C_2H_2)_3]$,[2] $[Mo^{VI}(S_2C_6H_4)_3]$,[3a] and $[Nb^{V}(S_2C_6H_4)_3]^-$,[3b] which are formally d^0 complexes, exhibit regular TP geometries around the metal atom, $[M^{IV}(mnt)_3]^{2-}$ (M = Mo or W; mnt = $S_2C_2(CN)_2{}^{2-}$)[4] and $[Mo^{IV}(S_2C_2(CO_2Me)_2)_3]^{2-}$,[5] formally d^2 complexes, exhibit an intermediate structure between octahedral and TP types.

Rather unexpected in this context is the almost perfect TP structure of $[Re(S_2C_2(C_6H_5)_2)_3]$, with the d^1 configuration,[1a] and also the pseudooctahedral structure of the d^0 $[Zr^{IV}(S_2C_6H_4)_3]^{2-}$ complex.[6] However, there is a great difference in metal size between these complexes, and a certain amount of caution should be exercised in this comparison since interligand sulfur−sulfur bonding was also believed to be a significant factor in stabilizing TP tris(dithiolene) complexes.[1,2]

At present, when a more extended series of complexes can be arranged according to the electronic configurations, no clear correlation results. The observation of a TP structure for $[Mo^{IV}(qdt)_3]^{2-}$ (qdt = quinoxaline-2,3-dithiolate) has been considered as unexpected, since its oxidized monoanionic Mo(V) derivative has a structure significantly distorted from the ideal TP geometry.[7] The most recent X-ray structures of $[M(S_2C_2(CH_3)_2)_3]^n$ complexes[8] (M = Mo and $n = 0{-}1, -2$; M = W and $n = -1, -2$) reveal that all they adopt regular TP stereochemistries. In general, structural data evidence that the geometry of a particular complex is not governed only by electronic factors. Ligand constraint, ligand field stabilization energy, proper matching of ligand and metal d orbital energies, the symmetry of ligand π orbitals, inter-donor atom bonding, and the overall charge of the complex have been suggested as important factors,[9,10] and thus, to correlate electronic configuration and molecular geometry, it is preferable to use compounds with identical ligands.

The current ligand has played a quite remarkable role in the study of factors stabilizing the TP geometry of tris(dithiolene) complexes. While tris(benzenedithiolate) complexes of Mo(VI) and Nb(V) are TP, the $[Zr^{IV}(S_2C_6H_4)_3]^{2-}$ structure is closer to octahedral.[11] Complex charge and interligand bonding might be responsible for the trend, but it was believed that stabilization of d orbital proceeding from Zr to Mo is the most important factor in stabilizing the TP structure of these complexes.[3,11] In an attempt to gain further information about the relative importance of electronic factors, we report here the improved synthesis of $(Bu_4N)[Mo(S_2C_6H_4)_3]$ and its structural characterization.

Results

The neutral $[Mo^{VI}(S_2C_6H_4)_3]$ complex was first prepared in moderate yield by refluxing solid $MoCl_5$ with a slight excess of benzenedithiol dissolved in Cl_4C.[1a] We have improved the synthesis by the use of $MoO_2(acac)_2$; the reaction does not require heat and prolonged reaction time and affords $[Mo^{VI}(S_2C_6H_4)_3]$ in yields of 70−80%. The reduced $Mo^{IV}(S_2C_6H_4)_3]^{2-}$ species was prepared in low yield from the reaction of $[MoCl_4(THF)_2]$ with $Li_2C_6H_4S_2$, whereas the $[Mo^{VI}(S_2C_6H_4)_3]$/$[Mo^{IV}(S_2C_6H_4)_3]^{2-}$ comproportionation reaction led to the isolation of the $[Mo^{V}(S_2C_6H_4)_3]^-$ monoanion.[12]

The CV of $[Mo^{VI}(S_2C_6H_4)_3]$ shows two reversible one-electron reductions at the formal potentials of +0.200 and −0.390 V, supporting the three-member $[Mo^{VI}(S_2C_6H_4)_3]^{0/-2}$ series, the existence of which was established much earlier for this and related tris(dithiolenes) of molybdenum.[13] The CV of a coulometrically fully reduced solution is identical to that of the unreduced solution, indicating effective stability of the reduced products. Thus, the preparation of these anions was herein attempted by direct reduction of $[Mo^{VI}(S_2C_6H_4)_3]$ with $(N(C_4H_9)_4)(SH)$ in dry, deoxygenated CH_2Cl_2. The redox reactions, monitored spectrophometrically, proceed with well-defined isosbestic points and stoichiometric conversions. The final spectra are that of $[Mo^{V}(S_2C_6H_4)_3]^-$ or $[Mo^{IV}(S_2C_6H_4)_3]^{2-}$, measured separately. EPR spectroscopy confirms these spectrophotometric results. When excess of bisulfide was added to a CH_2Cl_2 solution of $Mo^{VI}(S_2C_6H_4)_3$ kept under a stream of nitrogen, in situ measurements revealed the immediate appearance of a signal characteristic of a Mo(V) center ($\langle g\rangle = 2.006$; $\langle A\rangle(^{95,97}Mo) = 26.6 \times 10^{-4}\ cm^{-1}$). The concentration increases with time reaching a maximum and then disappears at a much slower rate, which indicates a further reduction to the EPR-

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Table 1. Crystal Data and Structure Refinement for $[Mo(S_2C_6H_4)_3]N(C_4H_9)_4$

empirical formula	$C_{34}H_{48}MoNS_6$
fw	758.75
temp	298(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	Pca2(1)
unit cell dimensions	$a = 19.749(4)$ Å
	$b = 11.019(3)$ Å
	$c = 17.324(5)$ Å
	$\alpha = 90°$
	$\beta = 90°$
	$\gamma = 90°$
volume, Z	3770(2) Å^3, 4
density (calcd)	1.273 Mg/m^3
absorption coeff	0.701 mm^{-1}
$F(000)$	1444
θ range for data collection	2.06 to 22.48 deg.
limiting indices	$0 \leq h \leq 21$, $0 \leq k \leq 11$, $0 \leq l \leq 18$
reflns collected	2555
independent reflns	2555
absorption correction	semiempirical from ψ scans
max and min transmission	0.2593 and 0.2451
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	2554/138/379
GOF on F∧2	1.046
final R indices $[I > 2\sigma(I)]$	R1 = 0.0863, wR2 = 0.0469
R indices (all data)	R1 = 0.2813, wR2 = 0.0739
absolute structure param	0.03(10)
largest diff peak and hole	0.398 and −0.460 eÅ^{-3}

Table 2. Bond Lengths (Å) and Angles (deg) for $[Mo(S_2C_6H_4)_3]N(C_4H_9)_4$

Mo(1)−S(3)	2.362(9)	Mo(1)−S(1)	2.379(9)
Mo(1)−S(5)	2.380(9)	Mo(1)−S(2)	2.382(9)
Mo(1)−S(6)	2.389(7)	Mo(1)−S(4)	2.400(8)
S(1)−C(1)	1.72(2)	S(2)−C(2)	1.73(2)
S(3)−C(7)	1.73(2)	S(4)−C(8)	1.70(2)
S(5)−C(13)	1.75(2)	S(6)−C(14)	1.71(2)
C(1)−C(2)	1.38(2)	C(7)−C(8)	1.38(2)
C(13)−C(14)	1.38(2)		
S(3)−Mo(1)−S(1)	106.6(3)	S(3)−Mo(1)−S(5)	157.3(3)
S(1)−Mo(1)−S(5)	90.1(3)	S(3)−Mo(1)−S(2)	86.9(3)
S(1)−Mo(1)−S(2)	82.0(3)	S(5)−Mo(1)−S(2)	111.0(3)
S(3)−Mo(1)−S(6)	87.0(3)	S(1)−Mo(1)−S(6)	158.4(3)
S(5)−Mo(1)−S(6)	82.1(3)	S(2)−Mo(1)−S(6)	82.1(3)
S(3)−Mo(1)−S(4)	81.6(3)	S(1)−Mo(1)−S(4)	87.0(3)
S(5)−Mo(1)−S(4)	84.2(3)	S(2)−Mo(1)−S(4)	161.1(3)
S(6)−Mo(1)−S(4)	112.0(3)		

silent $[Mo^{IV}(S_2C_6H_4)_3]^{2-}$ complex. The exposure of this fully reduced sample to air led to regeneration of the same Mo(V) EPR signal.

On a preparative scale, the tetrabutylammonium salts of these anionic Mo(V) and Mo(IV) complexes were isolated by simple filtration. Crystals of $[(C_4H_9)_4N][Mo(S_2C_6H_4)_3]$ are stable to aerial oxidation and proved suitable for structure analysis by X-ray diffraction. Crystallographic data are listed in Table 1, and selected bond lengths and angles are listed in Table 2. A perspective view of the molecular structure and numbering scheme is shown in Figure 1. Six sulfur atoms at the averaged distance of 2.382 Å form a polyhedron that is not close to either the TP or octahedral geometry. Its structure consists of two approximately parallel (dihedral angle 2.8°), roughly equilateral S_3 triangles, with an average side of 3.254 Å, separated by a distance of 2.927 Å. The Mo atom lies on the C_3 axis at 1.481 and 1.446 Å from S_3 planes. The upper right inset displays the individual chelate projection (twist) angles for each ligand (35.6, 34.4, and 30.4°). Hence, the triangles are twisted from each other by an averaged angle of 33.5°, a surprisingly high value which is slightly closer to the ideal octahedral value of 60° than to the TP limit of 0°.[14] Such a value is also the largest yet observed in a neutral, mono, or dianionic molybdenum tris(dithiolene) complex, with the examples having shorter interligand S···S distances and lower twisted angles of $[Mo^V(tfd)_3]^-$,[15] 3.11(4) Å (0°); $[Mo^V(qdt)_3]^-$,[7a] 3.16(5) Å (14.6°); $[Mo^{IV}(S_2C_2(CN)_2)_3]^{2-}$,[4] 3.188 Å (28°); $[Mo^{IV}(tfd)_3]^{2-}$,[16] 3.18(2) Å (16°); and $[Mo^{IV}\{S_2C_2(CO_2Me)_2\}_3]^{2-}$,[5] 3.18 Å (10.6°).

The dihedral angles between various planes in the MoS_6 polyhedron provide a more comprehensive measure of its shape.[17] Thus, the dihedral angle ρ is defined as the angle between the mean plane of the two S_3 triangles, and the chelate planes defined by the Mo and two S. The angles found here, S(1)MoS(2) = 66.5°, S(3)MoS(4) = 68.7°, and S(5)MoS(6) = 74.0° are slightly closer to an octahedral ($\rho = 54.7°$) than to a TP ($\rho = 90°$) geometry.

In the crystal structure, each anion is connected with two neighboring anions through C−H···S interactions that involve one phenyl C−H bond of one complex and a sulfur atom of the other. The net effect of such interactions is to generate discrete chains of anions oriented along [001]. Within each stack, the complexes are oriented in the same direction, and the close intrachain C−H···S contact observed is 2.904 Å for the aromatic H(16) atom of a complex unit and the S(4) atom of an adjacent molecule. There are no intermolecular contacts between chains. The Bu_4N^+ cations perfectly fit the holes among chains, with three of them sited around each complex anion. The shortest anion−cation distances always imply S and H atoms, and we do not believe that these anion−cation contacts dictate the distorted TP geometry of the anion.

Discussion

The structural shift from TP toward the octahedron as electrons are added to neutral Mo(VI) complexes can be first analyzed in terms of simple repulsion energy. To this regard, a comparison of the $[Mo^V(S_2C_6H_4)_3]^-$ structure with that observed for $[Nb^V(S_2C_6H_4)_3]^-$,[3b] which strongly resembles the Mo complex in metal size and also has the same charge, proves enlightening. In contrast to the distorted octahedral geometry of $[Mo^V(S_2C_6H_4)_3]^-$, $[Nb^V(S_2C_6H_4)_3]^-$ has a regular TP structure. This suggests that electrostatic repulsion is only a secondary factor in determining the structure of these monoanionic species, and, therefore, the distortion from TP symmetry is ultimately due to electronics effects.

For the discussion of the electronic structure, we shall use the MO scheme given in Figure 2 as a reasonably good one for TP tris(dithiolene) complexes.[18] In agreement with other early MO calculations,[1] the prism stability may be attributed to two kinds of π interactions: (1) between the d_{z^2} orbital, transforming as a_1', and a set of ligand orbitals from only sulfur p_z orbitals, which is responsible for $\sigma-\pi$ mixing, and (2) of $d_{x^2-y^2}$ and d_{xy} orbitals, transforming as e′, with thoroughly delocalized π orbitals from sulfur and carbon atoms normal to the principal planes of the ligands. This latter interaction accounts for the observed aromaticity of metalladithiolene rings[1b] and should tend

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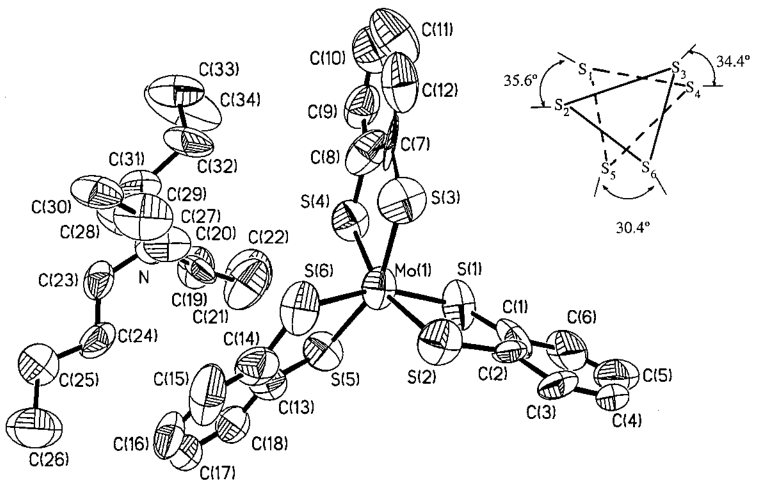

Figure 1. ORTEP drawing of structure and atom-labeling of $[(C_4H_9)_4N][Mo^V(S_2C_6H_4)_3]$. Thermal motion is represented by 50% probability ellipsoids. The coordination geometry of MoS_6 polyhedron as viewed down the approximate C_3 axis is shown in the insert.

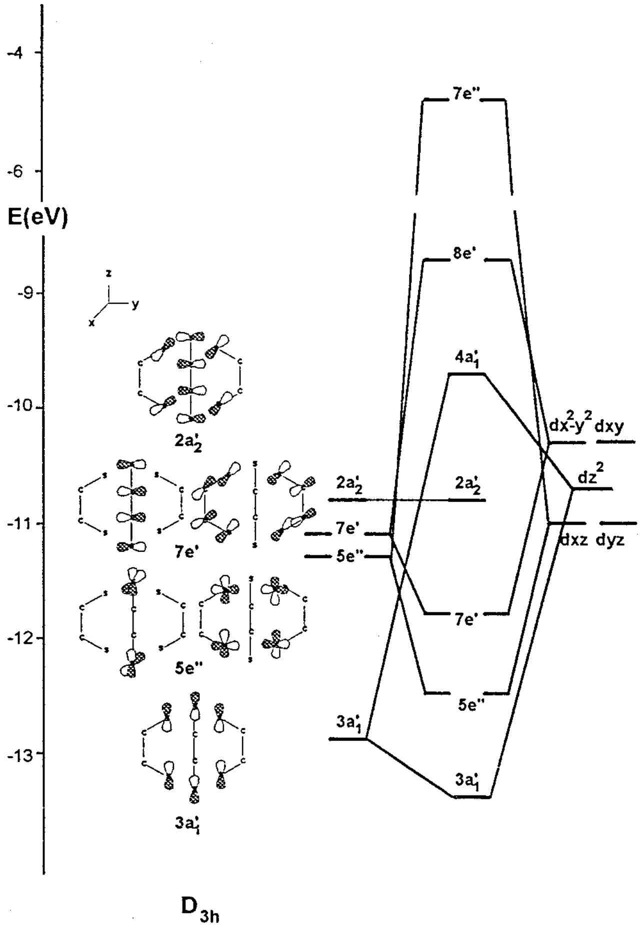

Figure 2. Molecular orbital diagram for $[Mo^{VI}(S_2C_2H_2)_3]$ showing the major d orbital interactions.

to lengthen the C−C bond connecting the sulfur atoms. Nevertheless, what is worth emphasizing here is that both (1) and (2) π-bonding interactions create interligand S···S distances and Mo−S bonds which are more covalent, stronger, and shorter. For the 12-electron $[Mo^{VI}(S_2C_6H_4)_3]$ complex, all bonding and nonbonding levels are occupied. Upon reducing this complex to form $[Mo^V(S_2C_6H_4)_3]^-$, the occupation of the π-antibonding level $4a_1'$ causes partial destabilization of both S···S distances and Mo−S bonds and induces distortion toward octahedral geometry. Consequently, in $[Mo^V(S_2C_6H_4)_3]^-$ the mean Mo−S bond length of 2.382 Å and interligand S···S distance of 3.254 Å are significantly longer than those reported for $[Mo^{VI}(S_2C_2H_2)_3]$, 2.367 and 3.110 Å, respectively.

Also, when the bend angle and the Mo−S bond length are increased, a less favorable π interaction of the $d_{x^2-y^2}$ and d_{xy} orbitals with the filled π ligand orbitals can be expected since no overlap can be achieved in the octahedral configuration. This is actually supported by close inspection of the metric parameters of the $Mo^VS_2C_2$ chelate ring. The most important information is provided by the shortening of C−C bonds between two sulfur atoms: 1.380 Å in $[Mo^V(S_2C_2H_4)_3]^-$ versus 1.412 Å in $[Mo^{VI}(S_2C_6H_4)_3]$. This feature reflects a sizable electronic delocalization from the aromatic C_6 rings to Mo under the D_{3h} symmetry of $[Mo^{VI}(S_2C_6H_4)_3]$ which cannot be achieved in the twisted $[Mo^V(S_2C_6H_4)_3]^-$.

Comparison of dimensional parameters of $[Mo^V(S_2C_6H_4)_3]^-$ with those reported for $[Nb^V(S_2C_6H_4)_3]^-$ further substantiates the importance of the π-bonding interactions. The Mo−S and the Nb−S distances differ by 0.059 Å, a value which is certainly less than the 0.074 Å value anticipated from the change in ionic radii of these metals. The 0.015 Å difference is virtually the same as that found for Mo−S distances in $[Mo^V(S_2C_6H_4)_3]^-$ and $[Mo^{VI}(S_2C_6H_4)_3]$, and again, the same π-bonding explanations, stabilizing the TP geometry reported for the Nb(V) complex, can be offered. Furthermore, one would expect the interligand S···S distance to be greater in the complex with the d^1 configuration, Mo(V), than in the d^0 Nb(V) complex. This S···S distance in $[Mo^V(S_2C_6H_4)_3]^-$ is in fact 0.022 Å longer than the interligand S···S distance in $[Nb^V(S_2C_6H_4)_3]^-$ (3.232 Å), and such difference is still far more significant if we take into account that the longer Nb−S bonds (2.441 Å) expand the S_6 cage.

Finally, it should be noted that the $[Sb^V(S_2C_6H_4)_3]^-$ structure[19] is of the octahedral type, with most parameters within 10% of octahedral values. This is in agreement with expectations for d^{10} complexes where all π-antibonding levels will be filled and the net interaction would be repulsive.

Another feature of the present structure that is worthy of mention is the planarity of benzenedithiolate ligands. The folding angles observed for individual ligands in $[Mo^V(S_2C_6H_4)_3]^-$, ca. 4.9, 5.6, and 6.8°, reveal no significant distortions from planarity. The previously reported bend of the S−C−C−S

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planes away from the S−Mo−S planes in $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}]$ (21.4°) has been explained by Harris et al.[20] using the results of Frenske−Hall MO calculations on the $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}]$ complex. This study suggests an electronic explanation for the ligand bending which is different from any of those previously proposed.[2] In the D_{3h} limit the HOMO is a nonbonding $2a'_2$ combination of ligand p_x and p_y orbitals, and the LUMO ($4a'_1$) consists primarily of the metal d_{z^2} orbital (Figure 2). Bending of the ligands reduces the symmetry from D_{3h} to C_{3h}, and both the HOMO and LUMO now transform as a′, which allows that they can mix together with the result that the HOMO is stabilized and LUMO is destabilized. This means that in the D_{3h} geometry (bend angle = 0°) the antibonding $4a_1'$ orbital of the theoretical $[\mathrm{Mo^{VI}(S_2C_6H_4)_3}]$ complex will be more antibonding, less stable than the corresponding a′ orbital of a C_{3h} geometry (bend angle ≠ 0°) with the same Mo−S distance. In complexes with additional electrons, the antibonding $4a_1'$ orbital (D_{3h}) is populated, and the driving force for bending is considerably less or nonexistent, which is consistent with the folding angles observed for $[\mathrm{Mo^{V}(S_2C_6H_4)_3}]^-$.

In conclusion, this study has demonstrated that the $[\mathrm{Mo^{V}(S_2C_6H_4)_3}]^-$ structure is deformed considerably toward octahedron and that there is a good electronic reason behind such distortion. Such a result clearly limits the previously reported postulate[3,11] that matching ligand orbital and metal d orbital energies is the most important factor in maintaining the trigonal prismatic geometry in tris(benzenedithiolate) complexes of transition metals.

Experimental Section

Materials. Tetra-*n*-butylammonium hydrogen sulfide was purchased from Fluka. $\mathrm{MoO_2(acac)_2}$ [21] and $\mathrm{C_6H_4(SH)_2}$ [22] were prepared by literature methods and characterized accordingly. Reagent grade solvents, distilled and dried by standard methods, were used in all cases. All operations and reactions were carried out under an atmosphere of dry N_2 or Ar with deaerated solvents.

Preparation of Complexes. $[\mathrm{Mo(S_2C_6H_4)_3}]$. $\mathrm{MoO_2(acac)_2}$ (0.5 g, 1.5 mmol) was dissolved in 15 mL of $\mathrm{CH_2Cl_2}$, and 0.65 g (4.6 mmol) of benzene-1,2-dithiol in 5 mL of $\mathrm{CH_2Cl_2}$ was added dropwise with stirring. The solution was stirred for 30 min at room temperature, after which the dark solid that formed was collected by filtration, washed with 5 × 10 mL portions of *n*-hexane, and dried in vacuo. Yield 70%. The complex was recrystallized from $\mathrm{CS_2}$/*n*-hexane (5:1) and dried in air to give deep-green crystals. Elemental analysis and spectroscopic parameters are in all respects identical with those previously reported for the same complex prepared from the reaction of solid $\mathrm{MoCl_5}$ with benzene-1,2-dithiol.[1a]

$[\mathrm{N(C_4H_9)_4}]_2[\mathrm{Mo(S_2C_6H_4)_3}]$. To 75 mL of a $\mathrm{CHCl_3}$ solution of $\mathrm{Mo(S_2C_6H_4)_3}$ (0.1 g, 0.2 mmol) was added dropwise an excess amount of $(\mathrm{Bu_4}^n\mathrm{N})\mathrm{HS}$ (0.22 g, 0.8 mmol) dissolved in 4 mL of $\mathrm{CHCl_3}$. The color immediately changed from green to olive green and finally to dark blue. The resulting air-sensitive reaction mixture was concentrated under vacuum, and the residual oil was diluted with 15 mL of MeCN. Cooling to −15 °C for 12 h yielded dark-blue crystals, which were filtered off, washed with 10 mL of cold MeCN, and dried in vacuo for 1 day; yield, 0.09 g, 45%. Anal. Calcd for $\mathrm{C_{50}H_{84}MoN_2S_6}$: C, 60.0; H, 8.4; S, 19.2; N, 2.8. Found: C, 59.7; H, 8.3; S, 18.8; N, 2.8. Absorption spectrum (THF): $\lambda_{\max}$ (ϵ_M) = 359 (13386), 584 (7693) nm.

$[\mathrm{N(C_4H_9)_4}][\mathrm{Mo(S_2C_6H_4)_3}]$. Method a. $[\mathrm{N(C_4H_9)_4}]_2[\mathrm{Mo(S_2C_6H_4)_3}]$ (0.1 g) was dissolved in 150 mL of 96% ethanol, and the blue solution was exposed to air, where it slowly became olive green. After 3 days at room-temperature, well-formed crystals of this complex salt were separated, washed with *n*-hexane, and dried in vacuo for 1 day; yield, 0.03 g (40%). Anal. Calcd for $\mathrm{C_{34}H_{48}MoNS_6}$: C, 53.8; H, 6.3; S, 25.3; N, 1.8. Found: C, 54.1; H, 6.6; S 24.9; N, 2.0. Absorption spectrum (THF) $\lambda_{\max}(\epsilon_M)$ = 414(14494), 614 (6229), 693 (5895).

Method b. Preparation of this compound was very similar to that of the Mo(IV) analogue. The reaction system $\mathrm{Mo(bdt)_3}$ (0.1 g, 0.2 mmol) and $(\mathrm{Bu_4}^n\mathrm{N})\mathrm{HS}$ (0.06 g, 0.2 mmol) in $\mathrm{CH_2Cl_2}$ gave a crude solid which was recrystallized from THF/*n*-hexane (5:1); yield, 0.11 g (68%).

Single-Crystal X-ray Diffraction. A well shaped, dark-green crystal of $[\mathrm{N(C_4H_9)_4}][\mathrm{Mo(S_2C_6H_4)_3}]$ with approximate dimensions 0.21 × 0.11 × 0.08 mm was mounted on a Siemens P4 four-circle diffractometer equipped with Mo Kα radiation. In the solution and refinement of the structure, the SHELXTL 5.0 software package was used.[23] The initial solutions were obtained by the heavy-atom method; coordinates of the metal atom were determined from Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier maps. The structure was refined by a full-matrix least-squares method against F^2 with statistical weighting and anisotropic displacement parameters for all non-hydrogen atoms. In the final stages of refinement, hydrogen atoms were added at idealized positions and refined as riding atoms with a uniform value of U_{iso}. Crystal data and final agreement factors are listed in Table 1. Observed and calculated structure factors, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles are given in the Supporting Information.

Other Physical Measurements. Absorption spectra were recorded on a HP8543 diode-array UV−vis spectrophotometer using quartz cells. Cyclic voltammetry and coulometry were performed in $\mathrm{CHCl_3}$, THF, or MeCN, with 0.1 M tetrabutylammonium hexafluorophosphate solutions as supporting electrolyte. Data were obtained at room temperature with use of a three-electrode cell described previously.[24] Potential measurements were made with the methanolic saturated calomel electrode (E = 0.00 V versus aqueous SCE); coulometric measurements were made at a potential 0.1 V more negative than the CV reduction peaks.

EPR spectra were obtained with a Bruker ER 200D X-band spectrometer. Samples from room-temperature reductions were transferred with a gastight syringe under Ar. EPR$\langle g \rangle$ and ^{95,97}Mo $\langle A \rangle$ values were obtained from the solution spectra, using DPPH as standard.

Supporting Information Available: X-ray crystallographic file and stereoview (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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