methyl group in **3a** compared to the doublet of the methyl group in **3b** indicate **3a** is the predominant isomer, approximately 95%, in CDCl₃.

Complexes **1** and **2** are not thermally interconvertible in hydrocarbon solution.[17] Complex **1** is stable up to 125 °C, whereupon it is decarbonylated to the edge-bridged amido complex **5**, similar to observations previously noted for the *N*-benzylformamido complex.[5b] Complex **2** is stable up to 150 °C, whereupon it is decarbonylated to the methylnitrene complex, **6** (Scheme I).

The relationship of the transformations observed in this work to a general syngas conversion on polynuclear centers is summarized in Scheme II; transformations observed in this work are represented by solid arrows with X = NHMe. The top portion of Scheme II indicates a possible role for the C,X-bonded species in the decarbonylation of the O,C-bonded species to a μ-X bridged species (analogous to transformation **1** → **5** in Scheme I). The dotted arrows represent possible extension to C₂ species based on the greater stability of the three-atom bridging unit (analogous to complex **2**, in Scheme I). These proposals supplement those recently advanced by Wilkinson and co-workers for syngas conversions at binuclear ruthenium centers.[18] Such transformations may occur in systems containing a polynuclear species as a principal component or in other systems[19] where such may exist only as a minor *but very active* constituent.

Figure 1. Two views of the MoS_9^{2-} anion. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 50% probability surfaces.

the existence of Mo–S coordination and the presence of two or three iron atoms at close proximity (~2.7 Å) to the molybdenum atom.

This information has stimulated an interest in the synthesis of polynuclear Fe–Mo–S complexes, several of which have been isolated and structurally characterized.[3,4] In our approach toward the synthesis of these polynuclear complexes, we have used effectively the tetrathiomolybdate anion, MoS_4^{2-}, as a chelating ligand for iron.[4]

The use of other molybdenum sulfur complexes as "reagents" for the synthesis of polynuclear aggregates containing Mo–S coordination is hindered by the limited availability of binary Mo–S complexes. With the exception of MoS_4^{2-} and polymeric molybdenum sulfides, the only other binary Mo–S complexes characterized, to date, are members of a series of polynuclear molybdenum complexes which contain the disulfide (S_2^{2-}) ligands.[5] One of the these complexes, $Mo_2S_{12}^{2-}$, recently has been reported to be an excellent reagent for the generation of the $Mo_2S_4^{2+}$ core and the subsequent synthesis of various complexes containing this core.[6] In this communication we report on the synthesis and structural characterization of *the first mononuclear Mo(IV) complex, with a MoS₅ coordination sphere, containing the MoS²⁺ group.*

The reaction of (Et₄N)₂MoS₄ with dibenzyl trisulfide, (C₇H₇)₂S₃, under dinitrogen in acetonitrile, CH₃CN, solution at ambient temperature is rapid, and red-brown crystals of (Et₄N)₂MoS₉ (I) are deposited almost instantly in 90% yield. Anal. Calcd for $MoS_9C_{16}H_{40}N_2$ (M_r = 645.1): C, 29.79; H, 6.26; N, 4.34; S, 44.73; Mo, 14.87. Found: C, 30.52; H, 6.40; N, 4.45; S, 44.08; Mo, 14.61. The synthesis of I can also be accomplished in excellent yields (ca. 70%) by the reaction of (Et₄N)₂MoS₄ with an equimolar amount of elemental sulfur in CH₃CN at ambient temperatures in a dinitrogen atmosphere. The electronic spectrum of I in dimethylformamide (DMF) solution shows a strong ab-

(16) The chemical shift of hydrogen bridging an edge of the metal cluster also bridged by a RC≡NR' group is characteristically found from −14.95 to −15.16 ppm: δ −15.02 in HOs₃(μ-PhC=NMe)(CO)₁₀. See: (a) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. δ −15.15 in HOs₃(μ-HC=NMe)(CO)₁₀ −15.16 in HOs₃(μ-HC=NPh)(CO)₁₀, and −14.95 in HOs₃(μ-HC=NPh)(CO)₉(P(OMe)₃). See: (b) Adams, R. D.; Golembeski, N. *J. Am. Chem. Soc.* **1979**, *101*, 2579. This provides additional support for the structure assignment in **3a**.

(17) This observation has also been made independently by R. D. Adams, N. M. Golembeski, and J. P. Selegue (private communication from R. D. Adams). These workers have isolated an O,C-bonded formamido cluster complex as a minor product in the reaction of *p*-tolyl isocyanate with H₂Os₃(CO)₁₀. They noted also that phosphine substitution in the starting cluster can markedly affect the product distribution in its reaction with isocyanate, an observation which we confirm in our work.

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A New Mo(IV) Thioanion Containing the Mo═S₁ Unit. Synthesis and Structural Characterization of (Et₄N)₂MoS₉

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Structural information concerning the Mo-containing site of nitrogenase has become available recently. Analyses of the Mo X-ray absorption fine structure in the Fe–Mo protein component of nitrogenase[1] and the nitrogenase cofactor[1,2] have established

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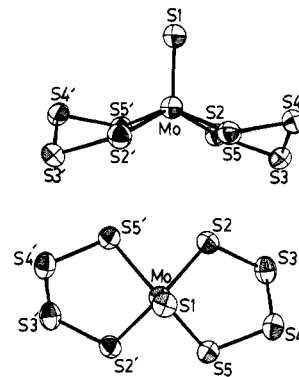(2) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249.

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Table I. Selected Structural Parameters in the MoS$_9{}^{2-}$-Dianion

Bond Lengths, Å			
Mo–S$_1$	2.128 (1)	S$_2$–S$_3$	2.166 (1)
Mo–S$_2$	2.331 (1)	S$_3$–S$_4$	2.012 (1)
Mo–S$_5$	2.387 (1)	S$_4$–S$_5$	2.107 (1)
Mo–S$_3$	3.735 (1)	S$_2$–S$_5$	3.345 (1)
Mo–S$_4$	3.535 (1)	S$_2{}'$–S$_5$	2.984 (1)

Bond Angle, deg			
S$_2$–Mo–S$_5$	90.32 (3)	Mo–S$_2$–S$_3$	112.28 (3)
S$_2{}'$–Mo–S$_5$	78.45 (3)	Mo–S$_5$–S$_4$	103.59 (3)
S$_1$–Mo–S$_2$	110.83 (3)	S$_2$–S$_3$–S$_4$	100.17 (4)
S$_1$–Mo–S$_5$	105.88 (3)	S$_3$–S$_4$–S$_5$	101.83 (5)

S$_2$–S$_3$–S$_4$/S$_3$–S$_4$–S$_5$ dihedral angle = 50.48 (6)

sorption at 316 nm (ϵ 15 750) and shoulders at 470, 405, and 340 nm. The Mo=S stretching vibration in the IR spectrum obtained in a KBr pellet occurs at 525 cm^{-1}.

Single crystals of I can be obtained by the slow diffusion of diethyl ether into a DMF solution of I.[7] X-ray diffraction data on a single crystal of I were collected on a Picker-Nuclear FACS-I automatic diffractometer using the θ–2θ scan technique and employing graphite monochromatized Mo Kα radiation (λ = 0.7107 Å, $2\theta_m$ = 12.2°). The data (full sphere to 2θ = 50°) corrected for Lorentz, polarization, and absorption effects were used for the solution of the structure by conventional, Patterson, direct methods, and Fourier techniques. Refinement was carried out by full-matrix least-squares methods. All hydrogen atoms were included at their calculated positions (C–H = 0.95 Å) but were not refined. Refinement on 145 parameters on 2146 data [$F_o{}^2 \geq 3\sigma(F_o{}^2)$] has converged to a conventional R factor of 0.025. All anisotropic temperature factors are normal and show no evidence for disorder or highly anisotropic thermal motions.

The structure of the anion in I (Figure 1) shows the Mo=S^{2+} unit coordinated by two S$_4{}^{2-}$ bidentate chelates. In the distorted square-pyramidal MoS$_5$ unit, the molybdenum atom is displaced from the basal plane of its square-pyramid toward S$_1$ by 0.73 Å. The MoS$_9{}^{2-}$ anion[8] is situated on a crystallographic twofold axis (at 0, $^1/_4$, z) that contains the Mo=S unit. The Mo=S distance at 2.128 (1) Å is near the upper end of the range for doubly bonded Mo–S distances[9] (1.937–2.129 Å). The "basal" Mo–S$_5$ and Mo–S$_2$ distances at 2.387 (1) and 2.331 (1) Å differ significantly from each other. At this time we do not have a satisfactory explanation for this difference;[10] however, a similar difference in chemically equivalent Mo–S bond lengths has been reported[11] for the anti form of Mo$_2$S$_4$(S$_2$C$_2$H$_4$)$_2{}^{2-}$ with Mo–S bridge bonds of 2.298 (3) and 2.344 (3) Å. The mean value of the basal Mo–S bonds in I, 2.36 (3) Å, is considerably shorter than the corresponding value reported for the oxobis(di-*n*-propyldithio-carbamato)molybdenum(IV) complex [2.413 (3) Å].[12]

The tetrasulfide ligand in I shows an interesting alternation in the lengths of the S–S bonds (Table I). Thus the two "terminal" S–S bonds (S$_2$–S$_3$, S$_4$–S$_5$) of 2.166 (1) and 2.107 (1) Å, respectively, are significantly longer than the $\overline{S–S}$ bond in orthorhombic sulfur[13] [2.037 (5) Å]. The S$_3$–S$_4$ "central" bond in I is signif-

icantly shorter than any of the above values at 2.012 (1) Å. This alternation in the S–S bond lengths is not observed for the S$_4{}^{2-}$ dianion in the structure[14] of BaS$_4$·H$_2$O ($\overline{S–S}$ = 2.069 (2) Å).

An alternation in the S–S bond lengths has also been observed for the S$_4{}^{2-}$ ligand in the structure of the (C$_5$H$_5$)$_2$MoS$_4$ complex[15] and has been rationalized as a result of significant Mo(d$_\pi$)–S(d$_\pi$) interactions. The rather short Mo(IV)–S bond lengths in I and the alternation in the S–S bond lengths within the S$_4{}^{2-}$ ligands could be rationalized in terms of a similar argument involving Mo(d$_\pi$)–S(d$_\pi$) and S(d$_\pi$)–S(d$_\pi$) interactions.[16]

In dimethyl sulfoxide solution, I is diamagnetic, as expected for a five-coordinate Mo(IV) complex with a d$_{xy}{}^2$ ground state in a pseudo C_{4v} geometry. Preliminary studies on the chemical reactivity of I indicate that the MoS$_9{}^{2-}$ anion is a rather reactive species. Upon refluxing in air, CH$_3$CN or DMF solutions of I slowly develop a green color. Golden green crystals of (Et$_4$N)$_2$MoOS$_8$ (II) can be isolated from these solutions following addition of ether to incipient crystallization and standing. Anal. Calcd for MoS$_8$OC$_{16}$H$_{40}$N$_2$ (M_r 629.1): C, 30.57; H, 6.37; N, 4.46. Found: C, 30.35; H, 6.46; N, 4.37.

The X-ray powder patterns of I and II are identical, and the infrared spectrum of II obtained in a KBr pellet shows a strong band at 930 cm^{-1} and no absorption at 525 cm^{-1}. We assign the 930-cm^{-1} absorption in II to the Mo=O$_t$ stretching vibration in a (S$_4$)$_2$MoO^{2-} anion, isostructural to (S$_4$)$_2$MoS^{2-}.

The formation of the MoS$_9{}^{2-}$ anion from MoS$_4{}^{2-}$ under apparently oxidizing conditions is intriguing. At present we can only speculate that the S$_4{}^{2-}$ chelating ligands and the Mo(IV) ion in I have been obtained as a result of intramolecular electron transfer in a S$_2$Mo^{VI}(S$_2$)$_2{}^{2-}$ unit. Such a unit could have been formed following S^0 addition to the MoS$_4{}^{2-}$ anion.

The (S$_4$)$_2$MoO^{2-} dianion appears to be a suitable model for dithionite-reduced sulfite oxidase. Both the oxidation state and the nature of the ligands encompassing the molybdenum agree with the EXAFS studies.[17] The apparent coordination unsaturation of the complex may allow for the interaction of a sixth ligand with the molybdenum atom. The molecular structure, redox properties, and reaction chemistry of this very interesting molecule are at present under study.

Supplementary Material Available: Observed structure factors for (Et$_4$N)$_2$MoS$_9$ and a table of atomic parameters (10 pages). Ordering information is given on any current masthead page.

(7) Crystal data for (Et$_4$N)$_2$MoS$_9$: cell dimensions, *a* = 15.594 (3), *b* = 13.264 (4), *c* = 27.577 (5); space group *Ibca*; Z = 8; d_{calcd} = 1.502 g cm^{-3}; d_{obsd} = 1.49 (2) g cm^{-1}; μ = 10.89 cm^{-1}.

(8) The two tetraethylammonium cations lie on crystallographic twofold axes at x, 0, $^1/_4$ and 0, $^1/_4$, z. The four independent C–N bond lengths span the range from 1.515 (3) to 1.520 (3) Å with a mean value of 1.517 (2) Å. Similarly the four independent C–C bonds are in the range between 1.502 (4) and 1.511 (4) Å with a mean value of 1.507 (4) Å.

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(10) Essentially the same differences in Mo–S and S–S bond lengths were found at the end of the isotropic refinement of the structure. Refinement on 718 data (2θ_{max} = 35°) conveyed to a conventional R value of 0.076. All of the isotropic temperature factors at this stage were small, in the range of 2.6–5.0 Å^2. The Mo–S$_2$ and Mo–S$_5$ bond lengths were 2.338 (5) and 2.382 (5) Å, respectively. The S$_2$–S$_3$, S$_4$–S$_5$, and S$_3$–S$_4$ bond lengths were 2.162 (8), 2.100 (7), and 2.021 (7) Å, respectively.

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Chemistry of Singlet Oxygen. 34. Unexpected Solvent Deuterium Isotope Effects on the Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$)

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In recent years it has become increasingly evident that the lifetime of singlet molecular oxygen ($^1\Delta_g$) is solvent dependent.[1-3]