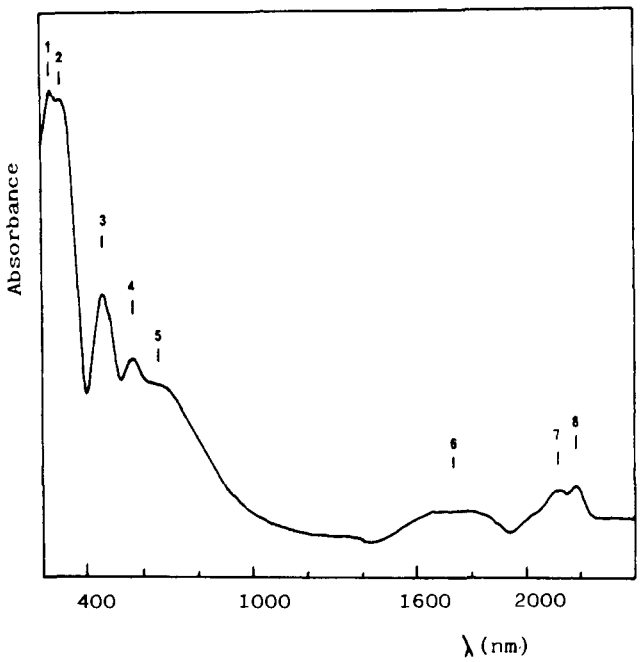

Figure 5. Diffuse-reflectance spectrum of $MnPO_4 \cdot 1.3H_2O$.

Table I. Diffuse-Reflectance Data for $MnPO_4 \cdot 1.3H_2O$

band	absorption		assignment
	nm	cm^{-1}	
1	255	39210	charge transfer
2	295	33900	charge transfer
3	455	21980	$^5B_{1g} \rightarrow {}^5E_g$
4	565	17700	$^5B_{1g} \rightarrow {}^5B_{2g}$
5	665	15040	$^5B_{1g} \rightarrow {}^5A_{1g}$
6	1600-1850	6250-5400	$2\nu(OH)^a$
7	2080	4810	$\nu(OH) + \delta(H_3O^+)$
8	2180	4590	$\nu(OH) + \delta(OHO)$

[a] Set of bands due to combination and overtones of OH stretching vibrations.

would be seen in its electronic reflectance spectrum. Mn(III) is a d^4 ion and in an octahedral environment one would expect only one absorbance band due to the $^5E_g \rightarrow {}^5T_{2g}$ transition, but in this case, the diffuse-reflectance spectrum (Figure 5) in the UV-vis region is formed by a set of five bands. Two bands near 255 and 295 nm (Table I) are too strong to be d-d transitions, and lying in the ultraviolet, they are assigned as oxygen to Mn(III) charge-transfer bands. The appearance of three bands in the visible region can only be explained by the presence of a strong Jahn-Teller effect. Table I lists the absorption maxima values and their assignments. The *Dq* parameter for this compound, read directly from the spectrum, has the value 1770 cm^{-1} because $10Dq$ coincides with the fourth transition energy $^5B_{1g} \rightarrow {}^5B_{2g}$. Analogous values are found for other compounds containing Mn(III), for example, 1790 cm^{-1} for $Mn(acac)_3$, 1780 cm^{-1} for $[MnF_6]^{3-}$, and 1667 cm^{-1} for $Mn(DMSO)_6^{3+}$.[19]

The ground-state splitting (GSS) coincides with the fifth band, and the excited-state splitting (ESS) is the difference between the third and the fourth bands. Thus, the GSS assumes a value of 15040 cm^{-1}, and the ESS, a value of 4280 cm^{-1}; both these values are of the same order but slightly higher than those found in the literature.[19,20] The assignments lead to fairly large values of McClure[21] parameters, $d\sigma = -5640$ cm^{-1} and $d\pi = -2140$ cm^{-1}. These are consistent with an elongated tetragonal distortion in which the oxygen to manganese π bonding is important. Definitively, the well-resolved splitting of the $^5T_{2g}$ state and the high values of *Dq*, $d\sigma$, and $d\pi$ picture of Mn(III) environment of tetragonal distorted-octahedral symmetry with a strong degree of covalence in the Mn-O bonding.

On the other hand, the diffuse-reflectance spectrum in the near-infrared region shows two sets of bands: (i) a very wide band (1550-1850 nm) due to the overtones and combinations of the different OH stretchings (ν(PO-H), ν(O-H), ν(MnO-H)) and (ii) two partially overlapping bands centered at 2080 and 2180 nm, which correspond to the $\nu(PO-H) + \delta(H_3O^+)$ and $\nu(PO-H) + \delta(OHO)$ combination vibrations, respectively.

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A Primary Molybdosulfenamide[1]

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A sulfide bridge of the Mo(V) dimer anion $[Mo_2(NC_7H_7)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CCH_3)]^-$ reacted with hydroxylamine-*O*-sulfonic acid to give the primary molybdosulfenamide $[Mo_2(NC_7H_7)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCH_3)(\mu\text{-}SNH_2)]$. This sulfenamide reacted with acetic anhydride to give the imide $[Mo_2(NC_7H_7)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCH_3)(\mu\text{-}SNHCOCH_3)]$. Treatment of sulfenamide with $(C_2H_5O)_2PS_2H$ or C_6H_5SH gave reductive S-N cleavage. The disulfide-bridged complex $[Mo_2(NC_7H_7)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCH_3)(\mu\text{-}S_2PS(OC_2H_5)_2)]$ was also prepared.

Introduction

The enzyme nitrogenase catalyzes the reduction of atmospheric dinitrogen to ammonia and has generated tremendous interest in agricultural, biological, genetic, and chemical arenas.[2-4] Much effort and emphasis have been placed on understanding the chemical structure and mechanism of action at the active binding site, but these yet remain unknown. The binding site is believed to be a Mo-Fe-S cluster, of which there are two per protein.[5-7]

(1) Reported in part at the Fourth International Conference on Bioinorganic Chemistry, Cambridge, MA, July 1989; Poster B023. Abstracted in: *J. Inorg. Biochem.* **1989**, *36*, 174.
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The "inorganic" composition of this cluster remains uncertain but is thought to be in the range $MoFe_{6-8}S_{4-9}$. X-ray crystallography of nitrogenase has been undertaken, and some preliminary results have been reported.[8,9] Structural information on the molybdenum site has been derived from X-ray absorption spectroscopy, which has revealed an environment of iron, sulfur, and either nitrogen or oxygen ligands.[10]

The interest in the biological system has spawned two independent paths of inorganic studies. The first concerns the chemistry of metal-coordinated dinitrogen and hypothetical intermediate ligands such as diazenido (RNN–), hydrazido (R_2NN–), and azo (RNNR) ligands.[11-14] More recently for molybdenum, these studies have steered into sulfur coligand complexes with an expressed interest to more closely represent a biological molybdenum site,[13,15-19] and a sulfur-only coligated dinitrogen complex, $[Mo(N_2)_2(C_{20}H_{40}S_4)]$, has been reported.[20] The second major pursuit of inorganic studies is in sulfido-molybdenum chemistry, especially in the area of Mo–Fe–S clusters, for which a variety of structural types and reactions have been described,[21-25] including reactions with nitrogenase model substrates.[26]

The mechanism of substrate binding and reduction by nitrogenase remains unknown. Traditionally the molybdenum is believed to be the initial dinitrogen binding site although there is little direct evidence.[27-30] A diversity of mechanistic schemes involving molybdenum have been proposed. These have invoked end-on or side-on binding of dinitrogen by one molybdenum and bridging by dinitrogen over two molybdenum sites (one from each cluster); various sequences of addition of H^+ and e^- then follow.[9,11-13]

Despite the heavy emphasis on molybdenum-centered proposals through the years, the very sanctity of this element as being primarily or even uniquely responsible for nitrogenase activity has recently been challenged. Two new, active forms of nitrogenase have been isolated, neither of which contains molybdenum and which are genetically distinct from the original Mo–Fe–S form. One alternate nitrogenase[31,32] contains a V–Fe–S cluster, while the second[33,34] apparently contains simply an Fe–S cluster in place of the heterometal cluster. These alternate forms are synthesized under Mo-depleted or Mo- and V-depleted conditions, respectively, thereby indicating a genetic priority scale with the Mo–Fe–S form at the top. Identification of these alternate forms resurrects questions regarding the nitrogen fixation mechanism. Furthermore, it is interesting to question roles for non-molybdenum atoms in the clusters. Iron has previously been suggested as involved in substrate interaction, and allusions to a direct role for sulfur have also been made.[7,30,35-38] These have not implied that Fe or S are necessarily a sole binding site but simply that these elements might also be involved (e.g., in addition to Mo) with substrate or its reduced intermediates at some point in the $6e^-$ reduction cycle. Direct research in this area is now of renewed, potential interest.

The preparation of a primary molybdosulfenamide, which contains the $Mo_2(\mu\text{-}SNH_2)$ group, and its reduction to liberate ammonia is described herein.

Experimental Section

Most operations were conducted open to air. Those indicated below to have been performed under N_2 were done on a vacuum line with dried, vacuum-transferred solvents.

N-Chlorosuccinimide was recrystallized from chloroform/ethanol/petroleum ether. $(EtO)_2PS_2H$ was vacuum distilled. Other commercial reagents were used as received. $[Mo(NTo)(S_2P(OEt)_2)S]_4$[39] and $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSPh)]$[40] (**5**) were prepared as previously described. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were obtained on a Varian XL300 spectrometer at 121, 75, and 300 MHz and are reported as downfield shifts from H_3PO_4 (^{31}P) and Me_4Si (^{13}C, ^1H). The solvent was $CDCl_3$. All NMR integrations were consistent with the assignments. IR spectra were obtained on a Perkin-Elmer 283 spectrophotometer as KBr pellets except as noted; only selected bands are listed. Galbraith Laboratories, Inc. (Knoxville, TN) performed the elemental analyses.

In all reactions, product identification was definitive by direct comparison to spectra of synthetic compounds or of commerical samples of the components.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNH_2)]$ (2). An orange-brown slurry of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.4184 g, 0.250 mmol), $MeCO_2H$ (0.11 mL, 1.9 mmol), and Et_3N (0.14 mL, 1.0 mmol) in THF (4

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mL)/EtOH (8 mL) was treated with NH_2OSO_3H (0.0622 g, 0.550 mmol) and then stirred 15 min. H_2O (10 mL) was added very slowly to the orange mixture, and the resulting precipitate was filtered out, washed (2:1 EtOH/H_2O), and dried to give a rust-colored powder (0.4156 g, 91%). Recrystallization was performed by evaporating a CH_2Cl_2 filtrate to small volume and treating with *i*-PrOH (3 mL, dropwise). Filtration, washing, (*i*-PrOH), and vacuum drying (18.5 h) gave red-orange crystals (0.3236 g, 71% overall). Anal. Calcd for $Mo_2C_{24}H_{39}N_3O_6P_2S_6$: C, 31.6; H, 4.3; N, 4.6; S, 21.1. Found: C, 31.4; H, 4.3; N, 4.6; S, 21.2. NMR data are as follows (ppm).[41] ^{31}P: 115.0 (115.0, 3 Hz upfield of major invertomer). ^1H: (6.74 d), 6.55 d, 6.46 d, To H; 4.25–3.95 m, $POCH_2$; (2.71 s), NH_2; (2.12 s), To CH_3; 2.08 s, NH_2 + To CH_3; 1.33 t, 1.21 t, $POCCH_3$; 1.31 s, O_2CCH_3. IR (cm^{-1}): 3364 w, 3280 w, 1530 m, 1442 s, 1050 sh, 1005 vs, 960 vs, 813 s, 794 s.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SND_2)]$. A solution of **2** (0.0911 g, 0.100 mmol) in THF (3 mL)/EtOD (0.5 mL)/D_2O (0.25 mL) was shaken gently for 10 min and then rotavapped. The residue was redissolved in fresh THF/EtOD/D_2O (same quantities) and again shaken 10 min. D_2O (4 mL) was then slowly added. The resulting precipitate was filtered out, washed (4:1 EtOD/D_2O), and vacuum-dried to give red-orange crystals (0.0825 g, 90%). The IR spectrum (cm^{-1}) showed ν(ND) at 2511 w and 2409 w. A Nujol spectrum showed no ν(NH), relative to a Nujol spectrum of **2**.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNHCOMe)]$ (3). An orange slurry of **2** (0.1826 g, 0.200 mmol) and $(MeCO)_2O$ (0.19 mL, 2.0 mmol) in 0.20 mL of CH_2Cl_2 was shaken gently for 30 min. The resulting solution was treated with petroleum ether (8.0 mL). The precipitate was filtered out, washed (petroleum ether), and vacuum-dried to give an orange powder (0.1787 g, 94%). Anal. Calcd for $Mo_2C_{26}H_{41}N_3O_7P_2S_6$: C, 32.7; H, 4.3; N, 4.4; S, 20.2. Found: C, 33.0; H, 4.4; N, 4.4; S, 21.1. NMR data are as follows (ppm)[41] (Roman numerals refer to specific isomers where discernible). ^{31}P: (114.8, III), 114.6, I, (114.6, IV, 10 Hz upfield of I), (114.3, II). ^1H: (6.79 d), (6.68 d), 6.63 d, I, (6.59 d, II), (6.50 d, II), 6.47 d, I, To H; (5.30 s, III), (5.15 s, IV), 4.90 s, I, (4.69 s, II), NH; 4.25–3.95 m, $POCH_2$; (2.76 s, II), (2.74 s), 2.05 s, I, $NCOCH_3$; (2.18 s), 2.09 s, To CH_3; 1.35 s, O_2CCH_3; 1.34 t, 1.19 t, $POCCH_3$. IR (cm^{-1}): 3370 w, 1691 m, 1534 m, 1443 s, 1036 sh, 1008 vs, 960 vs, 816 s, 793 s.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(S_2PS(OEt)_2)]$ (4). $(EtO)_2PS_2H$ (56 μL, 0.35 mmol) was added to a solution of *N*-chlorosuccinimide (0.04667 g, 0.350 mmol) in CH_2Cl_2 (1.0 mL). After 5 min, the yellow solution was added to a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2095 g, 0.125 mmol), $MeCO_2H$ (20 μL, 0.35 mmol), and Et_3N (49 μL, 0.35 mmol) in CH_2Cl_2 (2.0 mL), giving immediate fuming. This addition and all subsequent steps were conducted under dim light. The solution was stirred 10 min and then rotavapped. A THF filtrate (2.5 mL) of the residue was treated with 2:1 EtOH/H_2O (3.5 mL, dropwise). Filtration, washing (4:1 EtOH/H_2O), and drying gave orange crystals (0.2195 g, 81%). Recrystallization from CH_2Cl_2 (0.3 mL)/*i*-PrOH (0.9 mL) yielded deep orange crystals (0.1792 g, 66% overall). Anal. Calcd for $Mo_2C_{28}H_{47}N_2O_8P_3S_8$: C, 31.1; H, 4.4; N, 2.6; S, 23.7. Found: C, 31.2; H, 4.4; N, 2.5; S, 24.4. NMR data are as follows (ppm).[41] ^{31}P: (115.0), 114.4, $S_2P(OEt)_2$ bidentates; 87.2, (85.8), $S_3P(OEt)_2$ bridge. ^1H: (6.78 d), 6.58 d, 6.49 d, To H; 4.55 dq, bridge $POCH_2$; 4.25–3.95 m, bidentate $POCH_2$; (2.14 s), 2.10 s, To CH_3; 1.63 t, bridge $POCCH_3$; 1.34 t, 1.21 t, bidentate $POCCH_3$; 1.33 s, O_2CCH_3. IR (cm^{-1}): 1532 m, 1444 s, 1051 sh, 1006 vs, 965 vs, 814 s, 793 s.

Reaction of 2 with $(EtO)_2PS_2H$. To **2** (0.03426 g, 0.0376 mmol) in $CDCl_3$ (0.75 mL) was added $(EtO)_2PS_2H$ (36 μL, 0.22 mmol), causing rapid darkening and precipitation of colorless crystals. The sample was kept in the dark and periodically monitored by ^{31}P and ^1H NMR spectroscopy.

In a separate experiment, **2** (0.0455 g, 0.0499 mmol) in $CHCl_3$ (1.0 mL) was treated with $(EtO)_2PS_2H$ (48 μL, 0.30 mmol) and stirred 30 min. Addition of C_6H_6 (1.0 mL) followed by centrifugation and decantation left the precipitate, which was further rinsed three times with C_6H_6 (2.0 mL), each time followed by centrifugation and decantation. The dried crystals were shown by NMR (^{31}P and ^1H) and IR spectroscopy to be $(NH_4)S_2P(OEt)_2$ (0.0088 g, 87%).

Reaction of 2 with PhSH. An NMR tube containing **2** (0.04551 g, 0.0499 mmol), PhSH (50 μL, 0.49 mmol), and $CDCl_3$ (1.0 mL) was prepared under N_2 and then frozen, evacuated, and sealed. After initial NMR spectra were obtained, the sample was placed in a black rubber tube and immersed in a 60 °C water bath. Periodically the sample was removed from the bath and NMR spectra were obtained. Reaction times reported are for 60 °C time only. Preparation of the sample and subsequent handling were done under red light conditions.[39]

Reaction of 5 with PhSH. This reaction was performed exactly as for **2**/PhSH, using **5** (0.05034 g, 0.0501 mmol), PhSH (46 μL, 0.45 mmol), and $CDCl_3$ (1.0 mL).

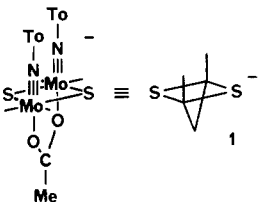
Reaction of 5 with PhSH and NH_3. This reaction was performed exactly as for **2**/PhSH, using **5** (0.05016 g, 0.0499 mmol), PhSH (46 μL, 0.45 mmol), NH_3 (1.2 mL, 0.05 mmol), and $CDCl_3$ (1.0 mL). For NH_3 addition, the gas was injected at the bottom of the $CDCl_3$ solution of other reagents while in a dry ice bath.

Reaction of 2 with $MeCO_2H$ and NH_3. This reaction was performed exactly as for **5**/PhSH/NH_3, using **2** (0.04558 g, 0.0500 mmol), $MeCO_2H$ (2.9 μL, 0.051 mmol), NH_3 (1.2 mL, 0.05 mmol), and $CDCl_3$ (1.0 mL).

Reaction of 3 with PhSH. This reaction was performed exactly as for **2**/PhSH, using **3** (0.04765 g, 0.0500 mmol), PhSH (50 μL, 0.49 mmol), and $CDCl_3$ (1.0 mL).

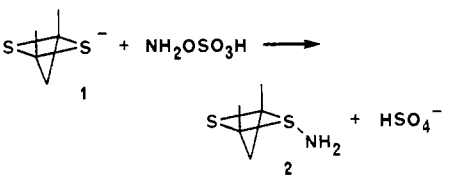
Results

The dimer anion $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^-$ (**1**) (see footnote 42 for abbreviations; dithiophosphates are omitted from the diagram for clarity) has an established sulfur-based



reactivity characterized by nucleophilic substitution and addition reactions.[40,43] Procedurally, the anion is generated in situ in a favorable equilibrium reaction[39] from the tetramer $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (hereinafter $[Mo_4]$) and acetate, which is herein supplied as $MeCO_2H$ + Et_3N.

The reaction of anion **1** with hydroxylamine-*O*-sulfonic acid has produced the primary molybdosulfenamide $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNH_2)]$ (**2**) (eq 1). This compound



(1)

contains the amide function bound to the bridge sulfur position and resembles primary organic sulfenamides, $RSNH_2$. This resemblance is a further parallel between $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]$ chemistry and that of RS, either as anions or as radicals, as has been previously described.[40,43-45]

The formulation of sulfenamide **2** is fully supported by elemental analyses, IR spectroscopy, and NMR spectroscopy. The IR spectrum shows ν(NH) at 3364 and 3280 cm^{-1}, in good agreement with published $RSNH_2$ values.[46-48] The NH_2 resonance is seen in ^1H NMR spectra, albeit indirectly. At normal temperatures (~19 °C) in $CDCl_3$, the minor invertomer (vide infra) NH_2 is seen at 2.71 ppm, but the major invertomer is coincident with the To CH_3 resonance at 2.08 ppm. This major NH_2 resonance, however, has a strong temperature dependence: at −60 °C the NH_2 peak is 0.16 ppm downfield of To CH_3, while at 60 °C the peak is 0.06 ppm upfield of To CH_3.

Sulfenamide protons readily exchanged with D^+. This was observable by NMR spectroscopy as a loss of NH_2 resonances upon shaking a $CDCl_3$ solution of **2** with D_2O. Isolated deuterio-**2** shows ν(ND) at 2511 and 2409 cm^{-1}, appropriately shifted relative to **2**.

(41) Where minor isomers are clearly discernible, their shifts are given in parentheses.

(42) Abbreviations: Me, methyl; Et, ethyl; Ph, phenyl; To, *p*-tolyl.
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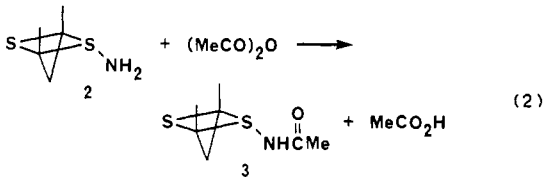
Initial X-ray crystallographic results for **2** have confirmed the structure.[49]

The molybdosulfenamide is a fully stable compound, unlike many primary organosulfenamides. Although substituted derivatives RSNHR′ and $RSNR'_2$ are well established, stable primary derivatives are limited.[46-48,50-52] The synthetic route to $RSNH_2$ using NH_2OSO_3H has been previously demonstrated.[46,53] In addition, Deutsch et al. have used this reagent to convert the cobalt-bound ligand $NH_2CH_2CH_2S^-$ to $NH_2CH_2CH_2SNH_2$.[54]

The molybdosulfenacetimide complex $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNHCOMe)]$ (**3**) is obtained in high yield by reaction of sulfenamide **2** with acetic anhydride (eq 2). This



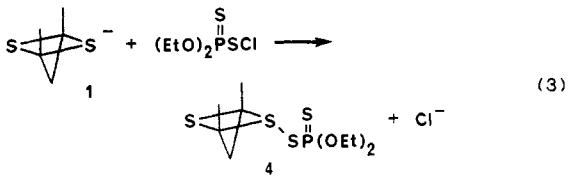
(2)

reaction parallels previous results for reactions of primary organosulfenamides with acid anhydrides,[46,55] or other carbonyl derivatives.[48,51]

The sulfenacetimide derivative, **3**, was characterized by IR and NMR spectroscopy. The NHCOMe group is evident in the IR spectrum by ν(NH) at 3370 cm^{-1} and ν(CO) at 1691 cm^{-1}; these are in addition to usual dimer absorptions.[40] NMR spectra are complicated by the presence of four conformational isomers (vide infra): these are most evident by clear observation of four ^{31}P and four NH (^1H) resonances; all four isomers are not resolvable for other positions. The assignment of NH resonances is unambiguous due to facile exchange with D_2O. The assignment of $NCOCH_3$ resonances is unambiguous due to the use of acetic anhydride-d_6 in alternate syntheses, which gives the μ-$SNHCOCD_3$ derivative. This deuterio product also shows a diminished $Mo_2(\mu\text{-}O_2CCH_3)$ resonance due to some $CD_3CO_2^-/CH_3CO_2^-$ bridge exchange.

Some hydrolysis of sulfenacetimide **3** occurs slowly in wet (air-exposed) $CDCl_3$ at 50–60 °C to give sulfenamide **2**, but the compound is otherwise of good stability.

The dithiophosphate disulfide-bridged dimer $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(S_2PS(OEt)_2)]$ (**4**) was prepared for definitive identification of reaction products described below. Synthesis of this compound is from dimer anion **1** and $(EtO)_2P(S)SCl$, generated in situ (eq 3). This preparation follows that

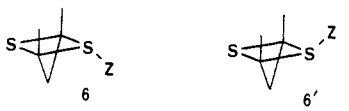


(3)

of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSPh)]$ (**5**) and homologues.[40] Compound **4** is prepared under reduced room light: initial studies suggest its photosensitivity to be between that of R = aryl and R = alkyl in the $Mo_2(\mu\text{-}SSR)$ series[44] of which **5** is a member.

Elemental analyses, IR spectroscopy, and NMR spectroscopy fully support the formulation of the dithiophosphate disulfide-bridged dimer. ^1H and ^{31}P NMR spectra clearly reveal bidentate and bridge dithiophosphates in 2:1 ratio. The bridge $(EtO)_2PS_3$ unit is seen at 87.2 and 85.8 ppm (invertomers, vide infra), comparable to the simple disulfide $(EtO)_2P(S)SSP(S)(OEt)_2$, whose resonance was separately found at 85.4 ppm.

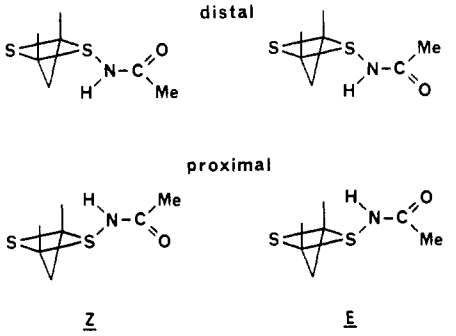
Conformational Isomerism. A variety of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SZ)]$ derivatives have displayed conformational isomerism related by bridge sulfur inversion. These are representable by formulations **6** and **6′**, wherein Z is distal or



proximal, respectively, relative to the tolylimido rings.[40,43] Currently, the sulfenamide, **2**, the sulfenacetimide, **3**, and the dithiophosphate disulfide-bridged dimer, **4**, show these invertomers in solution. For **2**, the invertomer ratio (**6**/**6′**) was estimated to be ~30 with significant uncertainty due to overlap of invertomer resonances. For the disulfide-bridged dimer, **4**, the ratio was measured to be 8.

For the sulfenacetimide complex, **3**, four isomers are seen by NMR spectroscopy. These are presently labeled I (66%), II (25%), III (5%), and IV (3%), where the percent distribution is derived from NH peak integrations. Where possible, resonances were assigned to the specific isomers as listed in the Experimental Section.

Isomers in addition to the usual sulfur invertomers are assigned to C–N rotamers within the acetamide group, consistent with established conformational isomerism of carboxamides.[56,57] The combination of sulfur invertomers and C–N rotamers gives four possible conformations as follows:



Actually the sulfenamide unit itself can again double the number of isomers due to restricted S–N rotation,[58,59] but no evidence for such has been found for **3**. All NMR spectra show end-to-end equivalence within the dimolybdenum fragment, consistent with enantiotopic tolyl and dithiophosphate groups. This allows treatment of the SNHCOC unit as lying in the plane perpendicular to the Mo–Mo vector midpoint. Thus, S–N rotation either is precluded or is very fast. The latter is reasonable, albeit not exclusively, based on a study of amide C–N and sulfenamide S–N rotation rates within a sulfenurethane.[60]

Consistent with a prior assignment of sulfur invertomers based on tolylimido ring proton resonances,[40] isomers I and II of sulfenacetimide **3** are assigned to distal invertomers; III and IV are then assigned to proximal invertomers. For *Z*/*E* distinction, a nuclear Overhauser experiment was performed (evacuated, sealed tube; dry $CDCl_3$; −20 °C) by irradiating individual $NCOCH_3$ isomer resonances while NH was observed. A 5% enhancement was observed for isomer I; no effect was observed for isomer II. Isomers III and IV were not similarly examined. Summarily, the results suggest isomer I is distal *Z*, II is distal *E*, and III and IV

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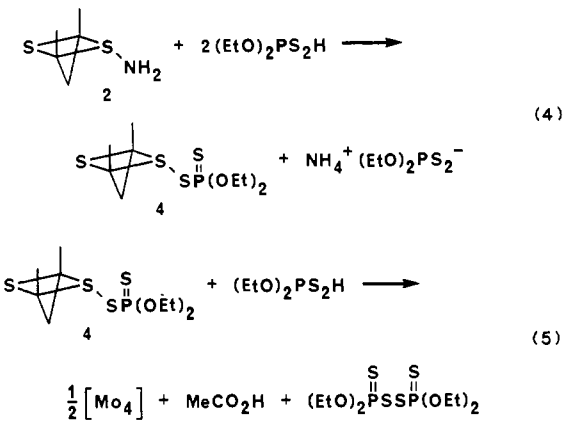
are proximal but not further defined.

Variable-temperature studies for **3** revealed coalescence of isomer I with II and coalescence of III with IV by 55–60 °C, but (I + II) remained yet separate from (III + IV). Thus, coalescence of C–N rotamers precedes that of sulfur invertomers.

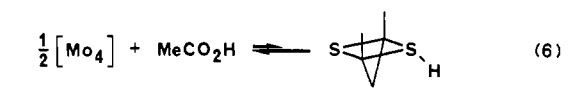
Reductions. Reductive cleavage of the sulfenamide functionality in **2** was investigated by using a thioacid, $(EtO)_2PS_2H$, and a thiol, PhSH.

Treatment of molybdosulfenamide **2** with 6-fold $(EtO)_2PS_2H$ resulted in a rapid reaction with copious precipitation. Monitoring the reaction by NMR spectroscopy (^{31}P and ^{1}H) revealed 6% unreacted **2**, 71% dithiophosphate-bridged dimer **4**, and 23% $[Mo_4]$ at 18 min; at 60 min the respective amounts were zero, 62%, and 38%. After 4 h, 31% **4** and 69% $[Mo_4]$ remained. Throughout, $(EtO)_2PS_2H$ decreased while the disulfide $(EtO)_2P(S)SSP(S)(OEt)_2$ increased. The initial precipitate was the salt $(NH_4)S_2P(OEt)_2$ obtainable in high yield from the reaction.

The results clearly indicate the two-step sequence given by eqs 4 and 5. Inherent to $[Mo_4]$ production is the unfavorable



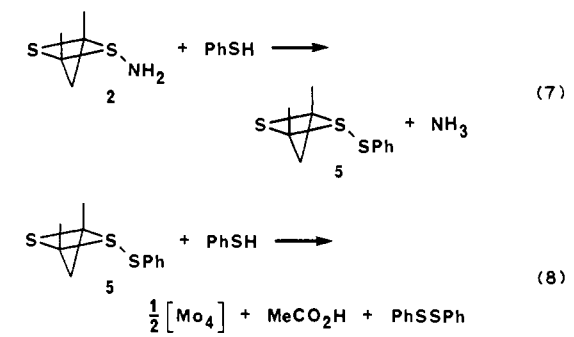
equilibrium of eq 6, involving a hydrosulfide-bridged dimer.[39] (The



deprotonated form of eq 6 lies to the right and constitutes the generation of dimer anion **1** mentioned above.)

While reaction with thioacid at room temperature was thus rapid and straightforward, reaction with 10-fold benzenethiol at 60 °C was slower and showed additional complexities, including enhanced decomposition at long times at the elevated temperatures employed. NMR monitoring of this reaction included ^{31}P, ^{1}H, and ^{13}C. The results showed 78% unreacted **2** and 22% $[Mo_4]$ at 4.0 h; those quantities were 28% and 58% at 12.0 h and 3% and 66% at 23.0 h with the balance of material as decomposition products. PhSSPh was clearly seen, but the PhSS-bridged dimer, **5**, was never observed. The system was further complicated by identification of free acetamide as a significant reaction product.

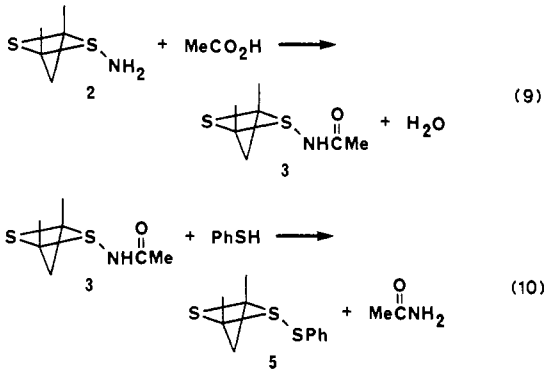
A two-step reaction had been anticipated analogous to eqs 4 and 5 but modified as shown by eqs 7 and 8. Here, ammonium



acetate was the expected precipitate; a colorless precipitate was indeed observable but in small amount. Nevertheless, the observation of acetamide required a decrease in ammonium acetate yield.

Failure to observe the PhSS-bridged dimer **5** was explicable by the relative rates of eqs 7 and 8. Separately, reaction of **5** and 9-fold PhSH was examined, equivalent to eq 8: after 1.0 h at 60 °C, 60% unreacted **5** and 40% $[Mo_4]$ were observed. Reaction was nearly complete at 4.0 h with only 3% **5** and 95% $[Mo_4]$. This reaction was even faster in the presence of 1 equiv of NH_3, as would be produced by eq 7: at 24 min at room temperature, only $[Mo_4]$ was seen in the ^{31}P NMR spectrum. No free acetamide was observed. Thus, eq 8 was indeed much faster than eq 7, accounting for the failure to observe **5** in the reduction of sulfenamide **2**.

The observation of acetamide in the overall reduction of sulfenamide **2** is explained by a side reaction producing the sulfenacetimide **3**, which is itself then reduced (eqs 9 and 10). Each



of these steps was also separately examined. Reaction of sulfenamide **2** with $MeCO_2H/NH_3$ at 60 °C (eq 9) was conducted. The NH_3 was included to mimic its presence via generation by eq 7. The solubility of ammonium acetate in $CDCl_3$ was very poor at room temperature but significantly greater at 60 °C. There is therefore a question in invoking $MeCO_2H$ or $MeCO_2^-$, but the former is indicated in eq 9 for simplicity. The results for this reaction showed 69% unreacted **2** and 31% **3** after 1.0 h; at 4.0 h, these quantities were 39% and 46% with the remainder as decomposition products. Reaction of sulfenacetimide **3** with 10-fold PhSH at 60 °C (eq 10) was plagued by enhanced decomposition, but $[Mo_4]$ was indeed the first observable product, with 6% observed at 15 min. At 1.0 h, 70% **3** and 21% $[Mo_4]$ were found, but by 4.0 h decomposition was already excessive. Acetamide was clearly observed throughout. This reaction was therefore itself two-step, in the sequence eqs 10 + 8.

Summarily, the reduction of sulfenamide **2** with excess benzenethiol follows two paths. The initial path is via eqs 7 + 8 until enough $MeCO_2H$ is generated to make the path via eqs 9 + 10 + 8 significant. The complexity of the spectra prohibit an accurate measure of the relative weights of the two pathways, although a reasonable estimate places acetamide yield in the 20–60% range. Studies of the individual reactions suggest eq 7 to be the slowest. The overall kinetics of the system are such that intermediates **3** and **5** never reach observable concentrations.

Discussion

Organosulfenamides have been studied for some time,[51,52] and examples are known for them to serve as S- or N-bound ligands.[54,61] The metallosulfenamide linkage, M_xSNR_2, is less established.[62]

The facile preparation and high stability of the current primary molybdosulfenamide **2** contrasts with the general poor stability of primary organosulfenamides, which tend to instead form bis(sulfen)imides, $(RS)_2NH$. This has been ascribed to nucleophilic attack by N of one $RSNH_2$ on S of a second $RSNH_2$, with liberation of ammonia[47] (eq 11). Isolable $RSNH_2$ are obtainable

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(62) A $PtSSNR_2$ complex has been reported: Shaver, A.; Hartgerink, J.; Lai, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938.

$$2RSNH_2 \rightarrow (RS)_2NH + NH_3 \quad (11)$$

when R is electron withdrawing[47] or when the reaction is presumably sterically precluded.[48] Either or both of these factors may be operating in the case of **2**. This reaction pathway may have some consequence on isolation of other primary metallosulfenamides, particularly those derived from metallosulfur complexes with two sulfur sites within interaction distance.

The thioacid and thiol reactions with molybdosulfenamide **2** fully parallel similar reactions with organic sulfenamides.[51] The mechanism involves nucleophilic attack by thio sulfur on sulfenamide sulfur, generating disulfide and free amine. This method has served as a means of preparing unsymmetrical disulfides.[63,64] The current results with **2** are consistent with a nucleophilic mechanism. Although radical chemistry has been established for a series of disulfide-bridged dimers (including **5**),[44] such has been entirely photoinitiated. Dark (red light) conditions were employed in the current work to eliminate interference from photohomolysis.

While the sulfenamide **2** has displayed some versatile chemistry to date (more results forthcoming), an inherent interest in the S–N linkage in general stems from considerations for a possible S–N interaction at some point in a biological nitrogen fixation cycle (see Introduction). This notion has been previously suggested,[35-38] but the background chemistry remains underdeveloped. The notion is, however, supported by several factors: the existence of three different forms of nitrogenase, all of which contain Fe and S; the large variety of reactions displayed by sulfur in recent years within a range of metallosulfur complexes;[65-80] and the chemistry of diazosulfides (RSNNR'),[81-83] sulfenylhydrazines (RSNR'NHR'),[84,85] thionitrosamines ($SNNR_2$),[86-88] etc., which contain sulfur bound to nitrogen units traditionally held as models for possible intermediates in nitrogen fixation.[12-14] Furthermore, the report of the binding of N_2 to sulfur in the benzenesulfenium cation under modest conditions remains intriguing.[89]

The current sulfenamide **2** undergoes facile reductive cleavage to liberate ammonia. This contrasts with metal amide conversion to ammonia, which involves protonation without redox. In terms of possible relevance to nitrogenase, either of these methods, taken by themselves, is reasonable, but the importance of this stage is probably minor. The more crucial question concerns prior mechanistic steps, especially the N_2 binding and first reduction step, since these are traditionally regarded as the chemically most difficult.[9,12,28] Thus, to invoke a sulfenamide opens the question as to where S–N interaction may have initiated.

Further studies are in progress.

Acknowledgment. This work was supported by research awards from the College of Arts and Sciences of the University of Louisville, the National Science Foundation (Grant No. RII-8610671), and the Kentucky EPSCoR Program.

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