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A Dimolybdosulfenamide: Condensations and Crystal Structures. Sulfur Invertomer Structural Effects

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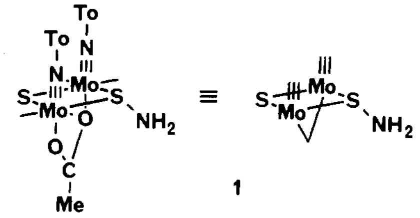
The H_2NS^- bridge of the sulfenamide $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCH_3)(\mu\text{-}SNH_2)]$ (**1**) reacted with RCHO (R = H, CH_3, $C(CH_3)_3$, $C_6H_4CH_3$) and $(CH_3)_2CO$ to give sulfenimines $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCH_3)(\mu\text{-}SN{=}CRR')]$ (**2**(R,R')) containing thiooximate bridges, $RR'C{=}NS^-$. Both sulfur and nitrogen inversion isomers were observed in solution by NMR (^1H, ^{31}P, and ^{15}N) spectroscopy. Crystal structures of **1**, **2**($H,C(CH_3)_3$), and **2**(CH_3,CH_3) were determined: **1**, $Mo_2C_{24}H_{39}N_3O_6P_2S_6$, a = 13.781 (2) Å, b = 14.524 (2) Å, c = 10.961 (2) Å, α = 104.48 (1)°, β = 106.39 (1)°, γ = 107.31 (1)°, triclinic, $P\bar{1}$, Z = 2; **2**($H,C(CH_3)_3$), $Mo_2C_{29}H_{47}N_3O_6P_2S_6$, a = 12.473 (3) Å, b = 28.197 (5) Å, c = 13.568 (3) Å, β = 114.81 (2)°, monoclinic, $P2_1/n$, Z = 4; **2**(CH_3,CH_3), $Mo_2C_{27}H_{43}N_3O_6P_2S_6$, a = 15.602 (2) Å, b = 15.618 (2) Å, c = 9.627 (2) Å, α = 91.13 (2)°, β = 96.25 (2)°, γ = 117.59 (2)°, triclinic, $P\bar{1}$, Z = 2. A comparison of the structures involving the two sulfur inversion orientations revealed that the primary structural differences between invertomers were associated with the Mo_2S_2 planarity and with the pyramidal nature of the tricoordinate sulfur.

Introduction

The organosulfenamide unit, $RSNR'_2$, is a well-established functionality, and much interest in it stems from a variety of applications in various fields including the rubber industry, agriculture, medicine, organic syntheses, bonding studies, and configurational studies.[1-5] Several metal complexes containing organosulfenamide ligands are known,[6,7] but metallosulfenamides themselves, as M_xSNR_2, are not well established, although a $PtSSNR_2$ complex (NR_2 = phthalimide) has been demonstrated.[8] The M_xSNR_2 unit, containing thiohydroxylamide R_2NS^- as a ligand, can be compared to the more established metal–hydroxylamine system which usually (albeit not exclusively) involves side-bound R_2NO^- ligands.[9,10]

The synthesis of a dimolybdosulfenamide, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNH_2)]$ (**1**), has been previously reported.[11] (See footnote[12] for abbreviations; dithiophosphates are omitted from the diagram of **1** for clarity). This compound contains the $Mo_2(\mu\text{-}SNH_2)$ linkage and is additionally notable as being a stable primary sulfenamide. Primary organosulfenamides, $RSNH_2$, are known but are less stable and are much fewer in number than the N-substituted derivatives, $RSNHR'$ or $RSNR'_2$.[13]



1

The primary organosulfenamide unit, where available, has provided a route to sulfenimines, $RSN{=}CR'_2$, via condensation reactions with aldehydes and ketones.[2,14] It was therefore of interest to investigate analogous chemistry for **1** as a route to dimolybdosulfenimines containing the thiooximate bridge, $R_2C{=}NS^-$. Although the thiooximate anion per se is known,[15] thiooxime complexes are not well documented, despite an extensive chemistry of oxime complexes.[16] In addition, $R_2C{=}NS^-$ is conceivably related to a resonance structure ($R_2N^+{=}NS^-$) for thionitrosoamines (R_2NNS),[17] which have been characterized as ligands in several metal systems.[18-21]

Syntheses and characterization of dimolybdosulfenimines are reported herein, as also is the crystal structure of **1** which was undertaken due to the unusual nature of the H_2NS^- bridge. Furthermore, during the course of the investigation, it became apparent that the dimolybdenum sulfenimines provided a way to study structural differences associated with inversion isomers for a dimetal sulfur bridge. Sulfur inversion at bridge sites in transition metal dimers has been well studied,[22-26] and much of

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the work has been concerned with the determination of inversion barriers and factors influencing the magnitude of that barrier. Less focus has been on specific structural differences between inversion isomers and the possible influence of structure on invertomer preference. The sulfenimines herein offered an initial opportunity to compare the Mo$_2$S$_2$ core structures between similar compounds differing in bridge sulfur invertomer orientation. For this reason, the structures of two dimolybdenum sulfenimines were also determined.

Experimental Section

Acetaldehyde was distilled and then vacuum transferred. Acetone was freshly dried over MgSO$_4$. Other commercial reagents were used as received. [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNH$_2$)] (**1**) was prepared as previously described;[11] its labeled, amide-^{15}N variant was prepared using ^{15}NH$_2$OSO$_3$H made from an adapted procedure.[27] ^{31}P-{^{1}H}, ^{15}N{^{1}H}, and ^{1}H NMR spectra were obtained on a Varian XL-300 spectrometer at 121, 30, and 300 MHz and are reported as downfield shifts from external 85% H$_3$PO$_4$, external MeNO$_2$, and internal Me$_4$Si. The solvent was CDCl$_3$. All coupling constants reported herein are absolute values. The NMR data, as listed below, give minor isomer shifts in parentheses when these were distinguishable. Furthermore, where four isomers were observed, these are simply designated as I (most abundant) through IV (least abundant), where distinguishable. All NMR integrations were consistent with the assignments. Infrared spectra were obtained on a Perkin-Elmer 283 IR spectrophotometer or a Nicolet 7199 FTIR spectrometer. In all cases, only selected bands are listed. Galbraith Laboratories, Inc. (Knoxville, TN) performed the elemental analyses.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNCH$_2$)], 2(H,H). A slurry of **1** (0.1322 g, 0.145 mmol) and paraformaldehyde (0.0439 g, 1.45 mmol of CH$_2$O) in CHCl$_3$ (2.5 mL) was heated at 50 °C in a water bath for 17 h. After the reaction was cooled to room temperature, benzene (1.5 mL) was added to settle the excess paraformaldehyde. Centrifugation and decantation yielded a red solution. The paraformaldehyde was further treated with C$_6$H$_6$ (1.0 mL), followed by centrifugation/decantation. The combined solutions were then rotavapped. The residue was dissolved in toluene (1.6 mL) and then treated slowly with petroleum ether (4.8 mL) to precipitate the product. Filtration, washing (petroleum ether), and vacuum drying gave a bright orange powder (0.0539 g, 40%). Anal. Calcd for Mo$_2$C$_{25}$H$_{39}$N$_3$O$_6$P$_2$S$_6$: C, 32.5; H, 4.3; N, 4.5. Found: C, 32.5; H, 4.2; N, 4.4. NMR data are as follows (ppm). ^{31}P: (114.9), 114.8. ^{15}N: (−28.7), −43.4. ^{1}H: (8.63 d), 8.50 d, 7.88 d, (7.74 d), SNCH$_2$; (6.62 d), 6.59 d, 6.48 d, To–H; 4.25–3.95 m, POCH$_2$; (2.10 s), 2.09 s, To–CH$_3$; 1.31 t, 1.22 t, POCCH$_3$; 1.22 s, O$_2$CCH$_3$. IR (cm^{-1}): 1535 m, 1444 s, 1007 vs, 958 vs, 815 s, 795 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNCHMe)], 2(H,Me). A solution of **1** (0.1988 g, 0.218 mmol) and acetaldehyde (24 μL, 0.43 mmol) in CHCl$_3$ (2.5 mL) was stirred 20 min and then rotavapped. The residue was dissolved in CH$_2$Cl$_2$ (0.9 mL), and this solution was treated slowly with petroleum ether (6.3 mL) to precipitate product. Filtration, washing (petroleum ether) and vacuum drying gave a red-orange powder (0.1549 g, 76%). Anal. Calcd for Mo$_2$C$_{26}$H$_{41}$N$_3$O$_6$P$_2$S$_6$: C, 33.3; H, 4.4; N, 4.5. Found: C, 33.3; H, 4.3; N, 4.4. NMR data are as follows (ppm). ^{31}P: (115.1), 115.0. ^{15}N: −54.7, (−71.1). ^{1}H: 8.81 m I + II, (8.42 q III), (8.21 q IV), SNCH; (6.65 d II), 6.58 d I, 6.48 m, To–H; 4.2–4.0 m, POCH$_2$; (2.74 d III), (2.70 d IV), 2.07 d I, (1.93 d II), SNCCH$_3$; (2.11 s II), 2.08 s I, To–CH$_3$; 1.31 t, 1.22 t, POCCH$_3$; 1.19 s, O$_2$CCH$_3$. IR (cm^{-1}): 1613 m, 1538 m, 1449 s, 1006 vs, 958 vs, 816 s, 796 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNCHCMe$_3$)], 2(H,CMe$_3$). A solution of **1** (0.2327 g, 0.255 mmol) and pivalaldehyde (0.17 mL, 1.5 mmol) in CHCl$_3$ (2.0 mL) was stirred for 30 min and then rotavapped. The residue was dissolved in CHCl$_3$ (0.40 mL); this solution was treated slowly with petroleum ether (4.0 mL) to precipitate the product. An orange powder (0.1951 g, 78%) was obtained after filtration, washing (petroleum ether), and vacuum drying. NMR data are as follows (ppm). ^{31}P: 115.2, (115.2, 1.6 Hz upfield). ^{15}N: −65.3, (−78.2). ^{1}H: (8.81 s), 8.78 s, SNCH; (6.73 d), 6.59 d, (6.49 d), 6.46 d, To–H; 4.2–4.0 m, POCH$_2$; (2.11 s), 2.08 s, To–CH$_3$; 1.30 t, 1.23 t, POCCH$_3$; 1.20 s, O$_2$CCH$_3$; 1.06 s, (1.10 s), SNCCCH$_3$. IR (cm^{-1}): 1607 m, 1546 m, 1445 s, 1012 vs, 960 vs, 819 s, 790 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNCHTo)], 2(H,To). A solution of **1** (0.2018 g, 0.221 mmol) and *p*-tolualdehyde (0.16 mL, 1.4 mmol) in CHCl$_3$ (3.0 mL) was stirred for 30 min and then rotavapped. The resulting red-orange residue was dissolved in CH$_2$Cl$_2$ (0.7 mL). Petroleum ether (5.3 mL) was added slowly to precipitate product. Filtration, washing (petroleum ether), and vacuum drying gave an orange powder (0.1574 g, 70%). Anal. Calcd for Mo$_2$C$_{32}$H$_{45}$N$_3$O$_6$P$_2$S$_6$: C, 37.9; H, 4.5; N, 4.1. Found: C, 38.4; H, 4.5; N, 4.0. NMR data are as follows (ppm). ^{31}P: (115.8 III + IV), (115.0 II, 3.5 Hz downfield from I), 115.0 I. ^{15}N: −56.0, (−73.6). ^{1}H: (9.43 s IV), (9.38 s II), 9.20 s I, (9.14 s III), SNCH; 7.54 d I, (7.34 d), (7.28 d II), 7.18 d I, (7.11 d II), SNCTo–H; (7.00 d), (6.89 d), (6.80 d), (SNC or MoN)To–H; 6.66 d, 6.63 d, 6.48 d I, (6.40 d II), MoNTo–H; 4.4–3.95 m, POCH$_2$; (2.39 s II), 2.37 s I, SNCTo–CH$_3$; (2.24 s), (2.16 s), (SNC or MoN)To–CH$_3$; 2.09 s, MoNTo–CH$_3$; 1.5–1.1 m, POCCH$_3$ + (O$_2$CCH$_3$); 0.94 s I, O$_2$CCH$_3$. IR (cm^{-1}): 1543 m, 1442 s, 1009 vs, 959 vs, 785 m.

[Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SNCMe$_2$)], 2(Me,Me). A solution of **1** (0.2840 g, 0.312 mmol) and acetone (4.5 mL, 61 mmol) was stirred over MgSO$_4$ for 8 days. The resulting mixture was filtered and washed with dried acetone. The filtrate was rotavapped, and the residue was stirred with petroleum ether (10 mL) for 20 min. Filtration, washing (petroleum ether), and vacuum drying gave an orange powder (0.2478 g, 87%). Anal. Calcd for Mo$_2$C$_{27}$H$_{43}$N$_3$O$_6$P$_2$S$_6$: C, 34.1; H, 4.6; N, 4.4. Found: C, 34.1; H, 4.9; N, 4.4. NMR data are as follows (ppm). ^{31}P: (115.3), 115.2. ^{15}N: −62.3, (−79.8). ^{1}H: 6.66 d, (6.57 d), (6.49 d), 6.47 d, To–H; 4.25–3.95 m, POCH$_2$; (2.75 s), 2.70 s, (2.12 s), 1.98 s, NCCH$_3$; 2.10 s, (2.09 s), To–CH$_3$; 1.31 t, 1.21 t, POCCH$_3$; 1.24 s, O$_2$CCH$_3$. IR (cm^{-1}): 1608 m, 1539 m, 1446 s, 1004 vs, 959 vs, 814 s, 749 m.

Crystallography. The crystal data and experimental details are given in Table I. Data were collected on an Enraf-Nonius CAD4 automated diffractometer with Mo Kα radiation (graphite monochromator), using the ω–2θ scan technique; computations utilized the Enraf-Nonius VAX/SDP programs.[28] Three representative reflections were measured every 60 min; their intensities remained constant within experimental error. Lorentz and polarization corrections were applied to the data. Scattering and anomalous dispersion factors were taken from ref 29.

For **1**, a red block crystal from CHCl$_3$/*i*-PrOH measuring 0.31 × 0.38 × 0.47 mm was used for data collection. Cell constants and an orientation matrix were obtained from least-squares refinement. No absorption correction was utilized; a secondary extinction correction (final coefficient, 1.6 (4) × 10^{-7}) was applied.

The structure was solved using the Patterson method, which revealed the positions of the two molybdenum atoms. The remaining atoms were located in succeeding difference Fourier syntheses. One ethoxy group, O(3)–C(17)–C(18), was disordered and was modeled with three O–C–C groups in the ratio 0.45:0.30:0.25. Hydrogen atoms on N(1) were included in observed positions; the positions of others were calculated and added to the structure factor calculations with B set to 1.3B_{eq} of the carbon atom to which each was bonded. Hydrogen parameters were not refined. The structure was refined by full-matrix least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F) + (0.005F)^2 + 1.0]^{-1}$. Selected results are given in Tables II, V and VI, and the structure is shown in Figure 1.

For **2**(H,CMe$_3$), a red plate crystal from C$_6$H$_6$/MeOH measuring 0.24 × 0.40 × 0.45 mm was used for data collection. An empirical absorption (ψ data) and a secondary extinction correction (final coefficient, 1.09 (2) × 10^{-7}) were applied.

The structure was solved by direct methods (MULTAN 78), which revealed the positions of the two molybdenum atoms. The remaining atoms were located in succeeding difference Fourier syntheses. The hydrogen atom on C(25) was included in observed positions; the positions of others were calculated. Solution and refinement were conducted as for **1** except there was no disorder, and $w = [\sigma^2(F) + (0.005F)^2 + 0.3]^{-1}$. Selected results are given in Tables III, V, and VI, and the structure is shown in Figure 2.

For **2**(Me,Me), a red, cut, block crystal from CH$_2$Cl$_2$/*i*-PrOH having approximate dimensions of 0.30 × 0.35 × 0.42 mm was used for data collection. An empirical absorption correction (ψ data) was applied.

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Table I. Crystallographic Data

	1	**2**(H,CMe$_3$)	**2**(Me,Me)
formula	$Mo_2C_{24}H_{39}N_3O_6P_2S_6$	$Mo_2C_{29}H_{47}N_3O_6P_2S_6$	$Mo_2C_{27}H_{43}N_3O_6P_2S_6$
fw	911.8	979.9	951.9
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	13.781 (2)	12.473 (3)	15.602 (2)
b, Å	14.524 (2)	28.197 (5)	15.618 (2)
c, Å	10.961 (2)	13.568 (3)	9.627 (2)
α, deg	104.48 (1)		91.13 (2)
β, deg	106.39 (1)	114.81 (2)	96.25 (2)
γ, deg	107.31 (1)		117.59 (2)
T, °C	23	23	23
V, Å^3	1871.0	4331.5	2060.3
Z	2	4	2
λ, Å	0.709 30 (Mo Kα)	0.709 30 (Mo Kα)	0.709 30 (Mo Kα)
ρ_{calcd}, g cm^{-3}	1.62	1.50	1.53
μ, cm^{-1}	11.0	9.5	10.0
transm coeff		0.955–0.999	0.878–1.000
octants	$\pm h,-k,\pm l$	$+h,-k,\pm l$	$\pm h,\pm k,+l$
no. of reflcns measd	7158	8027	8094
no. of reflcns with $I > 3\sigma(I)$	5801	5910	6080
$\Delta(\rho)$, e Å^{-3}	0.62 (6)	0.38 (7)	0.72 (6)
R[a]	0.030	0.034	0.033
R_w[b]	0.034	0.039	0.038
agreement est, %	0.5	1.9	0.8

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

Table II. Selected Positional Parameters for **1**

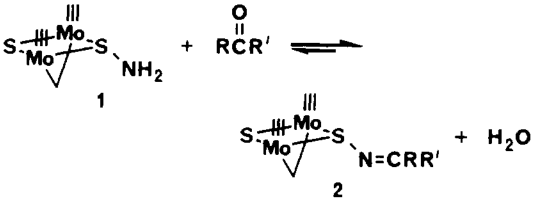
atom	x	y	z	B_{eq},[a] Å^2
Mo(1)	0.22060 (2)	0.36893 (2)	0.63745 (3)	3.529 (7)
Mo(2)	0.32494 (2)	0.25275 (2)	0.51910 (3)	3.510 (7)
S(1)	0.26333 (8)	0.37552 (6)	0.43846 (9)	4.20 (2)
S(2)	0.28475 (8)	0.25220 (6)	0.71330 (9)	4.20 (2)
S(3)	0.19359 (9)	0.41708 (9)	0.8589 (1)	5.57 (3)
S(4)	0.19422 (9)	0.53727 (8)	0.6516 (1)	5.92 (3)
S(5)	0.43447 (9)	0.15129 (8)	0.5909 (1)	5.75 (3)
S(6)	0.43710 (9)	0.25722 (8)	0.3688 (1)	5.32 (3)
P(1)	0.1880 (1)	0.5467 (1)	0.8326 (1)	6.66 (3)
P(2)	0.48959 (9)	0.16168 (9)	0.4436 (1)	5.96 (3)
O(1)	0.3925 (2)	0.4816 (2)	0.7514 (2)	4.14 (6)
O(2)	0.4744 (2)	0.3909 (2)	0.6585 (2)	4.27 (6)
N(1)	0.3670 (3)	0.4914 (3)	0.4775 (4)	6.8 (1)
N(2)	0.0854 (2)	0.2876 (2)	0.5359 (3)	4.02 (7)
N(3)	0.2062 (2)	0.1530 (2)	0.3933 (3)	3.94 (7)
C(1)	−0.0223 (3)	0.2207 (3)	0.4537 (3)	3.76 (8)
C(2)	−0.0916 (3)	0.2539 (3)	0.3745 (4)	5.2 (1)
C(6)	−0.0604 (3)	0.1192 (3)	0.4485 (4)	4.32 (9)
C(8)	0.1085 (3)	0.0751 (3)	0.2942 (3)	3.77 (8)
C(9)	0.0364 (3)	0.0966 (3)	0.1999 (4)	4.54 (9)
C(13)	0.0818 (3)	−0.0256 (3)	0.2924 (4)	4.6 (1)
C(15)	0.4765 (3)	0.4684 (3)	0.7433 (3)	3.94 (9)
C(16)	0.5871 (3)	0.5525 (3)	0.8390 (4)	5.6 (1)
NH(1)	0.385	0.535	0.563	8.3[b]
NH(2)	0.398	0.500	0.416	8.3[b]

[a] $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + ... + ab(\cos\gamma)\beta_{12} + ...]$. [b] Not refined.

Solution and refinement were conducted as for **1** except there was no disorder, and $w = [\sigma^2(F) + (0.005F)^2 + 0.6]^{-1}$. Selected results are given in Tables IV–VI, and the structure is shown in Figure 3.

Results

The primary dimolybdosulfenamide $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNH_2)]$ (**1**) reacted with aldehydes and with acetone to give sulfenimine products $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNCRR')]$, **2** or **2**(R,R′), via the condensation equilibrium of eq 1. Reactions using acetaldehyde, pivalaldehyde, or *p*-tolualdehyde were facile and straightforward (with the use of excess aldehyde). Reactions using acetone, however, were very slow and were never complete unless some drying agent was utilized. The use of $MgSO_4$ and long reaction times successfully provided clean product in high yield. Attempted reactions with a 10-fold amount of acetophenone or benzophenone in $CDCl_3$ were without any significant product after 35 days at room temperature.



(1)

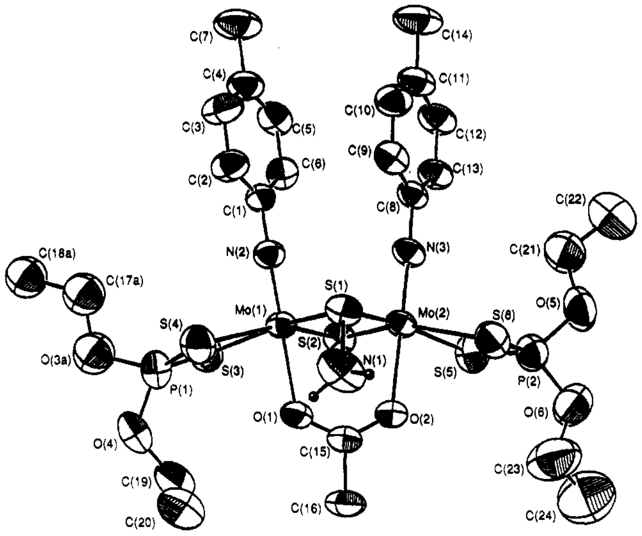


Figure 1. ORTEP view of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNH_2)]$ (**1**).

Reactions with formaldehyde employed thermolysis of paraformaldehyde. These reactions were not clean and other products, possibly oligomers at the C═N linkage, were observable in ^{31}P NMR spectra as minor products. Isolated samples contained 2–5% impurity as evidenced by a peak at δ 115.1 in the ^{31}P NMR spectra. Reactions of **1** in $CDCl_3$ with aqueous formaldehyde (two-phase mixture) also afforded the desired product **2**(H,H), but these reactions were less clean than those using paraformaldehyde.

Products were characterized by elemental analyses, NMR spectroscopy, IR spectroscopy, and X-ray crystallography. NMR spectra are complicated by stereoisomer equilibria (vide infra), but the results unambiguously show the presence of the double bond N═CRR′ unit in all the derivatives. To wit, N═CH

Table III. Selected Positional Parameters for **2**(H,CMe$_3$)

atom	x	y	z	B_{eq},^{a} Å^2
Mo(1)	0.92691 (3)	0.13632 (1)	0.34812 (3)	3.781 (8)
Mo(2)	0.86760 (3)	0.16255 (2)	0.52068 (3)	3.947 (9)
S(1)	0.73048 (9)	0.15866 (4)	0.32835 (9)	4.03 (3)
S(2)	1.0537 (1)	0.13963 (5)	0.53324 (9)	4.75 (3)
S(3)	1.0989 (1)	0.09667 (5)	0.3309 (1)	5.22 (3)
S(4)	0.8301 (1)	0.10292 (5)	0.15580 (9)	5.11 (3)
S(5)	0.9704 (1)	0.15454 (6)	0.7229 (1)	5.96 (4)
S(6)	0.6953 (1)	0.17025 (6)	0.5762 (1)	5.47 (3)
P(1)	0.9903 (1)	0.08167 (5)	0.1774 (1)	5.11 (3)
P(2)	0.8157 (1)	0.16691 (6)	0.7287 (1)	5.15 (3)
O(1)	0.8785 (2)	0.0662 (1)	0.3837 (2)	4.32 (7)
O(2)	0.8291 (2)	0.0867 (1)	0.5180 (2)	4.36 (7)
N(1)	0.6416 (3)	0.1092 (2)	0.2857 (3)	5.1 (1)
N(2)	0.9414 (3)	0.1925 (1)	0.3025 (3)	4.09 (9)
N(3)	0.8779 (3)	0.2230 (1)	0.5056 (3)	4.15 (9)
C(1)	0.9323 (3)	0.2352 (2)	0.2509 (3)	3.9 (1)
C(2)	0.8319 (4)	0.2450 (2)	0.1564 (4)	5.1 (1)
C(6)	1.0215 (4)	0.2692 (2)	0.2922 (4)	4.7 (1)
C(8)	0.8884 (4)	0.2697 (2)	0.4829 (3)	4.3 (1)
C(9)	0.8018 (4)	0.2929 (2)	0.3953 (4)	5.1 (1)
C(13)	0.9905 (4)	0.2944 (2)	0.5472 (4)	5.5 (1)
C(15)	0.8475 (4)	0.0561 (2)	0.4584 (4)	4.4 (1)
C(16)	0.8340 (5)	0.0050 (2)	0.4793 (4)	6.4 (2)
C(25)	0.5724 (5)	0.1004 (2)	0.3221 (5)	6.4 (2)
C(26)	0.4808 (4)	0.0611 (2)	0.2811 (5)	6.2 (1)
C(27)	0.5095 (6)	0.0271 (3)	0.2128 (6)	10.7 (2)
C(28)	0.4793 (8)	0.0364 (3)	0.3787 (7)	14.2 (3)
C(29)	0.3631 (6)	0.0838 (3)	0.2175 (9)	13.0 (4)

^{a} $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + ... + ab(\cos\gamma)\beta_{12} + ...]$.

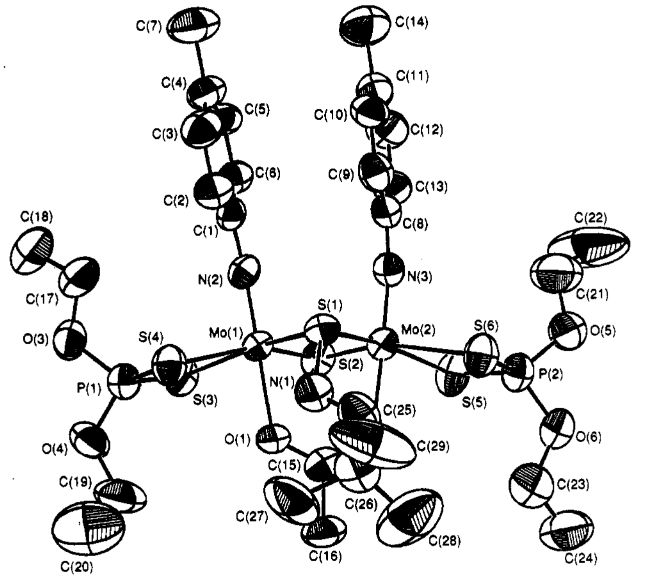


Figure 2. ORTEP view of [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SN=CHCMe$_3$)](**2**(H,CMe$_3$)).

resonances are observed at δ 7.74–8.81 for **2**(H,H), **2**(H,Me), and **2**(H,CMe$_3$) and at δ 9.14–9.43 for **2**(H,To). For **2**(H,H), $^2J_{HH}$ = 12.8 Hz (major) and 12.4 Hz (minor sulfur invertomer) for the NCH$_2$ protons, consistent with methanimine geminal coupling.[30] N=CCH$_3$ resonances are found at δ 1.93–2.75 for **2**(H,Me) and **2**(Me,Me). Assignments for **2**(Me,Me) were verified by the use of acetone-d_6 in alternate syntheses which gave the deuterio analogue **2**(CD$_3$,CD$_3$).

^{15}N NMR spectra for the imine nitrogens of the sulfenimines, **2**, were obtained using labeled compounds. These products were generated by reaction of the appropriate aldehyde with labeled **1**-$^{15}NH_2$. Resonances were observed at (–28.7) and –43.4 ppm for **2**(H,H), at –54.7 and (–71.1) ppm for **2**(H,Me), at –65.3 and (–78.2) ppm for **2**(H,CMe$_3$), at –56.0 and (–73.6) ppm for **2**(H,To), and at –62.3 and (–79.8) ppm for **2**(Me,Me). Parenthetical values are for the second most abundant isomer; for **2**(H,Me) and **2**(H,To), which show four isomers in solution, peaks for the two least abundant isomers were not found due to their low abundance. The shifts observed for all derivatives were within the normal range for organoimines.[31]

Table IV. Selected Positional Parameters for **2**(Me,Me)

atom	x	y	z	B_{eq},^{a} Å^2
Mo(1)	0.43316 (2)	0.24135 (2)	0.75577 (4)	3.873 (7)
Mo(2)	0.29709 (2)	0.04167 (2)	0.74580 (4)	3.649 (7)
S(1)	0.35691 (6)	0.13260 (6)	0.5428 (1)	4.03 (2)
S(2)	0.38642 (7)	0.14631 (7)	0.9453 (1)	4.54 (2)
S(3)	0.56366 (8)	0.36246 (8)	0.9383 (1)	5.39 (3)
S(4)	0.54829 (8)	0.36567 (8)	0.6049 (1)	5.80 (3)
S(5)	0.25587 (8)	–0.08574 (8)	0.9188 (1)	5.64 (3)
S(6)	0.22247 (7)	–0.11482 (7)	0.5853 (1)	5.20 (3)
P(1)	0.62934 (8)	0.43853 (8)	0.7829 (2)	5.51 (3)
P(2)	0.21080 (7)	–0.18541 (7)	0.7582 (2)	5.37 (3)
O(1)	0.5360 (2)	0.1835 (2)	0.7334 (3)	4.66 (6)
O(2)	0.4290 (2)	0.0273 (2)	0.7257 (3)	4.46 (6)
N(1)	0.2661 (2)	0.1586 (2)	0.4669 (4)	4.69 (7)
N(2)	0.3549 (2)	0.2914 (2)	0.7447 (3)	4.27 (7)
N(3)	0.1951 (2)	0.0579 (2)	0.7398 (3)	4.02 (7)
C(1)	0.3002 (3)	0.3405 (2)	0.7270 (5)	4.45 (9)
C(2)	0.2883 (3)	0.3756 (3)	0.5997 (6)	6.9 (1)
C(6)	0.2610 (3)	0.3579 (3)	0.8385 (6)	6.6 (1)
C(8)	0.1240 (2)	0.0870 (2)	0.7510 (4)	3.96 (8)
C(9)	0.0766 (3)	0.1051 (4)	0.6365 (5)	7.0 (1)
C(13)	0.1021 (3)	0.0992 (3)	0.8812 (5)	6.7 (1)
C(15)	0.5145 (2)	0.0950 (3)	0.7291 (4)	4.46 (9)
C(16)	0.5949 (3)	0.0678 (3)	0.7238 (6)	6.6 (1)
C(25)	0.2285 (3)	0.1222 (3)	0.3421 (4)	4.72 (9)
C(26)	0.1526 (3)	0.1490 (4)	0.2770 (5)	7.1 (1)
C(27)	0.2504 (3)	0.0572 (4)	0.2548 (5)	6.5 (1)

^{a} $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + ... + ab(\cos\gamma)\beta_{12} + ...]$.

Table V. Selected Bond Lengths (Å)

	1	**2**(H,CMe$_3$)	**2**(Me,Me)
Mo(1)–S(1)	2.431 (1)	2.433 (1)	2.4421 (9)
Mo(1)–S(2)	2.351 (1)	2.342 (2)	2.336 (2)
Mo(1)–S(3)	2.517 (1)	2.515 (2)	2.516 (2)
Mo(1)–S(4)	2.550 (1)	2.552 (1)	2.560 (1)
Mo(1)–O(1)	2.202 (2)	2.181 (3)	2.202 (4)
Mo(1)–N(2)	1.723 (2)	1.737 (4)	1.725 (4)
Mo(2)–S(1)	2.439 (1)	2.450 (1)	2.447 (2)
Mo(2)–S(2)	2.347 (1)	2.346 (1)	2.342 (1)
Mo(2)–S(5)	2.510 (1)	2.504 (1)	2.515 (1)
Mo(2)–S(6)	2.557 (1)	2.567 (2)	2.558 (1)
Mo(2)–O(2)	2.198 (2)	2.190 (3)	2.199 (3)
Mo(2)–N(3)	1.731 (3)	1.728 (4)	1.719 (3)
Mo(1)–Mo(2)	2.8283 (6)	2.8335 (6)	2.8378 (4)
S(1)–N(1)	1.709 (3)	1.724 (4)	1.739 (4)
S(3)–P(1)	1.995 (2)	1.996 (2)	1.993 (2)
S(4)–P(1)	1.982 (2)	1.985 (2)	1.987 (2)
S(5)–P(2)	1.988 (2)	1.995 (2)	1.990 (2)
S(6)–P(2)	1.988 (2)	1.985 (2)	1.993 (2)
O(1)–C(15)	1.253 (6)	1.260 (6)	1.260 (5)
O(2)–C(15)	1.255 (4)	1.267 (6)	1.258 (3)
N(2)–C(1)	1.382 (3)	1.374 (6)	1.388 (6)
N(3)–C(8)	1.388 (3)	1.372 (6)	1.393 (6)
N(1)–H(1)	0.903 (4)		
N(1)–H(2)	0.912 (5)		
N(1)–C(25)		1.186 (8)	1.274 (5)
C(25)–C(26)		1.520 (8)	1.508 (8)
C(26)–C(27)		1.48 (2)	
C(26)–C(28)		1.50 (1)	
C(26)–C(29)		1.499 (8)	
C(25)–C(27)			1.484 (8)

Infrared spectra show modest ν(C=N) bands at 1613 cm^{-1} for **2**(H,Me), at 1607 cm^{-1} for **2**(H,CMe$_3$), and at 1608 cm^{-1} for **2**(Me,Me); these are in addition to the usual dimer absorptions.[32]

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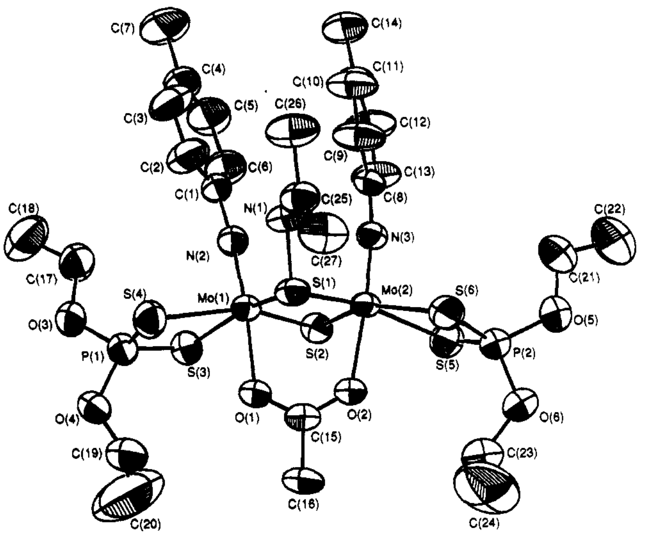


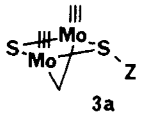
Figure 3. ORTEP view of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SN{=}CMe_2)]$(**2**(Me,Me)).

Table VI. Selected Bond Angles (deg)

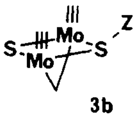
	1	**2**(H,CMe$_3$)	**2**(Me,Me)
S(1)–Mo(1)–S(2)	107.54 (4)	107.67 (5)	107.02 (3)
S(1)–Mo(1)–S(4)	86.83 (4)	87.73 (4)	87.54 (3)
S(2)–Mo(1)–S(3)	85.19 (4)	84.19 (4)	83.46 (4)
S(3)–Mo(1)–S(4)	78.10 (5)	78.28 (4)	78.00 (4)
O(1)–Mo(1)–N(2)	173.8 (1)	170.4 (1)	170.5 (1)
Mo(2)–Mo(1)–O(1)	81.42 (7)	82.1 (1)	82.52 (5)
Mo(2)–Mo(1)–N(2)	98.9 (1)	99.1 (1)	100.27 (8)
S(1)–Mo(2)–S(2)	107.41 (4)	107.00 (5)	106.67 (3)
S(1)–Mo(2)–S(6)	88.20 (4)	91.14 (5)	88.70 (4)
S(2)–Mo(2)–S(5)	84.03 (4)	81.91 (5)	82.93 (4)
S(5)–Mo(2)–S(6)	78.05 (5)	78.07 (4)	77.78 (4)
O(2)–Mo(2)–N(3)	172.0 (1)	171.3 (2)	172.5 (1)
Mo(1)–Mo(2)–O(2)	82.60 (8)	82.2 (1)	81.40 (6)
Mo(1)–Mo(2)–N(3)	97.0 (1)	95.8 (1)	96.03 (9)
Mo(1)–S(1)–Mo(2)	71.02 (3)	70.94 (3)	70.96 (3)
Mo(1)–S(2)–Mo(2)	74.02 (3)	74.38 (3)	74.68 (3)
Mo(1)–S(1)–N(1)	110.4 (1)	107.7 (2)	106.3 (1)
Mo(2)–S(1)–N(1)	114.3 (2)	117.2 (1)	107.1 (1)
Mo(1)–S(3)–P(1)	87.71 (7)	87.66 (7)	88.16 (5)
Mo(1)–S(4)–P(1)	87.06 (7)	86.87 (5)	87.07 (6)
Mo(2)–S(5)–P(2)	87.86 (6)	88.19 (5)	88.55 (6)
Mo(2)–S(6)–P(2)	86.58 (6)	86.66 (6)	87.32 (5)
S(3)–P(1)–S(4)	106.84 (8)	106.88 (9)	106.77 (6)
S(5)–P(2)–S(6)	106.75 (9)	106.74 (9)	106.17 (8)
Mo(1)–O(1)–C(15)	126.4 (2)	126.2 (3)	125.1 (2)
Mo(2)–O(2)–C(15)	125.0 (2)	125.4 (3)	126.8 (3)
Mo(1)–N(2)–C(1)	178.8 (4)	169.2 (2)	173.0 (3)
Mo(2)–N(3)–C(8)	177.7 (4)	173.1 (4)	169.1 (2)
O(1)–C(15)–O(2)	124.2 (2)	123.9 (4)	124.0 (5)
S(1)–N(1)–H(1)	111.3 (4)		
S(1)–N(1)–H(2)	119.2 (3)		
H(1)–N(1)–H(2)	129.4 (4)		
S(1)–N(1)–C(25)		120.6 (4)	116.5 (3)
N(1)–C(25)–C(26)		124.5 (6)	115.3 (4)
N(1)–C(25)–C(27)			127.7 (4)
C(26)–C(25)–C(27)			117.0 (4)

For **2**(H,To), assignment of ν(C=N) is uncertain due to the additional tolyl function and peaks thereof; for **2**(H,H) no additional peaks are observed in the region. These results are consistent with infrared results for organosulfenimines, whose ν(C=N) bands are commonly in the 1600–1620-cm^{-1} region (when not conjugated),[14] although some are also reported as inactive.[33]

Configurational Isomerism. NMR spectra of solutions of the sulfenimines **2** show the presence of both sulfur and nitrogen inversion isomers. Bridge sulfur invertomers are well established for compounds of the general formula, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SZ)]$.[32,34] These are denoted by **3a** and **3b** and are designated as distal and proximal, respectively,



3a



3b

dependent on the position of Z relative to the tolylimido groups. Furthermore, for the present derivatives, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SNCHR)]$ (**2**), *E* and *Z* isomers are also possible, allowing a total of four configurations. The *E–Z* isomerization is assumed to be due to nitrogen inversion, as has been described for organosulfenimine stereomutation.[2,14]

Specific isomer assignments are possible in most cases. For **2**(H,H) and for **2**(Me,Me), only sulfur invertomers are obtained. On the basis of prior methods of sulfur invertomer assignments,[32] the major solution isomer for **2**(H,H) is assigned the distal configuration and the invertomer ratio (**3a**/**3b**) is 4. For **2**(Me,Me), however, the major isomer is proximal, and the invertomer ratio is 0.5.

Configuration assignment for the **2**(H,R) derivatives was aided by use of the labeled $Mo_2S^{15}N{=}CHR$ compounds, which allowed measurement of $^2J_{NH}$ couplings from ^1H NMR spectra. For aldehyde-derived imine[35] and oxime[36] compounds, $^2J_{NH}$ is typically small (2–4 Hz) when H is syn to the nitrogen substituent, but the coupling is significantly larger (11–16 Hz) when H is anti. The great disparity in $^2J_{NH}$ values is also obtained in the present **2**(H,H) derivative: for the minor sulfur invertomer, the coupling constant is 15 Hz for the upfield $SN{=}CH_2$ resonance and 1.5 Hz for the downfield resonance; for the major invertomer, these values are 15 and ~1 Hz (incompletely resolved).

For **2**(H,Me), which has four isomers (designated I–IV by abundance), the two dominant isomers show $^2J_{NH}$ of 1–2 Hz, while the minor isomers show couplings of 17 (III) and 19 Hz (IV). The major isomers (I and II) are therefore assigned the *E* configuration while the minor isomers are assigned the *Z* orientation. These assignments are also supported by relative proton shifts of N=CH resonances. For aldehyde-derived oximes[37] and hydrazones,[38] the N=CH peak is more downfield when H is syn to the nitrogen substituent than when H is anti. For **2**(H,Me), the N=CH resonances of isomers I and II are the most downfield, consistent with their position as being syn to sulfur and of the *E* configuration overall. Full assignments of the isomers for **2**(H,Me) are therefore distal *E* as the most abundant (I, 53%), followed by proximal *E* (II, 40%), proximal *Z* (III, 4%) and distal *Z* (IV, 2%). Sulfur invertomer ratios are 1.3 for the *E* configuration and 0.5 for *Z*.

Four isomers are also seen for **2**(H,To) in an approximate distribution of 48%, 35%, 9%, and 8%. ^1H and ^{31}P NMR spectra show unusual shifts, however, and these rendered specific configuration assignments ambiguous. This is attributed to the presence of the imine tolyl group which adds bulk, contributes anisotropy to key resonances, and possibly conjugates with the N=C linkage.

For **2**(H,CMe$_3$), only two of four possible isomers are observed. Both are of the *E* configuration, based on spectral analogies to **2**(H,H) and **2**(H,Me) and on a small value of $^2J_{NH}$ (2 Hz). The major isomer is distal and the sulfur invertomer ratio is 4.

Variable-temperature ^{31}P and ^1H NMR studies for **2**(Me,Me) in C_6D_5Cl showed coalescence of sulfur invertomers by 112 °C. Syn/anti resonances failed to coalesce by 130 °C, indicating a

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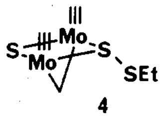
slower rate for nitrogen inversion. Studies of stereomutations in related organosulfenimines, RSN=CMe$_2$, have shown ΔG^* to be ~80 kJ/mol for *E–Z* isomerizations; coalescence temperatures (measured at 60 or 100 MHz) were in the range of 73–116 °C.[39,40]

Crystal Structures. The structure of the dimolybdosulfenamide **1** is shown in Figure 1. The structures for the dimolybdosulfenimines **2**(H,CMe$_3$) and **2**(Me,Me) are shown in Figures 2 and 3. The selection of derivatives **2** for crystallography was based on their major sulfur invertomer in solution: **2**(H,CMe$_3$) provided the distal isomer, while **2**(Me,Me) provided the proximal invertomer. Although the other aldimine derivatives showed distal as the major sulfur invertomer in solution, suitable crystals were not obtainable therefrom.

General metrical results for the molybdenum dimer components of the three structures parallel those found in the ethaneperthiolate-bridged dimer [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)-(SSEt)] (**4**).[41] In all cases, the imido linkages are linear and the acetate ligands bridge symmetrically. Mo–S bond distances within the Mo$_2$S$_2$ cores are longer for tricoordinate S(1) than for dicoordinate S(2). For the three present compounds, the Mo–S(1) bond lengths are 2.431 (1)–2.450 (1) Å while those for Mo–S(2) are 2.336 (2)–2.351 (1) Å. The shorter bonds to the dicoordinate sulfur have been discussed in terms of Mo–S π effects.[34]



4

For the dimolybdosulfenamide **1**, the Mo$_2$S$_2$ unit is reasonably planar with displacements of 0.01 Å from the least-squares plane. This is also reflected in the value of the dihedral angle between the separate MoS$_2$ planes of 178.2 (1)°. The salient feature of the structure is the bridging SNH$_2$ linkage. The amide function is attached to S(1) in the distal orientation, corresponding to the major solution invertomer as determined previously by NMR methods.[11] The S–N bond length, 1.709 (3) Å, suggests a single bond (sum of covalent radii = 1.74 Å[42]). For sulfenamides RSNR'$_2$, S–N bond lengths have been reported in the range 1.643–1.727 (7) Å;[43-48] for PhSN(CH$_2$Ph)$_2$ bound as a ligand (via S) to Cr(CO)$_5$, the S–N bond lengths are 1.697 (6) and 1.707 (5) Å (for the two independent molecules in the asymmetric unit).[7] An inorganic, primary sulfenamide analogue can be considered in S$_3$N$_2$NH$_2^+$ which contains exocyclic NH$_2$ bound to a tricoordinate sulfur of a ring; the S–N (amide) bond length therein is 1.566 (4) Å.[49] The shorter S–N bonds in the cited range for these compounds have been attributed to multiple bond character.

The amide nitrogen in **1** is notably planar with angles around N(1) adding to 359.9 (6)°. Prior sulfenamide structures[43-49] have shown planar and pyramidal nitrogens, with the former associated with a π-interaction to N. HSNH$_2$ itself has a pyramidal nitrogen,[50] although the question of planarity has been addressed in theoretical work.[51,52] The planarity found presently in **1** may be influenced by a weak hydrogen bond interaction as suggested by an intramolecular NH(1)···O(1) distance of 2.373 (5) Å and an intermolecular NH(2)···O(2') distance of 2.461 (5) Å. These are modestly less than the sum of van der Waals radii, 2.60 Å.[42]

For the dimolybdosulfenimine **2**(H,CMe$_3$), the Mo$_2$S$_2$ unit is reasonably planar with displacements of 0.01 Å from the least-squares plane; the dihedral angle between separate MoS$_2$ planes is 178.8 (1)°. The imine moiety is attached to S(1) in the distal *E* orientation, corresponding to the major solution isomer. The S–N bond length is 1.724 (4) Å, again indicative of a single bond. This bond is long compared to those of RSN=CR'$_2$ structures which are in the range 1.641 (3)–1.689 (2) Å;[53-57] the range extends to 1.56 (2) Å if ClSN=C$_5$Cl$_6$ is included.[57] The N=C bond length in **2**(H,CMe$_3$) is 1.186 (8) Å and is very short for a double bond; the corresponding bond lengths in RSN=CR'$_2$ compounds are 1.255 (7)–1.312 (5) Å.[53,55-57] Despite the unusual N=C bond length, the S(1)–N(1)–C(25) angle is normal, 120.6 (4)°.

For the dimolybdosulfenimine **2**(Me,Me), the Mo$_2$S$_2$ core is slightly puckered, with 0.06-Å displacements from the least-squares plane; the resulting MoS$_2$ dihedral angle is 169.9 (1)°. The imine function is attached to S(1) in the proximal orientation, corresponding to the major solution invertomer. The S–N bond length is 1.739 (4) Å; this is even longer than that in the structures of **1** and **2**(H,CMe$_3$) above. The N=C bond length of 1.274 (5) Å, however, is in the usual range.

Of interest in the current study is the direct comparison of the structures differing in sulfur invertomer configuration. Thus, proximal **2**(Me,Me) is compared to distal **2**(H,CMe$_3$), with reference also to the distal structures of **1** and of perthiolate **4**. The principal differences which are found, outside of the differences associated directly with the substituent on S(1), involve the Mo$_2$S$_2$ core; bond lengths and angles associated with imido, dithiophosphate, and acetate ligands are reasonably comparable in all derivatives to date.

For **2**(Me,Me) relative to the others, the primary difference structurally is the decrease in planarity of the Mo$_2$S$_2$ core (vide supra). This is not simply a bending of the MoS$_2$ planes, since the Mo–Mo distance is actually slightly longer. Instead, the effect is due to a drop in the position of S(1), tantamount to a bending of the Mo$_2$S planes. This can be seen in the dihedral angles between Mo$_2$S planes themselves and between separate Mo$_2$S planes and a reference plane defined by Mo(1), Mo(2), O(1), O(2), and C(15). The dihedral angles between Mo$_2$S planes overall are 179.1 (1)° for **2**(H,CMe$_3$) and 172.5 (1)° for **2**(Me,-Me). The dihedral angles between the Mo$_2$S(2) plane and the reference Mo$_2$O$_2$C plane are similar: 90.2 (1)° in **2**(H,CMe$_3$) and 91.4 (1)° in **2**(Me,Me); however, the dihedral angles between the Mo$_2$S(1) plane and the reference Mo$_2$O$_2$C plane are noticeably different: 88.9 (1)° in **2**(H,CMe$_3$) and 81.1 (1)° in **2**(Me,Me). Thus, the greater difference is associated with the lowered position of S(1) relative to the other components. In terms of actual displacements relative to the Mo$_2$S(2) plane, S(1)

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is 0.031 (1) Å lower in **2**(H,CMe$_3$), but it is 0.259 (1) Å lower in **2**(Me,Me).

In addition to the bending and longer Mo–Mo bond, there are also some differences in angles within the Mo$_2$S$_2$ core, but these are small and can be related geometrically to the above differences. One additional notable feature, not geometrically dependent on the Mo$_2$S$_2$ dimensions, is the sum of the angles about the tricoordinate sulfur, S(1). For **2**(Me,Me), this sum is 284.4 (2)°, and is distinctly smaller than the values of 295.7 (2)–296.3 (1)° [41] for the distal invertomer derivatives. Thus, along with bending down, S(1) has become more pyramidal in **2**(Me,Me).

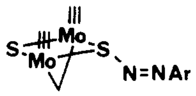
In the analysis of structural relationships and sulfur invertomer orientation, steric factors need also to be considered. The primary steric interactions expected for the bridge sulfur substituent are with the carboxylate group for the distal configuration and with the two arylimido groups for the proximal configuration. Comparison of nonbonding distances and the sum of van der Waals radii[42] yielded the following. For **2**(H,CMe$_3$), the only short contact is N(1)···C(15) which, at 3.05 Å, is 0.15 Å less than the van der Waals sum; N(1)···O(1) and N(1)···O(2) distances (2.94 and 3.10 Å) exceed (by 0.04 and 0.20 Å) the sum of the van der Waals radii. These relationships are also seen in **1**: the N(1)···C(15) distance is 3.03 Å, and N(1)···O(1) and N(1)···O(2) distances are 2.97 and 3.06 Å. For **2**(Me,Me), the N(1)···H(C9) distance, at 2.63 Å, is the only distance shorter (0.07 Å) than the van der Waals sum. All other distances from N(1) to N(2), C(1), C(2), H(C2), N(3), C(8), and C(9) exceed the sum of the van der Waals radii by 0.10 Å or more.

Discussion

The observed reactions of the thiohydroxylamide bridge in **1** parallel those of primary organosulfenamides,[1,2] which also follow the reactivity pattern aldehyde > ketone, as observed herein. Comparison can also be made to the condensation of a bound hydroxylamide ligand H$_2$NO$^-$ with ketones to give oxime complexes.[58,59]

The current imine derivative, **2**(H,H), is notable as possessing the methanimine (N=CH$_2$) linkage which is inherently prone to oligomerization unless sterically precluded.[60] Although the major product is unambiguously the imine, minor products may indeed be oligomers thereof.

In addition to the relationship to thionitrosoamines (see Introduction), the thiooximate ligand R$_2$C=NS$^-$ is furthermore isoelectronic and isostructural to the diazosulfide linkage, ArN=NS$^-$. Dimolybdenum diazosulfides **5** have been previously prepared and characterized; these compounds were observable in solution at low temperatures, but they were not isolable due to radical induced decompositions.[61] The diazosulfides **5** were also capable of distal/proximal sulfur invertomers and of *E*/*Z* nitrogen invertomers, but the latter were not observed spectroscopically.



5

The present aldehyde-derived dimolybdosulfenimines contain the Mo$_2$SN=CHR linkage; as such they can be considered as inverse products of normal metallo-S,H addition to nitriles or to HCN. Isomeric to Mo$_2$SN=CHR is the dimolybdothioimidate linkage, Mo$_2$SC(=NH)R; this has been proposed as an intermediate in the reduction of acetonitrile (R = Me) by [(C$_5$H$_5$)$_2$Mo$_2$(S$_2$CH$_2$)S(SH)]$^+$.[62] As a further note, organosulfenimines, PhSN=CHR, have been reported to eliminate nitrile upon treatment with base.[63]

The structures of **2**(H,CMe$_3$) and **2**(Me,Me) clearly show the thiooximate ligand as bridging via sulfur only. This contrasts to (mono)oxime complexes which generally involve O and N binding.[9]

The question of the preferred orientation for the sulfur invertomers can be considered in terms of electronic and steric factors. These factors could be quite different for the two isomers available to compounds of the general type [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SZ)] (**3**), due to the very different coligand environments above and below the Mo$_2$S$_2$ core. For such compounds, distal/proximal ratios have ranged from 0 to 30,[11,32,61,64,65] with no obvious dependence on the identity of the atom (C, N, P, or S) directly bonded to the tricoordinate S. Comparison of the current structures of **2**(H,CMe$_3$) and **2**(Me,Me) has revealed modest structural differences between the two different invertomers, and these are associated with a drop of S(1) out of the core plane and an increase in the pyramidal nature of that site. Steric effects of the two invertomer orientations are not very considerable, although there is apparently more contact for the distal configuration. Unfortunately, although the three structures to date of distal compounds show general similarities, the generality of the results for the proximal orientation are not established. For this reason, further structural comparisons, and also further evaluations of electronic factors, are in progress.

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Supplementary Material Available: Tables of full crystallographic parameters, positional parameters of all atoms, bond lengths and angles, general displacement parameters, and least-squares planes (43 pages). Ordering information is given on any current masthead page.

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