

# Bridging Disulfido Complexes of Molybdenum and Tungsten Formed by Reductive Sulfurization of Oxo–Molybdenum(VI) Complexes and Reductive Desulfurization of Thio(disulfido)–Tungsten(VI) Complexes

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Reactions of  $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  with boron sulfide in dichloromethane result in the formation of  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4](\text{BF}_4)_2$  [R = Et (1), Pr<sup>i</sup> (2), Bu<sup>i</sup> (3)] and  $[\text{Mo}(\text{S}_2\text{CNR}_2)_4]\text{BF}_4$ . Reactions of  $\text{WS}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2$  with  $\text{Me}_3\text{SiI}$  in dichloromethane produce  $[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4]\text{I}(\text{I}_3)$  (R = Et (4), Bu<sup>i</sup> (5)). The air stable, diamagnetic compounds have been characterized by microanalytical, mass spectral, IR, <sup>1</sup>H NMR and crystallographic studies. Orange **1**·2CHBr<sub>3</sub> crystallizes in triclinic space group  $P\bar{1}$  with  $a = 12.560$  (3),  $b = 13.000$  (4),  $c = 8.071$  (4) Å,  $\alpha = 94.16$  (4),  $\beta = 90.09$  (3),  $\gamma = 75.80$  (2)°,  $V = 1274$  (1) Å<sup>3</sup> and  $Z = 1$  dimer. Orange-red **4** crystallizes in triclinic space group  $P\bar{1}$  with  $a = 13.798$  (3),  $b = 11.876$  (3),  $c = 15.182$  (4) Å,  $\alpha = 106.95$  (2),  $\beta = 112.26$  (2),  $\gamma = 84.70$  (2)°,  $V = 2202$  (1) Å<sup>3</sup> and  $Z = 2$ . The structures were solved by Patterson and Fourier methods followed by least-squares refinements to conventional  $R$  values of 0.036 and 0.069 for **1** and **4**, respectively. The Mo- and W-containing cations exhibit dinuclear structures wherein  $\text{M}^{\text{V}}$  centers are bridged by two  $\mu\text{-}\kappa^2\text{S}, \text{S}'\text{:}\kappa^2\text{S}, \text{S}'\text{-S}_2^{2-}$  ( $\mu\text{-S}_2^{2-}$ ) ligands [S–S average 2.01 Å] and a metal–metal single bond [Mo–Mo = 2.808 (1) Å; W–W = 2.792 (3) Å]. Each metal atom is further coordinated by two bidentate dithiocarbamate ligands, the arrangement of which defines a  $\Delta\Delta$  diastereomer.

## Introduction

Current interest in molybdenum–sulfur and tungsten–sulfur chemistry stems from the importance of metal–sulfur systems in industrial<sup>2–6</sup> and biological catalysis.<sup>7–10</sup> Alumina supported, sulfided molybdenum–cobalt catalysts are extensively employed in large-scale commercial hydrotreating processes such as hydrodesulfurization, hydrogenation, isomerization, dehydration, and hydrocracking.<sup>2–6</sup> As well, two broad classes of molybdenum enzymes are known. The nitrogenases, which convert atmospheric dinitrogen into ammonia, contain an FeMo-cofactor rich in inorganic sulfide;<sup>7,8</sup> crystallographic studies have recently confirmed the presence of an Fe<sub>7</sub>MoS<sub>9</sub> cluster in the molybdenum nitrogenase.<sup>10</sup> The other known molybdenum enzymes are related by a common Mo-cofactor incorporating a 6-substituted pterin moiety postulated to bind to molybdenum by an unusual dithiolene functionality.<sup>7–9</sup> These enzymes catalyze net oxygen atom transfer reactions involving substrates such as

nitrate, sulfite, xanthine, and *N*- and *S*-oxides. Related pterin-containing tungsten enzymes appear to play a vital role in the growth and metabolism of hyperthermophilic archaea.<sup>9</sup> Although the active site structures of the enzyme systems are coming into focus,<sup>8–10</sup> less is known about the types of centers responsible for catalytic transformations on the surface of heterogeneous industrial catalysts. The synthesis and study of molecular “metal sulfides”, the sites and nature of their reactivity, and their conversion into heterometallic catalyst precursors are of interest in this regard.

The reactivity of metal–sulfur complexes may be centered on either the metal, the sulfur, or both of these centers. Facile redox interplay of molybdenum and sulfur, and to a lesser extent tungsten and sulfur, is manifest in many systems.<sup>11</sup> In induced internal electron transfer reactions, an external oxidant initiates metal–sulfur redox reactions. Examples include the reactions of  $\text{VS}_4^{3-}$  and  $\text{MoS}_4^{2-}$  with tetraalkylthiuram disulfides, which yield  $\text{V}^{\text{IV}}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4$ <sup>12,13</sup> and  $\text{Mo}^{\text{V}}(\text{S}_2)(\text{S}_2\text{CNR}_2)_3$ ,<sup>14,15</sup> respectively. Reduction of the metal center and the thiuram disulfide is coupled to oxidation of the thio ( $\text{S}^{2-}$ ) ligands to disulfido ( $\text{S}_2^{2-}$ ) and polysulfido ( $\text{S}_x^{2-}$ ) ligands. Reduction of tungsten does not occur when  $\text{WS}_4^{2-}$  is reacted with thiuram disulfides but partial oxidation of the thio ligands does take place

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to produce  $WS(S_2)(S_2CNR_2)_2$ ;<sup>14,15</sup> this is most likely due to the more negative (compared to molybdenum and vanadium) reduction potentials of tungsten. A number of related internal redox systems have been reported<sup>16–20</sup> and the mechanism of the reaction of  $MoS_4^{2-}$  with disulfides, which produces  $[Mo_2S_2(\mu-S)_2(S_2)_2]^{2-}$ , has been investigated.<sup>21</sup> The facile interconversion of other polysulfido complexes, such as  $[Mo_2S_2(\mu-S)_2(S_4)_2]^{2-}$  with  $[Mo_2(\mu-S)_2(S_2)_4]^{2-}$ , is further testimony to the subtle redox behavior of Mo–S systems.<sup>22</sup> Disulfido and polysulfido complexes can also be prepared by reductive sulfurization of high-valent oxo–molybdenum complexes.<sup>13,23–25</sup> Here the redox process involves reduction of the metal center and oxidation of reagent sulfide (from  $H_2S$ ,  $B_2S_3$  etc.) to di- or polysulfido ligands; these reactions may proceed via initial formation of thio complexes which may then undergo induced redox reactions of the type discussed above. The coordination chemistry of the disulfido ligand has been reviewed.<sup>26</sup>

A wealth of dialkyldithiocarbamate chemistry is known for molybdenum and tungsten.<sup>27–30</sup> With the exception of  $[M(S_2CNR_2)_4]^{0/+}$  complexes, the high valent dithiocarbamate chemistry of these elements is dominated by terminal oxo and thio complexes. Two types of dinuclear dithiocarbamate–M(V) complexes, viz.,  $M_2O_2(\mu-O)(S_2CNR_2)_4$  and  $M_2E_2(\mu-E)_2(S_2CNR_2)_2$  (E = O, S) predominate; all of these complexes feature terminal chalcogen ligands. We describe here the synthesis and characterization of a new type of dithiocarbamate complex of Mo(V) and W(V), the dinuclear bis- $\mu$ -disulfido complexes  $[M_2(\mu-S)_2(S_2CNR_2)_4]^{2+}$ . Our studies complement the chemistry of mononuclear disulfido–Mo and –W complexes,<sup>26–30</sup> related complexes such as  $[Mo_2(\mu-S)_2(S_2)_4]^{2-}$ ,<sup>23</sup>  $[Mo_2(\mu-S)_2X_8]^{2-}$  (X = Cl, Br),<sup>31</sup> and rather more esoteric  $\mu$ -disulfido di- and tetranuclear complexes such as  $\{[(S_2)_2MoO]_2S\}^{2-}$  and  $\{[(S_2)_2MoO]_2S\}_2^{2-}$ .<sup>32</sup> They also complement and extend previous work involving the analogous V(IV) and Nb(IV) complexes,  $V_2(\mu-S)_2(S_2CNR_2)_4$  (R = Bu<sup>t</sup>,<sup>12</sup> Et<sup>13</sup>) and  $Nb_2(\mu-S)_2(S_2CNEt_2)_4$ .<sup>33,34</sup> Some aspects of the molybdenum chemistry have been previously communicated.<sup>35</sup>

## Experimental Section

**Materials and Methods.** All reactions were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques and dry deoxygenated solvents. Samples of  $[MoO(S_2CNR_2)_3]BF_4$ ,  $MoOCl_2(S_2CNEt_2)_2$  and  $WS(S_2)(S_2CNR_2)_2$  were prepared by the methods of Young *et al.*,<sup>36</sup> Dirand *et al.*,<sup>37</sup> and Pan *et al.*,<sup>14</sup> respectively. Boron sulfide (Morton Thiokol) and  $Me_3SiI$  (Aldrich) were used without further purification. Infrared spectra were recorded as KBr disks on a Perkin–Elmer 1430 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-400 WB spectrometer equipped with an ASPECT 3000 computer and a C/H 5 mm dual probe head using tetramethylsilane as reference ( $\delta = 0$ ). Mass spectra were recorded on a Vacuum Generators VG ZAB 2HF mass spectrometer. Microanalyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

**Syntheses.**  $[Mo_2(\mu-S)_2(S_2CNEt_2)_4](BF_4)_2$  (**1**). A solution of  $[MoO(S_2CNEt_2)_3]BF_4$  (6.0 g, 9.3 mmol) in dichloromethane (150 mL) was treated with boron sulfide (0.37 g, 3.1 mmol) and the mixture was stirred for 28 h. The brown mixture was filtered in air and diethyl ether (200 mL) was slowly added to the filtrate to precipitate an orange solid. The yields were typically ca. 2.0 g (78%). Rapid addition of diethyl ether resulted in the contamination of **1** with  $[Mo(S_2CNEt_2)_4]BF_4$ . Contaminated products were recrystallized from acetonitrile by addition of diethyl ether or purified by column chromatography (silica,  $CH_2Cl_2/CH_3CN$  (2:1) eluant). Further addition of diethyl ether produced impure  $[Mo(S_2CNEt_2)_4]BF_4$  which was recrystallized ( $CH_2Cl_2$ /ether) to give black needles with infrared, EPR and UV–visible spectra identical to those in the literature.<sup>38</sup>

For **1**: Anal. Calcd for  $C_{20}H_{40}B_2F_8Mo_2N_4S_{12}$ : C, 22.10; H, 3.71; N, 5.16; S, 35.40. Found: C, 21.99; H, 3.70; N, 5.16; S, 35.27. IR:  $\nu(CN)$  1520 s, 1450 sh,m, 1440 m, 1380 m, 1275 m, 1200 m, 1150 m, ( $BF_4$ ) 1050 br,s, 850 m, 780 w, 600 w, 560 w, 530 m, 380 w, 370 w  $cm^{-1}$ . <sup>1</sup>H NMR ( $CDCl_3$ ):  $\delta$  1.1 to 1.4 (m, 24 H, 4 pair  $CH_3$ ), 3.95 and 3.74, 4.03 and 3.69, 3.81 and 3.69, 3.81 and 3.74 (each 2H (16 H total), <sup>2</sup> $J_{AB} = 14$  Hz, <sup>3</sup> $J = 7$  Hz, 4 pair  $H_{AB}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ( $CDCl_3$ ): 12.85, 13.00, 13.18, 13.32 ( $CH_3$ ); 46.11, 46.25, 46.52, 46.66 ( $CH_2$ ). <sup>95</sup>Mo NMR ( $CH_2Cl_2$ ):  $\delta$  –562,  $\Delta W_{1/2} = 90$  Hz. Mass spectrum  $m/z$  (% in multiplet): [**1** –  $BF_4$ ]<sup>+</sup> 991 (9), 992 (6), 993 (20), 994 (30), 995 (41), 996 (53), 997 (80), 998 (75), 999 (98), 1000 (94), 1001 (100), 1002 (87), 1003 (82), 1004 (55), 1005 (50), 1006 (24), 1007 (20), 1008 (8), 1009 (5); [**1** –  $2BF_4$ ]<sup>+</sup> 904 (9), 905 (3), 906 (17), 907 (25), 908 (40), 909 (45), 910 (80), 911 (66), 912 (99), 913 (89), 914 (100), 915 (84), 916 (86), 917 (53), 918 (55), 919 (24), 920 (23), 921 (8), 922 (6).

$[Mo_2(\mu-S)_2(S_2CNPt_2)_4](BF_4)_2$  (**2**). A solution of  $[MoO(S_2CNPt_2)_3]BF_4$  (0.4 g, 0.55 mmol) in dichloromethane (20 mL) was treated with boron sulfide (0.03 g, 0.25 mmol) and the mixture was stirred for 1 day. Upon evaporation of the solvent, the residue was dissolved in 10 mL of nitromethane. After filtering, the solution was loaded onto a silica gel chromatog-

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raphy column which was eluted with  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$  (2:1). The yellow compound was recrystallized from  $\text{CH}_3\text{CN}$ /diethyl ether. The yield was 0.13 g, 80%.

Anal. Calcd for  $\text{C}_{28}\text{H}_{56}\text{B}_2\text{F}_8\text{Mo}_2\text{N}_4\text{S}_{12}$ : C, 28.05; H, 4.71; N, 4.67; S, 32.09. Found: C, 28.07; H, 4.54; N, 4.68; S 32.00. IR:  $\nu(\text{CN})$  1500 s, 1450 sh,m, 1440 m, 1370 m, 1335 s, 1180 m, 1140 m, 1080 m,  $(\text{BF}_4)$  1050 br,s, 570 w, 515 w, 460 w, 380 w  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{NO}_2$ ):  $\delta$  1.50 (m, 48 H, 16  $\text{CH}_3$ ), 4.70 (m, 8H, 8 CH). Mass spectrum  $m/z$  (highest peak in multiplet):  $[\text{2} - \text{BF}_4]^+$  1113;  $[\text{2} - 2\text{BF}_4]^+$  1026.

$[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNBu}^i_2)_4](\text{BF}_4)_2$  (**3**). A solution of  $[\text{MoO}(\text{S}_2\text{CNBu}^i_2)_3]\text{BF}_4$  (1.0 g, 1.23 mmol) in dichloromethane (30 mL) was treated with boron sulfide (0.05 g, 0.42 mmol) and the mixture was stirred for 1 day. After filtering, the solution was carefully treated with diethyl ether to precipitate the orange complex. The yield was 0.27 g, 68%. The analytical sample was recrystallized from  $\text{CHBr}_3$ /ether and retains some  $\text{CHBr}_3$  of crystallization (observed by NMR).

Anal. Calcd for  $\text{C}_{36.25}\text{H}_{72.25}\text{B}_2\text{Br}_{0.75}\text{F}_8\text{Mo}_2\text{N}_4\text{S}_{12}$ : C, 31.68; H, 5.30; N, 4.08; S, 28.00. Found: C, 31.73; H, 5.41; N, 4.10; S 28.01. IR:  $\nu(\text{CN})$  1520 s, 1460 m, 1435 m, 1380 m, 1360 m, 1330m, 1250 s, 1150 s,  $(\text{BF}_4)$  1050 br,s, 630 m, 610 w, 510 w, 420 w, 380 w  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.88 (d, 24 H,  $^3J = 7$  Hz, 8  $\text{CH}_3$ ), 0.90 (d, 24 H,  $^3J = 7$  Hz, 8  $\text{CH}_3$ ), 2.14 (9 line, 8H, 8CH), 3.39 (A) and 3.50 (B) (m, 8H,  $J_{\text{AB}} = 13.8$  Hz,  $^3J = 7.5$  Hz, 4  $H_{\text{AB}}$ ), 3.45 (A) and 3.72 (B) (m, 8H,  $J_{\text{AB}} = 13.8$  Hz,  $^3J = 7.5$  Hz, 4  $H_{\text{AB}}$ ). Mass spectrum  $m/z$  (highest peak in multiplet):  $[\text{3} - \text{BF}_4]^+$  1225;  $[\text{3} - 2\text{BF}_4]^+$  1138.

$[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4]\text{Cl}_2$ . A solution of  $\text{MoOCl}_2(\text{S}_2\text{CNET}_2)_2$  (0.24 g, 0.5 mmol) in dichloromethane (15 mL) was treated with boron sulfide (0.02 g, 0.17 mmol) and the mixture was stirred for 4 days. After filtering, the solution was carefully treated with diethyl ether to precipitate the yellow complex. The yield was 0.14 g (60% based on Mo). Infrared spectroscopy and conversion to **1** upon reaction with  $\text{NaBF}_4$  in methanol identified the compound as  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4]\text{Cl}_2$ .

$[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4]\text{I}(\text{I}_3)$  (**4**). A mixture of  $\text{WS}(\text{S}_2\text{CNET}_2)_2$  (0.345 g, 0.6 mmol) and excess  $\text{Me}_3\text{SiI}$  (2.5 mL, 17.5 mmol) in dichloromethane (25 mL) was stirred at room temperature for 5 days. The green solution became deep red during this period and a small amount of yellow solid formed. Following filtration, addition of diethyl ether to the filtrate precipitated the red product which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethyl ether. Yield = 0.45 g, ca. 95%.

Cocrystallization of  $\text{I}^-$ ,  $\text{I}_3^-$  and mixed  $\text{I}^-(\text{I}_3^-)$  salts prevented consistent microanalytical results. IR:  $\nu(\text{CN})$  1525 s, 1470 m, 1440 s, 1380 w, 1360 m, 1280 s, 1210 m, 1160 m, 1080 w, 860 w, 780 w, 570 w, 550 br,w, 500 w, 470 w  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.38 (t, 12H,  $^3J = 7$  Hz, 4  $\text{CH}_3$ ), 1.40 (t, 12H,  $^3J = 7$  Hz, 4  $\text{CH}_3$ ), 3.6–3.9 (m, 12H, 6  $\text{CH}_2$ ), 3.9–4.1 (m, 4H, 2  $\text{CH}_2$ ). Mass spectrum  $m/z$  (highest peak in multiplet):  $[\text{4} - \text{I}_3]^+$  1215;  $[\text{4} - \text{I}_4 - \text{S}_2\text{CNET}_2]^+$  940;  $[\text{4} - \text{I}_4 - \text{S}_3\text{CNET}_2]^+$  908;  $[\text{4} - \text{I}_4 - 2\text{S}_2\text{CNET}_2]^+$  792;  $[\text{WS}(\text{S}_2\text{CNET}_2)_2]^+$  512.

$[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNBu}^i_2)_4]\text{I}(\text{I}_3)$  (**5**). A mixture of  $\text{WS}(\text{S}_2\text{CNBu}^i_2)_2$  (0.767 g, 1.1 mmol) and excess  $\text{Me}_3\text{SiI}$  (2.6 mL, 18.2 mmol) in dichloromethane (20 mL) was stirred at room temperature for 4 days. The green solution became deep red during this period. After reducing the solution volume to half, addition of diethyl ether precipitated the red product as an oil which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethyl ether. The yield was 0.8 g, 70%.

Cocrystallization of  $\text{I}^-$ ,  $\text{I}_3^-$  and mixed  $\text{I}^-(\text{I}_3^-)$  salts prevented consistent microanalytical results. Upon slow recrystallization  $[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNBu}^i_2)_4]\text{I}(\text{I}_3)$  (**6**) was obtained: Anal. Calcd for  $\text{C}_{36}\text{H}_{72}\text{I}_6\text{N}_4\text{S}_{12}\text{W}_2$ : C, 20.84; H, 3.50; N, 2.70; S, 18.54; W,

**Table 1.** Crystallographic data for  $1\cdot 2\text{CHBr}_3$  and **4**

	$1\cdot 2\text{CHBr}_3$	<b>4</b>
chem formula	$\text{C}_{11}\text{H}_{21}\text{BBr}_3\text{F}_4\text{MoN}_2\text{S}_6$	$\text{C}_{20}\text{H}_{40}\text{LN}_4\text{S}_{12}\text{W}_2$
fw	796.1	1596.7
space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
<i>a</i> , Å	12.560 (3)	13.798 (3)
<i>b</i> , Å	13.000 (4)	11.876 (3)
<i>c</i> , Å	8.071 (4)	15.182 (4)
$\alpha$ , deg	94.16 (4)	106.95 (2)
$\beta$ , deg	90.09 (3)	112.26 (2)
$\gamma$ , deg	75.80 (2)	84.70 (2)
<i>V</i> , Å <sup>3</sup>	1274 (1)	2202 (1)
<i>Z</i>	1 dimer	2
$\rho_{\text{calcd}}(\rho_{\text{meas}})$ , $\text{g}\cdot\text{cm}^{-3}$	2.075 (2.07)	2.409
$\mu$ , $\text{cm}^{-1}$	55.92	37.4
radiation, $\lambda$ (Å)	0.710 73 (Mo $K\alpha$ )	1.541 84 (Cu $K\alpha$ )
temp, °C	22	20
<i>R</i> <sup>a</sup>	0.036	0.069
<i>R</i> <sub>w</sub>	0.040	0.074

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

17.72; I, 36.70. Found: C, 21.89; H, 3.75; N, 2.59; S, 18.05; W, 17.30; I, 36.10. IR:  $\nu(\text{CN})$  1510 s, 1460 m, 1435 m, 1380 m, 1360 m, 1330 m, 1250 s, 1150 s, 1090 m, 800 w, 630 m, 610 w, 510 w, 420 w, 380 w.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.98 (d, 24 H,  $^3J = 7$  Hz, 8  $\text{CH}_3$ ), 1.00 (d, 24 H,  $^3J = 7$  Hz, 8  $\text{CH}_3$ ), 2.28 (9 line, 8H, 8  $H_{\text{AB}}$ ), 3.35–3.9 (m, 16H, 8  $H_{\text{AB}}$ ). Mass spectrum  $m/z$  (highest peak in multiplet):  $[\text{5} - \text{I}_3]^+$  1441;  $[\text{5} - \text{I}_4 - \text{S}_2\text{CNBu}_2]^+$  1108;  $[\text{5} - \text{I}_4 - \text{S}_3\text{CNBu}_2]^+$  1076;  $[\text{5} - \text{I}_4 - 2\text{S}_2\text{CNBu}_2]^+$  904;  $[\text{WS}(\text{S}_2\text{CNBu}_2)_2]^+$  624.

**Crystallography.** Crystals of **1** grown from  $\text{CH}_2\text{Cl}_2$ –diethyl ether or  $\text{CHCl}_3$ –diethyl ether mixtures were unstable due to loss of solvent of crystallization. Orange crystals suitable for an X-ray structure determination were eventually obtained by slow evaporation of a  $\text{CHBr}_3$  solution of **1**. Red platelike crystals of **4** and **6**<sup>39</sup> were obtained by slow diffusion of diethyl ether into dichloromethane solutions of **4** and **5**, respectively, at  $-20$  °C.

Intensity data for **1** were measured to a maximum Bragg angle of  $24.0^\circ$  using Mo  $K\alpha$  radiation and the  $\omega: 2\theta$  scan technique. Intensity data for **4** were measured using the  $\theta-2\theta$  scan technique over the  $2\theta$  ranges  $3.0-84.0^\circ$  ( $4.0^\circ/\text{min}$ ) and  $84.0-105.1^\circ$  ( $2.0^\circ/\text{min}$ ) employing Cu  $K\alpha$  radiation. The intensities of six check reflections recollected every 300 reflections dropped uniformly as a nearly linear function of exposure time. They were used to correct the data for degradation which amounted to 2.5% at the end of the first shell and 6% at the end of the second shell; no decomposition was detected for **1**. The data sets were corrected for Lorentz and polarization effects and analytical absorption corrections were applied.<sup>40</sup> Relevant crystallographic data are given in Table 1.

The structure of  $1\cdot 2\text{CHBr}_3$  was solved by the Patterson method and refined by a full-matrix least-squares procedure based on  $F_o$ .<sup>40a</sup> Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model in their calculated positions (C–H 0.97 Å). The refinement was continued until convergence employing a weighting scheme of the form  $w = 3.97/[\sigma^2(F) + 0.0008|F|^2]$ ; the analysis of variance showed no special features. The structure of **4** was solved by

(39) Crystal data for **6**: triclinic space group  $P\bar{1}$ ,  $a = 12.641$  (8),  $b = 15.135$  (7),  $c = 10.073$  (1) Å,  $\alpha = 93.49$  (2),  $\beta = 99.33$  (2),  $\gamma = 105.17$  (4) $^\circ$  with  $Z = 4$ . The structure was refined by a full-matrix least-squares procedure to  $R = 0.066$  for 5135 reflections with  $I \geq 2.5\sigma(I)$ . The structure of **6** is closely related to **4** except that two  $\text{I}_3^-$  anions per dication were present.

(40) (a) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination, Cambridge University, England, 1976. (b) Sheldrick, G. M. SHELXTL, University of Göttingen.

**Table 2.** Fractional Atomic Coordinates ( $\times 10^5$  for Mo,  $\times 10^4$  for Other Atoms) and Their Estimated Standard Deviations for 1·2CHBr<sub>3</sub>

atom	x	y	z
Mo	41159(4)	58975(4)	49336(6)
S(1)	4499(1)	4359(1)	2905(2)
S(2)	5555(1)	5282(1)	2825(2)
S(3)	4738(1)	7572(1)	4862(2)
S(4)	3147(1)	6990(1)	2716(2)
S(5)	2827(1)	7112(1)	6977(2)
S(6)	2298(1)	5425(1)	4946(2)
N(1)	3931(6)	8689(5)	2264(7)
N(2)	1021(4)	6430(4)	7518(6)
C(1)	3934(6)	7871(6)	3133(8)
C(2)	3323(8)	8813(8)	737(9)
C(3)	2214(10)	9538(9)	1009(12)
C(4)	4418(9)	9679(11)	2926(13)
C(5)	5387(11)	9302(10)	2271(12)
C(6)	1894(5)	6341(5)	6636(7)
C(7)	251(6)	5771(6)	7117(8)
C(8)	587(9)	4709(7)	7807(11)
C(9)	787(6)	7142(6)	9043(8)
C(10)	84(8)	8222(7)	8703(11)
B(1)	7084(9)	7045(10)	-531(12)
F(1)	7776(6)	7572(7)	108(8)
F(2)	7589(6)	6280(8)	-1625(11)
F(3)	6495(7)	6781(6)	562(8)
F(4)	6317(9)	7686(8)	-1480(11)
C(100)	-1434(6)	8504(6)	3530(8)
Br(1)	-2123(1)	7860(1)	5151(1)
Br(2)	150(1)	8011(1)	3635(1)
Br(3)	-1868(1)	10025(1)	3857(1)

direct methods and only the W, I and S atoms were refined anisotropically; the refinement, with H atoms in calculated positions, was continued until convergence employing a weighting scheme of the form  $w = 1/[\sigma^2(F) + 0.03|F|^2]$ .<sup>40b</sup> Fractional atomic coordinates for 1·2CHBr<sub>3</sub> and 4 are listed in Tables 2 and 3, respectively. Structures and numbering schemes are represented using ORTEP.<sup>41</sup> Selected bond distances and angles are given in Tables 4 and 5. The scattering factors for neutral Mo and W (corrected for  $f'$  and  $f''$ ) were from ref 42 and those for the remaining atoms were as incorporated in the SHELX76 and SHELXTL programs.<sup>40</sup>

## Results

Reaction of the oxo-Mo(VI) complexes  $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  (R = Et, Pr<sup>i</sup>, Bu<sup>t</sup>) with boron sulfide (Mo:S = 1:1.3) in dichloromethane produced the Mo(V) complexes  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4](\text{BF}_4)_2$  (R = Et (1), Pr<sup>i</sup> (2), Bu<sup>t</sup> (3)) and  $[\text{Mo}(\text{S}_2\text{-CNR}_2)_4]\text{BF}_4$ . Sonication of the heterogeneous reaction mixtures did not improve final yields or reaction times. The products were generally separated by fractional crystallization, then purified by recrystallization or column chromatography. Reaction of  $\text{MoOCl}_2(\text{S}_2\text{CNEt}_2)_2$  with boron sulfide produced the chloride salt,  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNEt}_2)_4]\text{Cl}_2$ . Compounds 1–3 are orange, diamagnetic, air-stable crystalline materials which are readily soluble in dichloromethane, alcohols, acetonitrile, and nitromethane but insoluble in saturated and aromatic hydrocarbons and diethyl ether. Pure  $[\text{Mo}(\text{S}_2\text{CNEt}_2)_4]\text{BF}_4$  was obtained upon recrystallization of the final fractional crystallization sample from the preparation of 1. The compound exhibited the distinctive electronic and EPR spectral properties characteristic of other salts containing the  $[\text{Mo}(\text{S}_2\text{CNEt}_2)_4]^+$  cation.<sup>38</sup>

**Table 3.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Their Estimated Standard Deviations for 4

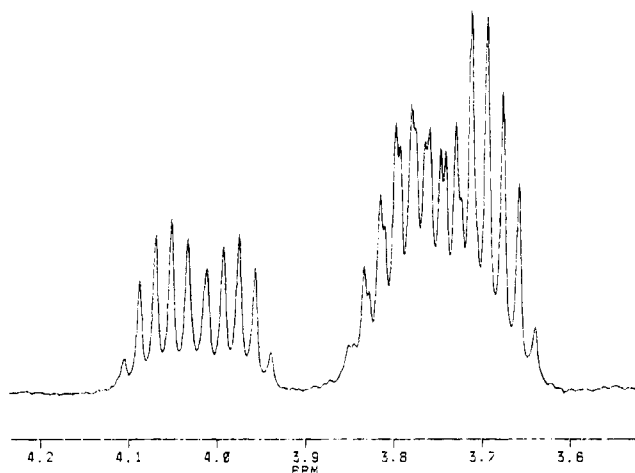
atom	x	y	z
W(1)	3109(1)	-378(1)	1377(1)
W(2)	2298(2)	148(2)	-440(2)
S(1)	3982(6)	-797(7)	191(7)
S(2)	3936(7)	932(7)	887(8)
S(3)	1491(7)	-1178(8)	57(9)
S(4)	1415(7)	564(8)	737(7)
S(11)	2403(8)	-1088(8)	2437(8)
S(12)	3411(7)	-2545(8)	1198(8)
S(21)	3389(8)	1414(8)	2839(9)
S(22)	4878(8)	-408(8)	2669(8)
S(31)	2105(7)	-1642(7)	-1840(8)
S(32)	552(7)	91(8)	-1749(8)
S(41)	3017(8)	847(8)	-1497(9)
S(42)	1979(8)	2301(7)	-285(8)
N(1)	2393(21)	-3400(21)	2094(25)
N(2)	5309(23)	1481(23)	4165(28)
N(3)	170(24)	-1844(24)	-3271(29)
N(4)	2784(24)	3122(24)	-1302(28)
C(11)	2771(28)	-2426(28)	1998(33)
C(12)	2653(39)	-4661(39)	1641(48)
C(13)	3510(33)	-5068(33)	2373(40)
C(14)	1781(32)	-3332(32)	2694(38)
C(15)	671(49)	-3326(47)	1973(59)
C(21)	4710(28)	896(28)	3449(33)
C(22)	6520(39)	1025(39)	4755(48)
C(23)	7172(36)	1476(35)	4226(43)
C(24)	5133(32)	2649(31)	4912(37)
C(25)	4593(41)	2463(40)	5529(49)
C(31)	791(27)	-1191(27)	-2415(33)
C(32)	-940(29)	-1461(29)	-3618(35)
C(33)	-1021(40)	-534(38)	-4218(48)
C(34)	337(41)	-3118(39)	-3736(50)
C(35)	287(36)	-3163(35)	-4768(43)
C(41)	2692(33)	2138(33)	-1071(39)
C(42)	3411(32)	2980(32)	-1936(38)
C(43)	2769(27)	2575(27)	-3043(31)
C(44)	2368(26)	4295(27)	-927(31)
C(45)	1740(33)	4891(34)	-1779(41)
I(1)	5427(2)	3524(2)	938(3)
I(2)	6491(2)	4326(2)	3191(3)
I(3)	7468(3)	5286(3)	5294(3)
I(4)	981(3)	3127(2)	1857(3)

Reaction of the thio-W(VI) complexes  $\text{WS}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2$  (R = Et, Bu<sup>t</sup>) with excess trimethylsilyl iodide followed by precipitation of the product with diethyl ether yielded  $[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNEt}_2)_4]\text{I}(\text{I}_3)$  (4) and  $[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNBu}^t)_4]\text{I}(\text{I}_3)$  (5), respectively. No reactions were observed when  $\text{Me}_3\text{SiO}_2\text{CCF}_3$  or  $\text{NBu}^n\text{I}$  were substituted for  $\text{Me}_3\text{SiI}$ . The tungsten compounds are red-brown, diamagnetic, air-stable crystalline materials with essentially the same solubility properties as their molybdenum analogues (4 is less soluble than 1 in most solvents).

The IR spectra of the molybdenum compounds were dominated by bands due to the dithiocarbamate ligands ( $\nu(\text{CN})$  ca.  $1500\text{ cm}^{-1}$ ) and a strong broad feature due to the  $\text{BF}_4^-$  anion ( $1050\text{ cm}^{-1}$ ). Weak bands associated with the  $\text{S}_2^{2-}$  ligands (for 1 at  $530\text{ cm}^{-1}$ ) were observed.<sup>26</sup> The IR spectra of the tungsten compounds were also dominated by bands due to the dithiocarbamate and  $\text{S}_2^{2-}$  ligands. The positive ion fast atom bombardment mass spectrum (FAB-MS) of 1 exhibited peak clusters at  $m/z$  1001 and 914 assignable to the  $[\text{1-BF}_4]^+$  and  $[\text{1-2BF}_4]^+$  ions, respectively. Quite analogous mass spectra were observed for the other molybdenum compounds. The highest  $m/z$  cluster in the FAB-MS of 4 and 5 corresponded to the ion pair  $\{[\text{W}_2(\text{S}_2)_2(\text{S}_2\text{CNR}_2)_4]^{2+}\text{I}^-\}^+$ . Stronger peaks due to  $[\text{W}_2\text{S}_4(\text{S}_2\text{CNR}_2)_3]^+$  and  $[\text{WS}(\text{S}_2\text{CNR}_2)_2]^+$  were also observed for these compounds.

(41) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(42) Ibers, J. A.; Hamilton, W. C. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp. 99, 149.



**Figure 1.** Methylene resonances in the 400 MHz  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  at 20  $^\circ\text{C}$ .

**Table 4.** Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg) for **1**<sup>a</sup>

Mo-S(1)	2.443(2)	Mo-S(2)	2.430(2)
Mo-S(1')	2.444(2)	Mo-S(2')	2.426(2)
Mo-S(3)	2.491(2)	Mo-S(4)	2.493(2)
Mo-S(5)	2.492(2)	Mo-S(6)	2.506(1)
Mo-Mo'	2.808(1)	S(1)-S(2)	1.999(2)
S(3)-C(1)	1.732(6)	S(4)-C(1)	1.704(6)
S(5)-C(6)	1.729(6)	S(6)-C(6)	1.733(6)
C(1)-N(1)	1.314(8)	C(6)-N(2)	1.284(8)
$\langle\text{N}-\text{C}_{\text{Et}}\rangle_{\text{av}}$	1.500(9)	$\langle\text{C}-\text{C}\rangle_{\text{av}}$	1.445(14)
Mo-S(1)-Mo'	70.1(1)	Mo-S(2)-Mo'	70.6(1)
S(1)-Mo-S(2)	48.4(1)	S(1)-Mo-S(1')	109.9(1)
S(2)-Mo-S(2')	109.4(1)	S(1)-Mo-S(2')	90.0(1)
Mo-S(1)-S(2)	65.4(1)	Mo-S(2)-S(1)	66.1(1)
S(1)-Mo-S(3)	128.1(1)	S(1)-Mo-S(4)	88.3(1)
S(1)-Mo-S(5)	149.3(1)	S(1)-Mo-S(6)	79.8(1)
S(2)-Mo-S(3)	81.9(1)	S(2)-Mo-S(4)	83.8(1)
S(2)-Mo-S(5)	160.2(1)	S(2)-Mo-S(6)	125.7(1)
S(3)-Mo-S(4)	69.7(1)	S(3)-Mo-S(5)	78.3(1)
S(3)-Mo-S(6)	135.6(1)	S(4)-Mo-S(5)	87.6(1)
S(5)-Mo-S(6)	69.6(1)	Mo-S(3)-C(1)	88.6(2)
Mo-S(4)-C(1)	89.2(2)	Mo-S(5)-C(6)	89.4(2)
Mo-S(6)-C(6)	88.9(2)	S(3)-C(1)-S(4)	111.9(4)
S(5)-C(6)-S(6)	110.9(4)		

<sup>a</sup> Primed atoms are related by crystallographic center of inversion.

The  $^1\text{H}$  NMR spectrum of **1** in the methylene region ( $\delta$  3.6–4.1) is shown in Figure 1. Decoupling of the methyl resonances reduced this complex spectrum to a set of four AB quartets. The geminal coupling  $^2J_{\text{AB}}$  was found to be 14 Hz, while the vicinal coupling  $^3J_{\text{HH}}$  obtained from the one-dimensional spectrum was found to be 7 Hz. Two-dimensional homonuclear  $J$ -resolved and COSY spectroscopy<sup>43,44</sup> confirmed the above coupling constants and revealed five unique chemical shifts for the methylene protons; these were  $\delta$  3.69 (4H), 3.74 (4H), 3.81 (4H), 3.95 (2H), 4.03 (2H). COSY spectra allowed identification of coupled pairs of  $\text{H}_{\text{AB}}$  protons.  $^1\text{H}$  NMR chemical shifts and coupling constants are summarized in the Experimental Section. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** revealed four methyl and four methylene resonances. The spectrum of **3** (Figure 2a) consisted of two overlapping doublets at  $\delta$  0.89, a 9-line resonance at  $\delta$  2.14, and two multiplet features at  $\delta$  3.5–3.8. Decoupling at  $\delta$  2.14 simplified the remaining resonances; two peaks were observed at  $\delta$  0.89 and two AB quartets were

**Table 5.** Selected Interatomic Distances ( $\text{\AA}$ ) and Angles (deg) for **4**

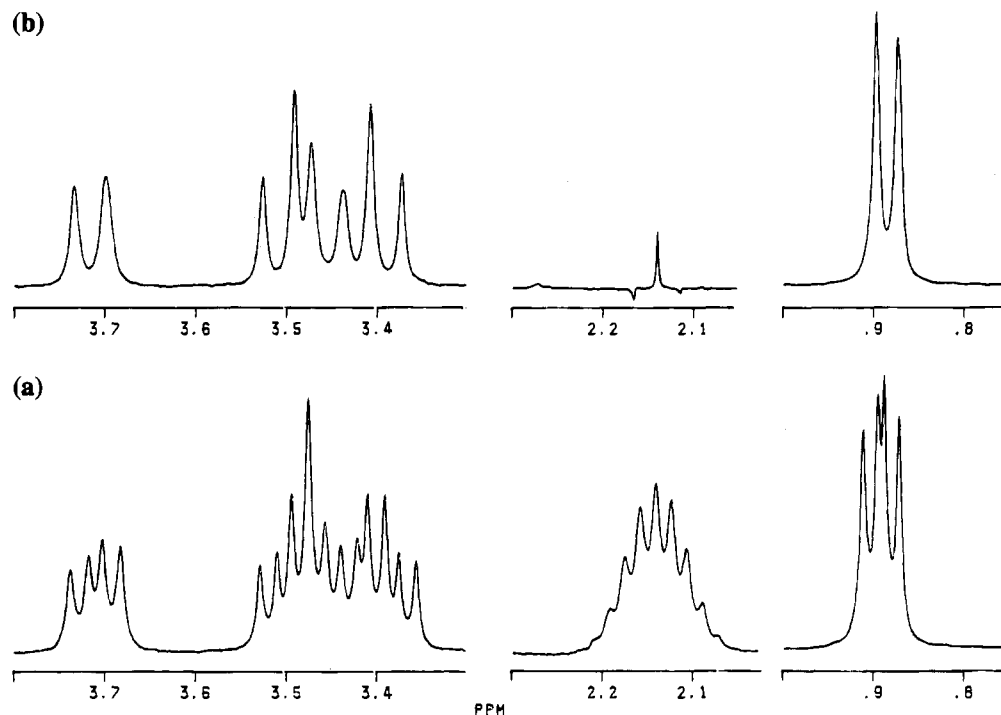
W(1)-S(1)	2.44(1)	W(1)-S(2)	2.43(1)
W(1)-S(3)	2.41(1)	W(1)-S(4)	2.47(1)
W(2)-S(1)	2.46(1)	W(2)-S(2)	2.43(1)
W(2)-S(3)	2.44(1)	W(2)-S(4)	2.44(1)
W(1)-W(2)	2.792(3)	S(1)-S(2)	2.02(1)
S(3)-S(4)	2.04(1)	W(1)-S(11)	2.53(1)
W(1)-S(12)	2.52(1)	W(1)-S(21)	2.52(1)
W(1)-S(22)	2.49(1)	W(2)-S(31)	2.48(1)
W(2)-S(32)	2.47(1)	W(2)-S(41)	2.53(2)
W(2)-S(42)	2.51(1)	I(1)-I(2)	3.053(5)
I(2)-I(3)	2.865(5)		
W(1)-S(1)-W(2)	69.5(3)	W(1)-S(2)-W(2)	70.1(3)
W(1)-S(3)-W(2)	70.4(3)	W(1)-S(4)-W(2)	69.4(3)
W(1)-S(1)-S(2)	65.3(5)	W(2)-S(1)-S(2)	64.7(3)
W(1)-S(2)-S(1)	65.6(5)	W(2)-S(2)-S(1)	66.3(3)
W(1)-S(3)-S(4)	66.8(3)	W(2)-S(3)-S(4)	65.3(5)
W(1)-S(4)-S(3)	63.8(3)	W(2)-S(4)-S(3)	65.3(5)
S(1)-W(1)-S(2)	49.1(3)	S(1)-W(2)-S(2)	49.0(3)
S(3)-W(1)-S(4)	49.4(3)	S(3)-W(2)-S(4)	49.4(3)
S(1)-W(1)-S(3)	90.1(4)	S(1)-W(2)-S(3)	89.0(3)
S(1)-W(1)-S(4)	110.4(4)	S(1)-W(2)-S(4)	110.7(4)
S(2)-W(1)-S(4)	89.8(4)	S(2)-W(2)-S(4)	90.7(4)
S(1)-W(1)-S(11)	149.5(3)	S(1)-W(1)-S(12)	80.8(4)
S(1)-W(1)-S(21)	126.7(4)	S(1)-W(1)-S(22)	86.7(4)
S(2)-W(1)-S(11)	158.8(3)	S(2)-W(1)-S(12)	127.6(4)
S(2)-W(1)-S(21)	80.7(4)	S(2)-W(1)-S(22)	84.7(4)
S(3)-W(1)-S(11)	84.5(4)	S(3)-W(1)-S(12)	79.9(3)
S(3)-W(1)-S(21)	128.5(3)	S(3)-W(1)-S(22)	157.0(3)
S(4)-W(1)-S(11)	88.6(4)	S(4)-W(1)-S(12)	126.8(3)
S(4)-W(1)-S(21)	81.8(3)	S(4)-W(1)-S(22)	151.6(3)
S(11)-W(1)-S(12)	68.7(4)	S(11)-W(1)-S(21)	78.1(4)
S(11)-W(1)-S(22)	86.7(4)	S(12)-W(1)-S(21)	133.9(4)
S(12)-W(1)-S(22)	77.1(3)	S(21)-W(1)-S(22)	69.8(3)
S(1)-W(2)-S(31)	78.9(3)	S(1)-W(2)-S(32)	149.1(3)
S(1)-W(2)-S(41)	88.1(4)	S(1)-W(2)-S(42)	127.5(3)
S(2)-W(2)-S(31)	125.3(3)	S(2)-W(2)-S(32)	159.9(3)
S(2)-W(2)-S(41)	84.3(4)	S(2)-W(2)-S(42)	81.3(3)
S(3)-W(2)-S(31)	80.8(4)	S(3)-W(2)-S(32)	84.3(4)
S(3)-W(2)-S(41)	158.5(3)	S(3)-W(2)-S(42)	128.2(4)
S(4)-W(2)-S(31)	127.6(4)	S(4)-W(2)-S(32)	87.3(4)
S(4)-W(2)-S(41)	149.9(3)	S(4)-W(2)-S(42)	81.0(4)
S(31)-W(2)-S(32)	70.2(3)	S(31)-W(2)-S(41)	77.8(4)
S(31)-W(2)-S(42)	134.9(4)	S(32)-W(2)-S(41)	87.4(4)
S(32)-W(2)-S(42)	78.6(3)	S(41)-W(2)-S(42)	68.9(4)
I(1)-I(2)-I(3)	175.0(1)		

observed in the  $\delta$  3.5–3.8 region (Figure 2b). The  $^1\text{H}$  NMR spectrum of **4** exhibits two triplet methyl resonances and two multiplet resonances in the  $\delta$  3.6–4.1 region. The  $^{95}\text{Mo}$  NMR spectrum of **1** in dichloromethane exhibited a sharp signal at  $\delta$  -562 ( $\Delta W_{1/2} = 90$  Hz).

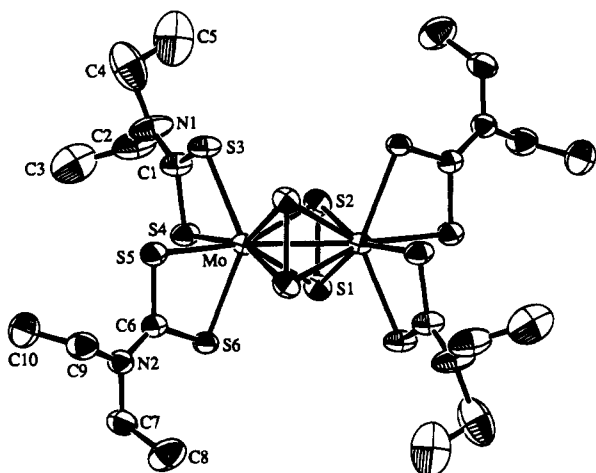
**Description of Structures.** The dimeric, centrosymmetric  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNEt}_2)_4]^{2+}$  cation (Figure 3) is composed of molybdenum atoms separated by a distance of 2.808 (1)  $\text{\AA}$  and bridged by two  $\mu\text{-S}_2^{2-}$  ligands. The bridge is characterised by Mo-S(1) and Mo-S(2) distances of 2.443 (2) and 2.430 (2)  $\text{\AA}$ , respectively, and an S(1)-S(2) distance of 1.999 (2). The nonbonding contact distances between the sulfur atoms of the  $\text{S}_2^{2-}$  ligands are: S(1)·S(2') = 3.443 (3)  $\text{\AA}$ , S(1)·S(1') = 3.999 (3)  $\text{\AA}$  and S(2)·S(2') = 3.962 (3)  $\text{\AA}$ . The four sulfur atoms of the bridge are planar and both Mo atoms are 1.404 (1)  $\text{\AA}$  out of the plane. The atoms of the  $[\text{Mo}_2(\text{S}_2)_2]^{6+}$  core have a rectangular bipyramidal (distorted octahedral) geometry with axial Mo and equatorial S atoms. Each Mo atom is further coordinated by two bidentate dithiocarbamate ligands with Mo-S distances ranging from 2.491 (2)–2.506 (1)  $\text{\AA}$ . The coordination environment of the Mo atoms may be described as distorted octahedral if the midpoints of the  $\text{S}_2^{2-}$  ligands are considered as single vertices of the polyhedron. The larger  $[\text{Mo}_2\text{S}_{12}]$  fragment may be envisaged to form from two distorted hexahedra interpenetrating along a pair of vertices to

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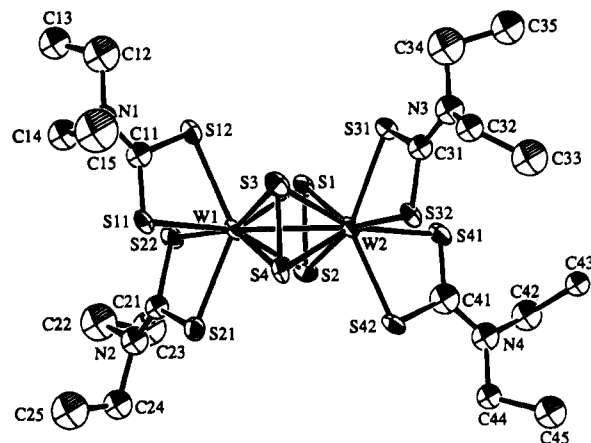
**Figure 2.** (a)  $^1\text{H}$  NMR spectrum of **3** ( $\text{CDCl}_3$ , 400 MHz). (b) Selectively decoupled ( $\delta$  2.14)  $^1\text{H}$  NMR spectrum of **3** ( $\text{CDCl}_3$ , 400 MHz) (both at  $20^\circ\text{C}$ ).



**Figure 3.** Structure of the cation of **1** drawn at the 40% probability level.

form a rectangular midsection, comprised of the atoms of the two  $\mu\text{-S}_2^{2-}$  ligands. Although not strictly octahedral, the  $\text{M}(\text{bidentate})_2(\text{monodentate})_2$  moieties formed when the midpoints of the  $\text{S}_2^{2-}$  ligands are taken to be imaginary monodentate ligands may be described by  $\Delta$  and  $\Lambda$  chirality designators.<sup>45</sup> Using this method, the chirality of the Mo and Mo' metal centers may be designated  $\Lambda$  and  $\Delta$ , respectively, i.e., the complex is a meso isomer.

The dimeric  $[\text{W}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4]^{2+}$  cations in **4** (Figure 4) and **6**<sup>39</sup> both exhibit structures analogous to that described above for  $[\text{Mo}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNEt}_2)_4]^{2+}$ . The following description applies to both structures (parameters for **6** follow in square brackets those for **4**). The dinuclear cations are composed of tungsten atoms separated by a distance of 2.792 (3) [2.803 (6)] Å and bridged by two  $\mu\text{-S}_2^{2-}$  ligands. The bridges are char-

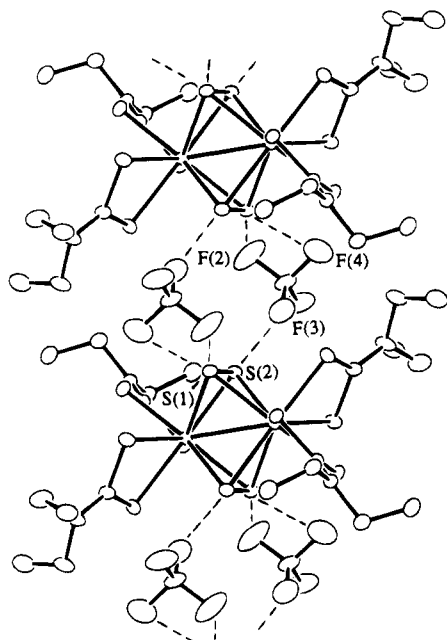


**Figure 4.** Structure of the cation of **4** drawn at the 40% probability level.

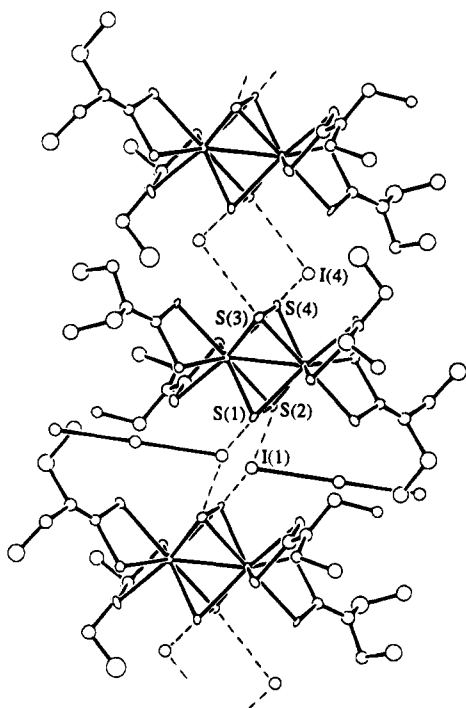
acterised by average W-S and S(1)-S(2) and S(3)-S(4) distances of 2.44 [2.50], 2.02 [2.04] and 2.04 Å, respectively. The nonbonding contact distances between the sulfur atoms of the  $\text{S}_2^{2-}$  ligands of **4** include: S(1)·S(3) = 3.430 Å, S(2)·S(4) = 3.459 Å, S(1)·S(4) = 4.028 Å and S(2)·S(3) = 3.969 Å. The sulfur atoms of the bridge are planar to  $\pm 0.007$  Å and the W(1) and W(2) atoms are 1.393 and 1.397 Å out of the plane, respectively. The atoms of the  $[\text{W}_2(\text{S}_2)_2]^{6+}$  core have a rectangular bipyramidal geometry with axial W and equatorial S atoms. The coordination environments of the W atoms and the geometries of the  $[\text{W}_2\text{S}_{12}]$  units closely resemble those described above for **1**. The coordination spheres of the W atoms are completed by two bidentate dithiocarbamate ligands the configuration of which define the  $\Delta\Delta$ -diastereomer in both cases.

A number of interactions involving the cations, anions and solvent molecules in **1**, **4** and **6** are observed. In **1**, each F atom forms one contact with neighboring entities. Thus F(1) forms a hydrogen bond to the  $\text{CHBr}_3$  molecule such that F(1)·H(100) is 2.23 Å and the F(1)-H(100)-C(100) angle is  $170.8^\circ$ . The remaining contacts involve the bridging  $\text{S}_2^{2-}$  units

(45) (a) Tentative Proposals for Nomenclature of Absolute Configurations Concerned with Six-Coordinated Complexes Based on the Octahedron. *Inorg. Chem.* **1970**, *9*, 1. (b) Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Chemical Nomenclature*; American Chemical Society: Washington, 1990; Chapter 16, pp 141-153.



**Figure 5.** Association of the  $\text{BF}_4^-$  anions with the cations in centrosymmetric **1**.



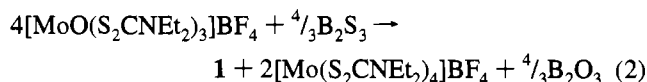
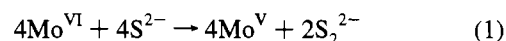
**Figure 6.** Association of the  $\text{I}_3^-$  and  $\text{I}^-$  anions with the cations in **4**.

such that  $\text{S}(1) \cdots \text{F}(2'')$  is 3.094 Å,  $\text{S}(2) \cdots \text{F}(3)$  is 3.190 Å and  $\text{S}(1) \cdots \text{F}(4'')$  is 3.214 Å; these interactions are shown in Figure 5. The iodide and triiodide counter-anions of **4** are positioned close to the disulfido ligands, in a pair-wise, alternating arrangement with the cations (Figure 6);  $\text{S} \cdots \text{I}$  distances are in the range 3.15 (1) to 3.93 (1) Å. The closest  $\text{S} \cdots \text{I}$  interactions are  $\text{S}(1) \cdots \text{I}(1') = 3.38$  (1) Å and  $\text{S}(4) \cdots \text{I}(4) = 3.15$  (1) Å. Longer  $\text{S} \cdots \text{I}$  distances include  $\text{S}(2) \cdots \text{I}(1) = 3.82$  (1) Å,  $\text{S}(3) \cdots \text{I}(4'') = 3.93$  (1) Å. The  $\text{S} \cdots \text{I}$  interactions in **6** range from 3.83 to 3.96 Å.

### Discussion

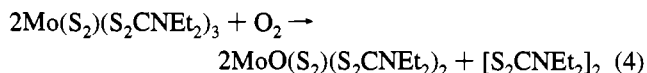
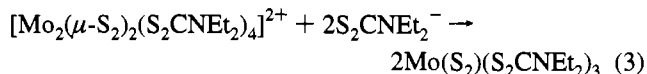
The molybdenum compounds are formed in reductive desulfurization reactions. Coupled redox (eq 1) and ligand redistribution processes are involved in these reactions; overall, eq 2

may pertain ( $\text{R} = \text{Et}$ ). The dithiocarbamate ligands do not

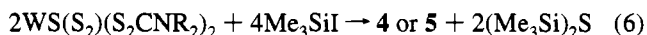
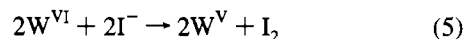


appear to be redox active and are maintained as bidentate ligands in both products. Boron sulfide has proved a valuable reagent for the conversion of oxo ligands to their thio counterparts and has been exploited in reactions involving  $\text{V}(\text{IV})$ ,<sup>46</sup>  $\text{Mo}(\text{VI})$ ,<sup>47</sup>  $\text{Mo}(\text{V})$ ,<sup>48</sup>  $\text{Mo}(\text{IV})$ ,<sup>49</sup>  $\text{W}(\text{VI})$ ,<sup>50</sup>  $\text{Tc}(\text{V})$  and  $\text{Re}(\text{V})$ .<sup>51</sup> Its application in high valent  $\text{V}(\text{V})$  and  $\text{Mo}(\text{VI})$  chemistry is extremely limited due to the propensity of sulfide to reduce these metal centers. Thus, the thio- $\text{Mo}(\text{VI})$  complexes  $[\text{MoS}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  are not observed in the reactions of  $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  and boron sulfide. Interestingly, the analogous  $\text{W}(\text{VI})$  complex  $[\text{WS}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  has been described.<sup>52</sup> Reaction of  $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4$  and  $(\text{Me}_3\text{Si})_2\text{S}$  in acetonitrile is extremely slow, even at reflux, and is ineffective for the synthesis of the title compounds. The related  $\text{V}(\text{IV})$  complex  $\text{V}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4$  may be synthesised by reaction of  $\text{VO}(\text{S}_2\text{CNET}_2)_3$  and  $\text{B}_2\text{S}_3$ .<sup>13</sup> In contrast, only a small amount of  $\text{Nb}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4$  is produced in the reaction of  $\text{NbO}(\text{S}_2\text{CNET}_2)_3$  and  $\text{B}_2\text{S}_3$ , the major products being  $\text{NbS}(\text{S}_2\text{CNET}_2)_3$  and  $\text{Nb}(\text{S}_2)(\text{S}_2\text{CNET}_2)_3$ .<sup>34</sup> Reaction of  $\text{Cs}_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$  with  $\text{NaS}_2\text{CNET}_2$  provides much better yields of  $\text{Nb}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4$ .<sup>33</sup>

Complex **1** reacts with  $\text{NaS}_2\text{CNET}_2$  or  $\text{Me}_3\text{SiS}_2\text{CNET}_2$ , according to eq 3, to produce brown  $\text{Mo}(\text{S}_2)(\text{S}_2\text{CNET}_2)_3$ , identified by EPR spectroscopy ( $g$  1.975,  $a$  38 G).<sup>14,15</sup> This mononuclear complex is oxidized in air to blue  $\text{MoO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2$ <sup>53</sup> according to eq 4.



The tungsten compounds **4** and **5** are formed in reductive desulfurization reactions. The important redox reactions and proposed overall reactions for their formation are given in eqs 5 and 6, respectively. The reactions involve reduction of  $\text{W}(\text{VI})$



to  $\text{W}(\text{V})$  by iodide with concomitant desulfurization to produce  $(\text{Me}_3\text{Si})_2\text{S}$ ; it would appear that both Lewis acid ( $\text{Me}_3\text{Si}^+$ ) and reductant ( $\text{I}^-$ ) are required for the reaction. The presence of  $\text{I}^-$  and  $\text{I}_3^-$  anions at the completion of the reactions permits the crystallization of a variety of salts of the  $\text{W}(\text{V})$  cations, under

(46) Sato, M.; Miller, K. M.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981**, *20*, 3571.

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different conditions. Thus, attempts to grow single crystals of the isobutyl derivative produced crystals of the bis(triiodide) salt **6**.<sup>39</sup>

Microanalytical, IR and mass spectrometric data for **1–5** were consistent with the proposed formulations. Infrared spectra were dominated by the characteristic bands of the dithiocarbamate ligands, weak bands due to the disulfido ligands and (where present) the  $\text{BF}_4^-$  anions. The dimeric structures of **1–3** were confirmed by FAB-MS, which revealed peak clusters assignable to the  $[\text{M}-\text{BF}_4]^+$  and  $[\text{M}-2\text{BF}_4]^+$  ions. It is possible that the interaction of the  $\text{BF}_4^-$  ion with an  $\text{S}_2^{2-}$  ligand observed in the solid state is maintained in the gas phase  $[\text{M}-\text{BF}_4]^+$  ion pairs. Peak clusters from ion pairs were also observed in recent FAB-MS studies of triangular  $[\text{Mo}_3\text{S}(\text{S}_2)_3]^{4+}$  complexes reported by Hegetschweiler and co-workers.<sup>54–56</sup> The dimeric structures of **4** and **5** were also confirmed by FAB-MS, which revealed peak clusters assignable to the  $[\text{M}-\text{I}_3]^+$  and related fragment ions.

The  $^1\text{H}$  NMR spectra of freshly prepared samples of **1** sometimes exhibit broad resonances, particularly in the methylene region. With time these broad signals are replaced by well resolved multiplet resonances (Figure 1). Paramagnetic impurities are not responsible for the broad signals initially observed. The initial presence of a number of isomers which convert to a single thermodynamically stable isomer may be inferred from the spectral change. Intimate overlap of the methyl resonances of **1** produces a broadened triplet resonance consistent with the methyl groups having very similar environments. Two-dimensional NMR techniques confirm the presence of four unique  $\text{H}_{\text{AB}}$  methylene groups but the assignment of resonances to individual groups within the complex is not possible. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1** are consistent with four chemically unique ethyl groups in the dimeric molecule.

The symmetry of the  $[\text{M}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNR}_2)_4]^{2+}$  complexes is dictated principally by the configuration ( $\Delta$  or  $\Lambda$ ) at each metal center and by distortions within the  $[\text{M}_2(\text{S}_2)_2]^{6+}$  core. The  $\Delta\Delta$  and  $\Delta\Lambda$  (or  $\Lambda\Lambda$ ) isomers possess  $C_{2h}$  and  $D_2$  symmetry, respectively, only if an idealized, regular  $[\text{M}_2(\text{S}_2)_2]^{6+}$  core is present. Complexes with  $C_{2h}$  and  $D_2$  symmetries would possess only two chemically unique alkyl group environments and geminal groups (e.g.,  $\text{CH}_2$ ) would be diastereotopic. Irregularities within the  $[\text{M}_2(\text{S}_2)_2]^{6+}$  core would reduce the symmetry of both diastereomers; the  $\Delta\Lambda$  and  $\Delta\Delta$  (or  $\Lambda\Lambda$ ) isomers would possess  $C_i$  and  $C_2$  symmetry, respectively. In both cases four unique alkyl group environments would result and geminal groups would again be diastereotopic. Clearly, it is not possible to distinguish unambiguously between the  $\Delta\Lambda$  and  $\Delta\Delta/\Lambda\Lambda$  isomers on the basis of available NMR data.

The high resolution  $^1\text{H}$  NMR spectrum of **1** indicates the presence of a single stereochemically rigid diastereomer, the symmetry of which is consistent with the structure established by X-ray crystallography (vide supra). The inequivalence of the ethyl groups may result from an asymmetric  $[\text{Mo}_2(\text{S}_2)_2]^{6+}$  core, possibly arising from an interaction of the bridging sulfur atoms with a  $\text{BF}_4^-$  anion. The  $^1\text{H}$  NMR spectrum of  $[\text{Mo}_2(\text{S}_2)_2]$

$(\text{S}_2\text{CNPr}^i)_4(\text{BF}_4)_2$  is complex and consistent with the presence of a number of isomers. The  $^1\text{H}$  NMR spectrum of **3** consisted of resonances assignable to methyl groups coupled to an adjacent methine proton (dd,  $\delta$  0.89), methine protons (9-line,  $\delta$  2.14), and diastereotopic methylene protons (m,  $\delta$  3.5–3.8). The spectrum and decoupling experiments are consistent with only two chemically unique *i*-butyl groups in this molecule (cf., the four chemically unique ethyl groups of **1**). The complex must therefore possess a regular  $[\text{Mo}_2(\text{S}_2)_2]^{6+}$  core (possibly time averaged, or devoid of an ion-pair interaction) and although it is not possible to unambiguously assign a structure, the complex may exhibit the  $\Delta\Delta/\Lambda\Lambda$  structure crystallographically established for its vanadium analogue.<sup>12</sup> Complex **4** exhibits spectra consistent with two chemically unique ethyl groups and a regular or time averaged  $[\text{W}_2(\text{S}_2)_2]^{6+}$  core. The  $^{95}\text{Mo}$  NMR signal of **1** was considerably shielded relative to the signal of the oxo-Mo(VI) starting material ( $\delta$  80<sup>57</sup>) and those of other dinuclear Mo(V) complexes ( $\delta > 320$ ).<sup>58–60</sup>

Finally, we turn our attention to the solid state structures of **1**, **4** and **6**. The geometry of the  $[\text{Mo}_2(\text{S}_2)_2]^{6+}$  core is similar to those previously observed in compounds such as  $\text{MoS}_2\text{Cl}_3$ ,<sup>61</sup>  $(\text{NH}_4)_2[(\text{S}_2)_2\text{Mo}(\mu\text{-S}_2)_2\text{Mo}(\text{S}_2)_2]^{23}$  and salts of  $[\text{Mo}_2(\mu\text{-S}_2)_2\text{X}_8]^{2-}$ .<sup>31</sup> An extended lattice of the type  $z[\text{Mo}_2(\text{S}_2)_2\text{Cl}_4\text{Cl}_{4/2}]$  with  $\text{Mo}-\text{S} = 2.43 \text{ \AA}$ ,  $\text{S}-\text{S} = 1.98 \text{ \AA}$ ,  $\text{Mo}\cdots\text{Mo} = 2.833 \text{ \AA}$  is observed in the case of  $\text{MoS}_2\text{Cl}_3$ . The previously mentioned anions contain Mo(V) centers linked by two  $\text{S}_2^{2-}$  ligands (average  $\text{S}-\text{S} = 2.01 \text{ \AA}$ ) and a metal-metal bond (average  $2.842 \text{ \AA}$ ). Although the cores of the halo complexes are regular within experimental error, the core of the  $[(\text{S}_2)_2\text{Mo}(\mu\text{-S}_2)_2\text{Mo}(\text{S}_2)_2]^{2-}$  anion exhibits an irregular structure in both its molecular forms. The M-M distances and the diamagnetism of **1**, **4** and **6** indicate the presence of a single metal-metal bond in all three compounds. Extended Hückel MO calculations<sup>62</sup> confirmed the metal-metal bonding orbital as the HOMO. The dimeric complexes contain  $\Delta$  and  $\Lambda$  metal centers as previously defined and are therefore achiral. The ethyl substituents of the dithiocarbamate ligands occupy chemically unique environments due to their disposition with respect to the bridging  $\text{S}_2^{2-}$  ligands and counterions. This ligand arrangement contrasts with that determined for  $\Delta\Delta/\Lambda\Lambda\text{-V}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNBu}^i)_4$ <sup>12</sup> and  $\text{Nb}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4$ <sup>33</sup> but is the same as that reported for  $\Delta\Lambda\text{-V}_2(\mu\text{-S}_2)_2(\text{S}_2\text{CNET}_2)_4$ .<sup>13</sup>

The three cationic complexes exhibit close intermolecular interactions involving the bridging disulfido ligands. In **1**, there are several intermolecular contacts in the crystal lattice involving the cations, anions and solvent of crystallization. The interactions with the  $\text{BF}_4^-$  anions persist in the gas phase (as indicated by FAB-MS studies) and possibly in solution (NMR). Close  $\text{S}\cdots\text{I}$  interactions are present in the crystal structures of **4** and **6**. Interactions between sulfur and iodide have been observed in a wide variety of systems.<sup>63</sup> The closest of the interactions

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in **4** and **6** is 0.36 Å shorter than the S···I interactions in 1,2,4-trithiolane salts such as  $[\text{OC}_4\text{H}_8\text{NCS}_3\text{CNC}_4\text{H}_8\text{O}]_2\text{I}_{16}$ <sup>64</sup> and in  $[\text{Et}_2\text{NCS}_3\text{CNET}_2][\text{Hg}_2\text{I}_6]$ .<sup>65</sup> A number of triangular  $[\text{Mo}_3\text{S}(\text{S}_2)_3]^{4+}$  complexes also exhibit S···X interactions with halide counterions. In the recently reported structure of  $[\text{Mo}_3\text{S}(\text{S}_2)_3(\text{S}_2\text{-CNET}_2)_3]\text{I}$ , the iodide is associated with the axial sulfur atoms of all three  $\mu\text{-S}_2^{2-}$  ligands, with S···I distances of ca. 3.25–3.30 Å.<sup>55</sup> Shorter S-I bonds of ca. 2.62 Å are characteristic of compounds containing formal I<sup>+</sup> centers, e.g.  $\{[(\text{NH}_2)_2\text{C}=\text{S}]_2\text{I}\}^+$ <sup>66</sup> and  $\{[(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)]_2\text{I}\}^{5+}$ ,<sup>67</sup> where the polarization of the S-I interaction is reversed. The sulfur-anion interactions

observed in **4** and **6** reflect considerable partial positive charge on the sulfur atoms and an enhanced electrophilicity due to electron donation to the high-valent metal centers.

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**Supplementary Material Available:** Tables of crystal data, bond distances and angles, anisotropic thermal parameters and calculated hydrogen atom positions (13 pages). Ordering information is given on any current masthead page.

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