synthesis of NS_2^+ from thiazyl salts and sulfur, the corresponding reaction with selenium produces the five-membered ring $N_2S_2SeCl^+$. This cation is also formed from NS^+ and alkylselenium chlorides. The instability of the Se=N double bond in selenodiimides, RN=Se=NR,[40] is well documented, and the current work indicates that this functionality is not stabilized in the $[Se{=}N{=}S]^+$ cation (as the $AlCl_4^-$ salt).

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Supplementary Material Available: Listings of thermal parameters, contact distances (<3.6 Å), and crystallographic parameters and a figure showing a stereoscopic view of the packing in $[N_2S_2SeCl][AlCl_4]$ (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Synthesis, X-ray Structures, and Spectroscopic and Magnetic Properties of a Series of Isomeric Binuclear Molybdenum(III) Complexes of General Formula $Mo_2Cl_6L_3$ (L = Thioether): Large Structural Influence of Bridging Ligands in Confacial Bioctahedral Complexes

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The syntheses, spectroscopic characterization, and X-ray crystal structures of two isomeric forms of $Mo_2Cl_6(THT)_3$ (THT = C_4H_8S, tetrahydrothiophene) are reported and compared with those of $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ and the anion $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]^-$. The most notable feature of these structures, which have a confacial bioctahedral framework, is that those which have the core structure $Mo(\mu\text{-}Cl)_3Mo$ have relatively long Mo–Mo bond lengths and display antiferromagnetic behavior, while those with one μ-Cl replaced by a μ-thioether have much shorter Mo–Mo bonds, in the range expected for Mo≡Mo bonding, and are diamagnetic. By following the interconversion of two isomers of $Mo_2Cl_6(Me_2S)_3$ in $C_2D_2Cl_4$ solution at 70 °C by ^1H NMR spectroscopy, it was inferred that the process is intramolecular, likely involving ligand exchange between terminal and bridging sites. The complex $(THT)Cl_2Mo(\mu\text{-}THT)(\mu\text{-}Cl)_2MoCl_2(THT)$ (**4**) crystallizes with 1 mol of CH_2Cl_2 in the triclinic space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 8.595$ (1) Å, $b = 11.165$ (4) Å, $c = 15.143$ (3) Å, $\alpha = 70.60$ (2)°, $\beta = 73.94$ (1)°, and $\gamma = 77.33$ (2)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R = 0.071$ and $R_w = 0.050$ for 5583 unique observed reflections. The complex *meso*-$(THT)Cl_2Mo(\mu\text{-}Cl)_3MoCl(THT)_2$ (**5a**) crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$ in a cell of dimensions $a = 10.522$ (2) Å, $b = 12.124$ (2) Å, $c = 18.262$ (3) Å, and $\beta = 98.91$ (1)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R = 0.083$ and $R_w = 0.043$ for 7938 unique observed reflections.

Introduction

There is currently renewed interest in confacial bioctahedral molybdenum(III) and tungsten(III) chemistry, both from the point of view of structural variations[2-4] and potential catalytic properties.[5] Earlier, we reported[6] on the syntheses and structures of two such complexes, $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ (**1**) (C_{2v}) and $[PPh_4][(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]$ (**2**) the latter complex being derived from the structural isomer of **1**, $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2]$ (**3**). This complex (**3**) was shown, on the basis of spectroscopic data, to exist as two stereoisomers, namely a C_s isomer, which we termed the meso isomer, **3a**, and an enantiomeric pair ((+)/(−)) of C_1 isomers, **3b** (Figure 1; L = Me_2S). The surprising feature of the structural analysis of these complexes was that by replacing the μ-Me_2S ligand in **1** by a μ-Cl to give the anion of **2**, the Mo–Mo bond length increased from 2.462 (2) to 2.746 (9) Å. An accompanying change in the magnetic properties, as detected from ^1H NMR measurements at different temperatures, suggested that whereas **1** was diamagnetic, the anion of **2** and its precursor **3** were antiferromagnetic.

We now report on the synthesis of the tetrahydrothiophene (THT) analogues of **1** (**4**) and **3a** (meso isomer, **5a**), their crystal structures, and solution behavior and provide a more detailed analysis of the magnetic properties of **2** and **3** and the interconversion of the various isomers in solution. Complete experimental details of the synthetic procedures for making **1**, **2**, and **3** and their spectroscopic characterization are provided, to supplement the preliminary report of their syntheses and structures.[6]

The facile synthesis of the C_{2v} isomer of $[(C_4H_8S)Cl_2Mo(\mu\text{-}C_4H_8S)(\mu\text{-}Cl)_2MoCl_2(C_4H_8S)]$ (**4**) will enable its chemistry to be compared with that of the analogous complexes of niobium and tantalum, which have been shown to be highly reactive toward alkynes.[7,8] Preliminary results suggest that this comparison will prove to be of considerable interest and potential catalytic significance.

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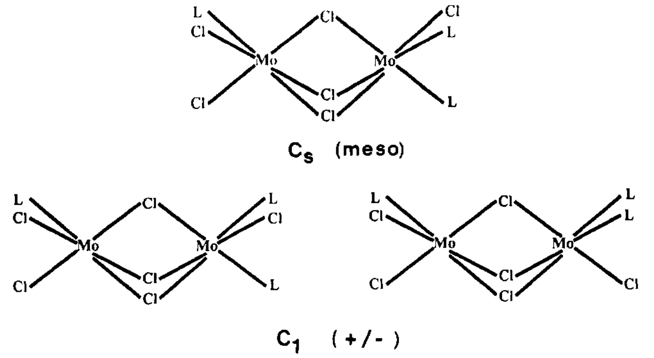

Figure 1. Possible isomeric forms of complexes of general formula $Cl_2(L)Mo(\mu\text{-}Cl)_3MoCl(L)_2$, where L = THT or Me_2S. Molecule labeling scheme used: L = Me_2S, meso = **3a**; (+)/(-) pair = **3b**; L = THT, meso = **5a**; (+)/(-) = **5b**.

Experimental Section

General Procedures and Techniques. All the starting materials and reaction products in this work were potentially air and moisture sensitive; hence, they were handled under an atmosphere of dry nitrogen by using standard Schlenk tube and glovebox techniques. Acetonitrile, dichloromethane, tetrahydrothiophene, dimethyl sulfide, and hexanes were dried over calcium hydride and distilled under nitrogen before use. Tetrahydrofuran was dried over sodium/benzophenone and then distilled under nitrogen. Elemental analyses either were performed by the University of Calgary Department of Chemistry Microanalytical and Spectroscopy Laboratory or were obtained commercially (Canadian Microanalytical Laboratories; Galbraith Laboratories, Inc.). ^1H NMR spectra were obtained with either a Bruker ACE-200 or a Varian XL-200 FT NMR spectrometer. Infrared spectra were recorded as Nujol mulls between CsI plates by using either a Nicolet 8000 FT or a Perkin-Elmer 467 grating spectrophotometer. Variable-temperature magnetic susceptibilities were determined at Queen Mary College by using equipment and procedures described previously.[9] Room-temperature measurements were made routinely at the University of Calgary by using the Faraday technique.

Preparation of Starting Materials. $MoCl_4(MeCN)_2$,[10] $MoCl_4(THF)_2$,[11] and $MoCl_3(THF)_3$[12] were prepared by using the literature methods. Although $MoCl_3(THT)_3$ has been reported previously,[13] it was made by a different procedure. $MoCl_3(THF)_3$ (4 g, 9.55 mmol) was reacted overnight in a Schlenk tube with THT (30 mL). The resulting red-orange liquid was reduced in volume to ca. 20 mL and hexane (50 mL) slowly added with concomitant shaking. After 3 h orange-red crystals had separated, and cooling to 0 °C produced a second crop, which in total gave a yield of 3.7 g (83%). Anal. Calcd for $MoCl_3(C_4H_8S)_3$: C, 30.88; H, 5.18. Found: C, 30.85; H, 5.02. $MoCl_4(Me_2S)_2$ was prepared by reaction of $MoCl_4(THF)_2$ (15.0 g, 39.3 mmol) with Me_2S (12.7 g, 204 mmol) in CH_2Cl_2 (150 mL). After the mixture was stirred for ca. 1 h the addition of hexane (ca. 50 mL) caused the precipitation of a small amount of unreacted $MoCl_4(THF)_2$ and the mixed-adduct $MoCl_4(THF)(Me_2S)$, which was filtered off to yield a dark orange-red filtrate. This was evaporated to dryness, giving a dark red solid (11.7 g), which after drying in vacuo (3 h) was identified as $MoCl_4(Me_2S)_2$. Anal. Calcd: C, 13.27; H, 3.34; Cl, 39.17. Found: C, 13.31; H, 3.45; Cl, 38.73. IR data (2000–250 cm^{-1}, Nujol mull, CsI plates): 1435 (m), 1320 (m), 1304 (sh), 1032 (m), 977 (m), 956 (sh), 850 (w, br), 725 (m), 678 (m), 338 (301, sh) (vs) (ν(Mo–Cl)), 261 (s). This spectrum is consistent with the presence of coordinated Me_2S and the absence of THF. ^1H NMR data (200 MHz, CD_2Cl_2 solution, 23 °C): $\delta = -29.3$ ppm, singlet (peak width at half-height 375 Hz). The product obtained from this route is more pure than that produced by direct reaction of Me_2S with $MoCl_4$.

Preparation of the $Mo_2Cl_6(Me_2S)_3$ Complexes. These preparations utilized $MoCl_4(Me_2S)_2$ as the starting material, and reduction with Et_3SiH yielded a mixture of the various isomers of the binuclear Mo(III) complexes. The detailed procedure was as follows. To a stirring solution of $MoCl_4(Me_2S)_2$ (11.6 g, 32.0 mmol) in CH_2Cl_2 (100 mL) was added Et_3SiH (14.62 g, 125.7 mmol). Over a period of ca. 5 h the solution changed from orange-red to red-purple to a dark purple color. Gas evolution was noticed during the early part of the reaction period. Qualitative gas chromatographic analysis of the head gases in the reaction vessel indicated that the major product was HCl, but a minor amount of hydrogen was also detected when an appropriate column was used. After an additional period of 10 h at 22 °C the solution was filtered and the sovlent removed under vacuum. The glassy red-purple solid so produced was shaken with CH_2Cl_2 (~15 mL), pumped to dryness, then again shaken with CH_2Cl_2 (~75 mL), and filtered. A purple residue left on the frit was found to be pure *meso*-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$ (**3a**). Yield: 0.21 g, ~2%, based on Mo. Addition of hexane (ca. 20 mL) to the filtrate caused a tarry red-purple material to deposit, and this process was repeated until no further deposition of the red-purple tar occurred. The solution was then cooled to 5 °C and left overnight, whereupon an amorphous purple powder was precipitated. This proved to be a mixture of the C_s (meso) and C_1((+)/(-)) isomers of $(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$, on the basis elemental analyses and ^1H NMR data. Eventually, after further addition of hexane and precipitation of purple powder, the solution was cooled to -20 °C for ca. 20 h, which yielded a mixture of the purple C_s/C_1 isomers and $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ (**1**). Finally, the mother liquor assumed an orange-red color and addition of more hexane and cooling to -20 °C gave rise to orange-brown crystals of **1**. Yield: 0.32 g, ~3%, based on Mo.

meso-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$ (**3a**) prepared as above is purple. Anal. Calcd for $Mo_2Cl_6S_3C_6H_{18}$: Cl, 35.99. Found: 35.57. IR data (2000–250 cm^{-1}, KBr disk): 1412 (s), 1433 (sh), 1421 (sh), 1320 (mw), 1297 (vw), 1035 (ms), 988 (ms), 979 (ms), 958 (w), 922 (w), 732 (w, br), 678 (mw), 346 (s), 336 (sh), 320 (m), 306 (s).

$(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ (**1**) prepared as above is orange. Anal. Calcd for $Mo_2Cl_6S_3C_6H_{18}$: Cl, 35.99. Found: 35.24. IR data (2000–250 cm^{-1}, KBr disk): 1421 (s), 1406 (sh), 1322 (mw), 1307 (w), 1287 (vw), 1036 (ms), 983 (s), 970 (ms), 920 (vw), 738 (w), 683, 670 (w, sh), 353 (vs), 338 (ms) 317 (vs), 298 (ms).

The C_1 ((+)/(-)) isomers of $(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$ (**3b**) were always obtained with a large excess of the C_s isomer, and all attempts to separate them failed, presumably because of the isomerization of the C_1 species in solution. This is discussed in the NMR section of the text.

Preparation of $[PPh_4][(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]$ (2). To a stirring solution of **3a** (0.14 g, 0.24 mmol) in CH_2Cl_2 (30 mL) was added PPh_4Cl (0.27 g, 0.72 mmol). The color changed from purple to a red-purple, and after ca. 10 h the solution was filtered and stripped of solvent under vacuum. The resultant glassy solid was redissolved in CH_2Cl_2 (20 mL), hexane (5 mL) added, and the solution cooled to -20 °C for 72 h. Red-purple crystals of **2** were filtered off and dried. Yield: 0.09 g, ~42%. The IR spectrum of this compound is dominated by absorptions due to the cation, and hence details are not given here.

Preparation of New THT (Tetrahydrothiophene, C_4H_8S) Complexes. $MoCl_3(THT)_3$ (2.5 g, 5.3 mmol) was placed in a Schlenk tube with toluene (50 mL). The color immediately became dark red, and after being stirred for 24 h the solution was shown by ^1H NMR spectroscopy to contain a complex mixture of isomers. After 72 h at 22 °C a purple solid precipitated. This solid (1.3 g) was filtered off (leaving an orange solution) and redissolved in CH_2Cl_2 (10 mL), and then hexane (15 mL) was added. Cooling to 5 °C for 24 h yielded dark purple crystals (0.6 g, ~17%) whose X-ray crystal structure (below) proved that their identity was $(THT)Cl_2Mo(\mu\text{-}Cl)_3MoCl(THT)_2$ (meso, C_s isomer) (**5a**). Anal. Calcd for $Mo_2Cl_6S_3C_{12}H_{24}$: C, 21.54; H, 3.61. Found: C, 21.40; H, 3.37. IR (cm^{-1}, Nujol mull, CsI plates): 1438 (s), 1377 (s), 1305 (m), 1270 (m), 1256 (m), 1208 (w), 1137 (w), 1078 (w), 954 (m), 883 (m), 734 (m), 662 (m), 516 (m), 479 (w), 345 (vs), 307 (vs). ^1H NMR ($CDCl_3$, 23 °C; δ, ppm): 3.71 (s, broad, 4 H), 3.50 (s, broad, 4 H), 3.24 (s, broad, 4 H), 0.24 (s, broad, 12 H).

Isolation of $(THT)Cl_2Mo(\mu\text{-}THT)(\mu\text{-}Cl)_2MoCl_2(THT)$ (4). The orange-red solution obtained as above was reduced in volume to ca. 30 mL and cooled to -20 °C. Dark orange crystals were produced (0.44 g), which apparently lost solvent when dried under vacuum. NMR spectra of the fresh crystals confirmed the presence of toluene of crystallization. ^1H NMR ($CDCl_3$; δ, ppm): 7.25–7.15 (m, 5 H, aromatic protons of toluene of crystallization), 4.07 (m, 4 H, α-H on μ-THT), 3.32 (m, 8 H, α-H on terminal THT), 2.55 (m, 4 H, β-H on μ-THT), 2.35 (s, 3 H, Me protons of toluene), 2.04 (m, 8 H, β-H on terminal THT). IR data (cm^{-1}, Nujol mull, CsI plates): 1429 (s), 1377 (s), 1332 (w), 1304 (m), 1268 (m), 1255 (m), 1246 (m), 1220 (w), 1129 (s), 1107 (w), 1100 (w), 1076 (w), 1066 (w), 1035 (w), 958 (m), 883 (m), 805 (m), 723 (w), 661 (m), 514 (w), 476 (w), 352 (vs), 340 (s), 324 (vs), 306 (m).

Crystallographic quality crystals were obtained from the toluene solvate of **4** by recrystallization from CH_2Cl_2, which yielded a dichloromethane solvate of formula $Mo_2Cl_6(THT)_3.CH_2Cl_2$. Anal. Calcd for $Mo_2Cl_8S_3C_{13}H_{26}$: C, 20.71; H, 3.47. Found: C, 20.43; H, 3.35. ^1H NMR ($CDCl_3$; δ, ppm): 5.30 (s, 2 H, CH_2Cl_2), 4.08 (m, 4 H), 3.34 (m,

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Table I. Crystallographic Data for $Mo_2S_3Cl_6C_{12}H_{24}{\cdot}CH_2Cl_2$ (**4**) and $Mo_2Cl_6S_3C_{12}H_{24}$ (**5a**)

$Mo_2S_3Cl_6C_{12}H_{24}{\cdot}CH_2Cl_2$ (**4**)	
$a = 8.595$ (1) Å	fw = 754.03
$b = 11.165$ (4) Å	$P\bar{1}$
$c = 15.143$ (3) Å	$\lambda = 0.71069$ Å
$\alpha = 70.60$ (2)°	$D_c = 1.933$ g cm^{-3}
$\beta = 73.94$ (1)°	$\mu = 16.81$ cm^{-1}
$\gamma = 77.33$ (2)°	$R = 0.071$
$V = 1295.55$ Å^3	$R_w = 0.050$
$Z = 2$	abs cor = 0.714–1.105
$T = 25$ °C	
$Mo_2Cl_6S_3C_{12}H_{24}$ (**5a**)	
$a = 10.522$ (2) Å	fw = 669.10
$b = 12.124$ (2) Å	$P2_1/n$
$c = 18.262$ (3) Å	$\lambda = 0.71069$ Å
$\beta = 98.91$ (1)°	$D_m = 1.94$ (2) g cm^{-3}
$V = 2301.55$ Å^3	$D_c = 1.931$ g cm^{-3}
$Z = 4$	$\mu = 19.55$ cm^{-1}
$R = 0.083$	$R_w = 0.043$
$T = 25$ °C	abs cor = 0.685–1.865

8 H), 2.56 (m, 4 H), (2.05 (m, 8 H), THT assignments as above.

Alternate Route to 4. $MoCl_3(THF)_3$ (4 g, 9.5 mmol) was stirred in CH_2Cl_2 (30 mL) for 48 h, and then the solution was pumped to dryness. Addition of THT (30 mL) and stirring for 12 h yielded a pink precipitate (2.7 g). This powder was washed with hexanes, dried, and recrystallized from CH_2Cl_2/hexane to yield a dark purple powder, which was shown to be spectroscopically identical with samples of **4** obtained as described above. The material was suspected from its NMR spectrum of being paramagnetic and was shown to possess the following magnetic properties: $\chi_g = 0.441 \times 10^{-6}$, $\chi_M = 295 \times 10^{-6}$, and χ_M' (corrected for diamagnetism) = 603×10^{-6} cgsu; $\mu_{eff} = 1.19$ μ_B ($T = 293$ K).

X-ray Crystallography

The experimental data for compounds **1** and **2** were given previously.[6] The data collection, reduction, solution, and refinement for compounds **4** and **5a** are described here.

Data Collection. A suitable crystal of **4** (as the CH_2Cl_2 solvate), a deep red plate, was embedded in epoxy resin on a glass fiber and mounted on a CAD4 diffractometer. A similar mounting procedure for **5a** utilized a deep purple, block-shaped crystal. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $9.57 < \theta < 13.86°$ and $8.93 < \theta < 15.91°$ for **4** and **5a**, respectively. Crystal and instrumental instability were monitored through the measurement of three standard reflections every 1 h of X-ray exposure time. There was no indication of crystal decomposition in either case. The net intensities were corrected for reflection width, scale variation, and Lorentz and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics. The crystal data and experimental details for both crystals are given in Table I and in the supplementary material (Table S1).

Table II. Non-Hydrogen Atom Coordinates and Thermal Parameters for **4**

atom	x	y	z	10^3U, Å^2
Mo(1)	0.79517 (7)	0.23528 (5)	0.16312 (4)	40.0
Mo(2)	0.67684 (7)	0.03294 (5)	0.24133 (4)	38.4
Cl(1)	0.6437 (2)	0.4365 (1)	0.1023 (1)	54.1
Cl(2)	0.5768 (2)	0.2118 (1)	0.3136 (1)	43.1
Cl(3)	0.9652 (2)	0.0367 (1)	0.2395 (1)	40.8
Cl(4)	0.3962 (2)	0.0146 (2)	0.2639 (1)	47.0
Cl(5)	1.0233 (2)	0.2646 (2)	0.0310 (1)	52.2
Cl(6)	0.7703 (2)	−0.1568 (1)	0.1925 (1)	51.1
S(1)	0.6768 (2)	0.1487 (1)	0.0747 (1)	35.4
C(11)	0.7894 (8)	0.0939 (6)	−0.0290 (4)	41.0
C(12)	0.685 (1)	0.1510 (9)	−0.0994 (6)	94.8
C(13)	0.541 (1)	0.2212 (9)	−0.0719 (6)	102.3
C(14)	0.4952 (8)	0.2292 (6)	0.0267 (4)	45.6
S(2)	0.9195 (2)	0.3255 (2)	0.2596 (1)	49.9
C(21)	1.1373 (9)	0.3220 (7)	0.2132 (5)	64.8
C(22)	1.166 (1)	0.4544 (9)	0.1727 (7)	95.9
C(23)	1.038 (1)	0.5351 (7)	0.2200 (7)	93.1
C(24)	0.876 (1)	0.4970 (7)	0.2303 (6)	79.1
S(3)	0.6557 (2)	0.9005 (2)	0.4189 (1)	45.7
C(31)	0.7693 (9)	0.9591 (7)	0.4776 (5)	56.9
C(32)	0.915 (1)	0.8604 (8)	0.4978 (6)	82.8
C(33)	0.873 (1)	0.7347 (8)	0.5095 (6)	91.4
C(34)	0.789 (1)	0.7484 (7)	0.4302 (5)	73.1
C(1)	0.383 (2)	0.6704 (9)	0.3718 (7)	136.3
Cl(11)	0.3387 (4)	0.6659 (3)	0.4904 (2)	123.0
Cl(12)	0.3640 (6)	0.5571 (3)	0.3386 (2)	202.2

Table III. Non-Hydrogen Atom Coordinates and Thermal Parameters for **5a**

atom	x	y	z	10^3U, Å^2
Mo(1)	0.90670 (3)	0.29657 (2)	0.12134 (2)	34.8
Mo(2)	1.05170 (3)	0.32526 (2)	0.25476 (2)	34.6
Cl(1)	1.03688 (8)	0.46117 (7)	0.15292 (5)	42.7
Cl(2)	1.08412 (9)	0.19610 (8)	0.35365 (6)	57.3
Cl(3)	1.08861 (8)	0.17602 (8)	0.16736 (6)	51.1
Cl(4)	0.81834 (8)	0.28925 (8)	0.23757 (5)	50.3
Cl(5)	0.9690 (1)	0.2957 (1)	0.00226 (5)	63.7
Cl(6)	1.0222 (1)	0.47215 (9)	0.33542 (6)	62.5
S(1)	1.28967 (9)	0.36233 (8)	0.28287 (6)	47.3
C(11)	1.3779 (3)	0.2328 (3)	0.2972 (2)	56.1
C(12)	1.4859 (4)	0.2425 (4)	0.2538 (3)	72.5
C(13)	1.4420 (4)	0.2993 (5)	0.1863 (3)	100.1
C(14)	1.3550 (4)	0.3956 (4)	0.1978 (3)	80.9
S(2)	0.71587 (9)	0.41582 (8)	0.07432 (5)	46.3
C(21)	0.7460 (4)	0.5029 (3)	−0.0025 (2)	56.9
C(22)	0.6948 (4)	0.6146 (3)	0.0134 (2)	58.2
C(23)	0.7407 (4)	0.6346 (3)	0.0945 (2)	55.2
C(24)	0.7084 (4)	0.5335 (3)	0.1368 (2)	55.8
S(3)	0.7505 (1)	0.13989 (9)	0.08939 (7)	64.7
C(31)	0.8106 (5)	0.0165 (4)	0.1342 (3)	78.8
C(32)	0.8453 (8)	−0.0536 (6)	0.0788 (5)	166.0
C(33)	0.7754 (7)	−0.0331 (7)	0.0077 (4)	140.9
C(34)	0.7532 (7)	0.0840 (5)	−0.0019 (3)	146.9

Solutions and Refinement. The structures were solved by locating the molybdenum and chlorine atoms in the core of each molecule in an E map, with phases derived from symbolic addition.[14] The remaining non-hydrogen atoms were located in difference maps after refining the scale and thermal parameters. The data were corrected for absorption with DIFABS[15] after isotropic refinement. At this stage of both refinements, all of the hydrogen atoms were located in difference Fourier maps. All non-hydrogen atoms were refined anisotropically, with the hydrogen atoms calculated in idealized positions with fixed isotropic temperature factors, which were not refined. Convergence was reached at $R = 0.071$ and 0.083 for **4** and **5a**, respectively. The final values of the positional and isotropic temperature factors are given in Tables II and III. Tables of hydrogen atom positions, thermal parameters, comprehensive bond distances, and angles and tables of F_o, F_c, and $\sigma(F)$ are available as supplementary material.[16] Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[17] No corrections for extinction were made. All calculations were performed on a Zenith 386 computer running a UNIX V.3 operating system with the program package XTAL.[18]

Results

Syntheses. The series of binuclear Mo(III) complexes involving dimethyl sulfide ligands were originally prepared[6] as a result of an alternate goal. $WCl_4(Me_2S)_2$ had been shown[19] to react with triethylsilane to produce the hydrido-bridged, bis(thioether)-bridged ditungsten(III) complex $(Me_2S)Cl_2W(\mu\text{-}H)(\mu\text{-}Me_2S)_2WCl_3$ as the major tungsten-containing product. Hence, it had been anticipated that the analogous molybdenum reaction might yield a similar product. However, the reaction proceeded differently, and after the metathesis of Mo–Cl and Si–H the transient molybdenum(IV) hydrido complex decomposes to yield

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(14) Schenk, H.; Hall, S. R. SIMPEL, XTAL2.4 User's Manual. Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1988.

(15) Program DIFABS: Walker, N.; Stewart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(16) See paragraph at end of paper concerning supplementary material.

(17) *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(18) Hall, S. R., Stewart, J. M., Eds. XTAL2.4 User's Manual. Universities of Western Australia and Maryland, 1988.

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Table IV. Important Bond Lengths (Å) and Bond Angles (deg) for $(C_4H_8S)Cl_2Mo(\mu\text{-}C_4H_8S)(\mu\text{-}Cl)_2MoCl_2(C_4H_8S)$ (**4**) and $(C_4H_8S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(C_4H_8S)_2$ (**5a**)

4		**5a**	
	Bond Lengths		
Mo(1)-Mo(2)	2.470 (1)	Mo(1)-Mo(2)	2.6896 (6)
Mo(1)-Cl(1)	2.365 (2)	Mo(1)-Cl(1)	2.4385 (9)
Mo(1)-Cl(2)	2.488 (2)	Mo(1)-Cl(3)	2.451 (1)
Mo(1)-Cl(3)	2.487 (2)	Mo(1)-Cl(4)	2.447 (1)
Mo(1)-Cl(5)	2.366 (2)	Mo(1)-Cl(5)	2.366 (1)
Mo(1)-S(1)	2.409 (2)	Mo(1)-S(2)	2.515 (1)
Mo(1)-S(2)	2.562 (3)	Mo(1)-S(3)	2.521 (1)
Mo(2)-Cl(2)	2.467 (2)	Mo(2)-Cl(1)	2.471 (1)
Mo(2)-Cl(3)	2.480 (2)	Mo(2)-Cl(2)	2.375 (1)
Mo(2)-Cl(4)	2.386 (2)	Mo(2)-Cl(3)	2.483 (1)
Mo(2)-Cl(6)	2.373 (2)	Mo(2)-Cl(4)	2.465 (1)
Mo(2)-S(1)	2.409 (2)	Mo(2)-Cl(6)	2.362 (1)
Mo(2)-S(3)	2.565 (2)	Mo(2)-Cl(1)	2.517 (1)
	Bond Angles		
Cl(1)-Mo(1)-Cl(5)	95.01 (6)	Cl(1)-Mo(1)-Cl(3)	91.53 (3)
Cl(1)-Mo(1)-S(1)	88.15 (7)	Cl(1)-Mo(1)-Cl(4)	95.71 (3)
Cl(1)-Mo(1)-Cl(3)	172.79 (8)	Cl(1)-Mo(1)-Cl(5)	89.75 (4)
Cl(1)-Mo(1)-Cl(2)	86.47 (6)	Cl(1)-Mo(1)-S(2)	89.99 (3)
Cl(1)-Mo(1)-S(2)	92.20 (7)	Cl(1)-Mo(1)-S(3)	173.58 (4)
Cl(5)-Mo(1)-S(1)	88.24 (7)	Cl(3)-Mo(1)-Cl(4)	93.58 (3)
Cl(5)-Mo(1)-Cl(3)	85.94 (6)	Cl(3)-Mo(1)-Cl(5)	89.99 (4)
Cl(5)-Mo(1)-Cl(2)	172.51 (8)	Cl(3)-Mo(1)-S(2)	178.40 (3)
Cl(5)-Mo(1)-S(2)	92.43 (7)	Cl(3)-Mo(1)-S(3)	94.39 (4)
S(1)-Mo(1)-Cl(3)	99.02 (6)	Cl(4)-Mo(1)-Cl(5)	173.39 (3)
S(1)-Mo(1)-Cl(2)	99.16 (7)	Cl(4)-Mo(1)-S(2)	85.78 (3)
S(1)-Mo(1)-S(2)	179.22 (5)	Cl(4)-Mo(1)-S(3)	81.47 (4)
Cl(3)-Mo(1)-Cl(2)	91.68 (5)	Cl(5)-Mo(1)-S(2)	90.51 (4)
Cl(3)-Mo(1)-S(2)	80.62 (7)	Cl(5)-Mo(1)-S(3)	92.72 (4)
Cl(2)-Mo(1)-S(2)	80.17 (7)	S(2)-Mo(1)-S(3)	84.07 (4)
Cl(6)-Mo(2)-Cl(4)	92.96 (7)	Cl(1)-Mo(2)-Cl(2)	175.41 (3)
Cl(6)-Mo(2)-S(1)	87.78 (6)	Cl(1)-Mo(2)-Cl(3)	90.00 (4)
Cl(6)-Mo(2)-Cl(2)	172.59 (5)	Cl(1)-Mo(2)-Cl(4)	94.40 (3)
Cl(6)-Mo(2)-Cl(3)	87.29 (7)	Cl(1)-Mo(2)-Cl(6)	88.14 (3)
Cl(6)-Mo(2)-S(3)	90.37 (6)	Cl(1)-Mo(2)-S(1)	88.81 (3)
Cl(4)-Mo(2)-S(1)	88.10 (6)	Cl(2)-Mo(2)-Cl(3)	89.43 (4)
Cl(4)-Mo(2)-Cl(2)	86.50 (7)	Cl(2)-Mo(2)-Cl(4)	90.17 (3)
Cl(4)-Mo(2)-Cl(3)	172.86 (6)	Cl(2)-Mo(2)-Cl(6)	92.30 (4)
Cl(4)-Mo(2)-S(3)	87.29 (6)	Cl(2)-Mo(2)-S(1)	86.64 (3)
S(1)-Mo(2)-Cl(2)	99.58 (6)	Cl(3)-Mo(2)-Cl(4)	92.35 (3)
S(1)-Mo(2)-Cl(3)	99.04 (6)	Cl(3)-Mo(2)-Cl(6)	177.58 (4)
S(1)-Mo(2)-S(3)	174.94 (7)	Cl(3)-Mo(2)-S(1)	90.66 (3)
Cl(2)-Mo(2)-Cl(3)	92.34 (7)	Cl(4)-Mo(2)-Cl(6)	89.33 (4)
Cl(2)-Mo(2)-S(3)	82.22 (6)	Cl(4)-Mo(2)-S(1)	175.60 (4)
Cl(3)-Mo(2)-S(3)	85.57 (6)	Cl(6)-Mo(2)-S(1)	87.76 (4)
Mo(1)-S(1)-Mo(2)	61.78 (6)	Mo(1)-Cl(2)-Mo(2)	66.43 (3)
Mo(1)-Cl(2)-Mo(2)	59.81 (4)	Mo(2)-Cl(3)-Mo(2)	66.06 (3)
Mo(1)-Cl(3)-Mo(2)	59.65 (4)	Mo(2)-Cl(4)-Mo(2)	66.38 (3)

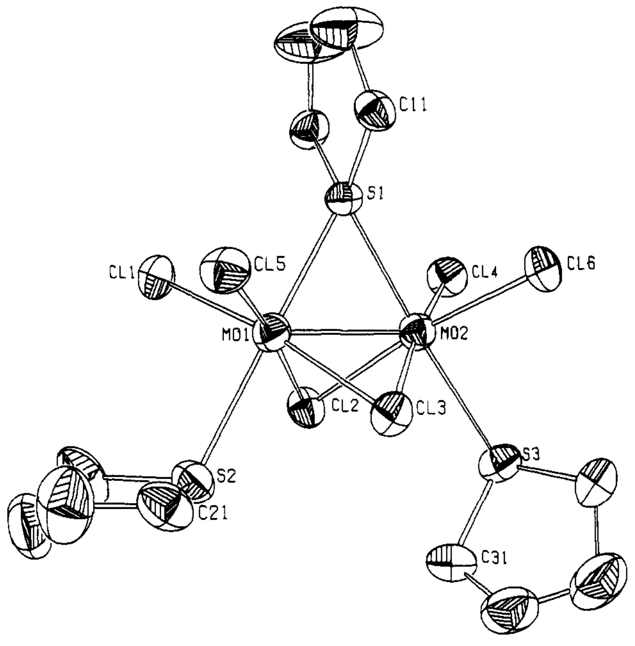

Figure 2. ORTEP plot of $(THT)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}THT)MoCl_2(THT)$ (**4**) drawn at the 50% probability level.

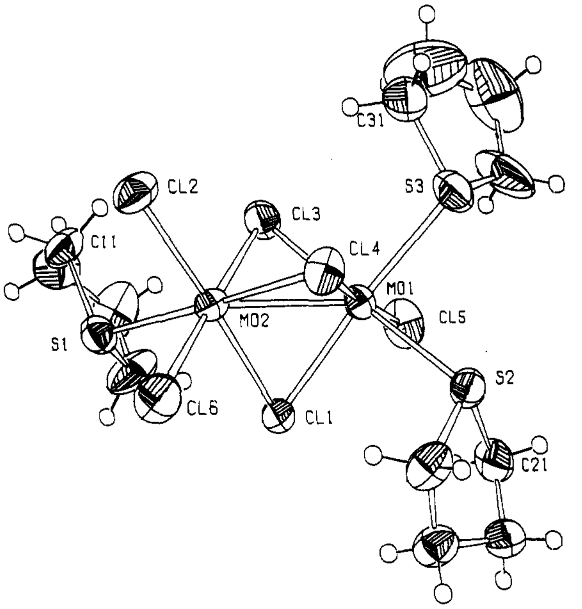

Figure 3. ORTEP plot of $(THT)Cl_2Mo(\mu\text{-}Cl)_3MoCl(THT)_2$ (**5a**) drawn at the 50% probability level. Hydrogen atoms are drawn as 0.1-Å spheres.

the characterized dimolybdenum(III) complexes. A plausible reaction sequence is as follows:

$$MoCl_4(Me_2S)_2 + Et_3SiH \rightarrow MoCl_3H(Me_2S)_2 + Et_3SiCl \quad \text{(i)}$$

$$MoCl_3H(Me_2S)_2 + MoCl_3H(Me_2S)_2 \rightarrow Mo_2Cl_6(Me_2S)_3 + H_2 + Me_2S \quad \text{(ii)}$$

$$MoCl_3H(Me_2S)_2 + MoCl_4(Me_2S)_2 \rightarrow Mo_2Cl_6(Me_2S)_3 + HCl + Me_2S \quad \text{(iii)}$$

Alternative pathways involving the generation of dihydrodimolybdenum(IV) intermediates cannot be ruled out, especially in view of the 4:1 molar ratio of silane to molybdenum employed in the reaction. However, the simple scheme suggested above accounts for all the products observed, namely H_2, HCl, Me_2S, and $Mo_2Cl_6(Me_2S)_3$. The strategy for direct synthesis of the tetrahydrothiophene complexes utilized the Mo(III) complexes first reported by Westland.[13] The method was also shown to be capable of producing the dimethyl sulfide complexes.[20] No synthesis was found that yielded only one isomer of $Mo_2Cl_6(R_2S)_3$; hence, a somewhat tedious separation process is required to isolate pure products. As discussed below, the separation process is made more complicated by the solution processes that can interconvert the various isomers.

Structures. The crystal structures of the two isomers of $Mo_2Cl_6(THT)_3$, **4** and **5a**, demonstrate that the principal feature noted in the earlier report on dimethyl sulfide derivatives is also prevalent here. That is, the substitution of a chloro bridge (in **5a**) by a thioether bridge (in **4**) results in a substantial change in the Mo–Mo bond distance. The ORTEP plots of the new THT complexes are given in Figures 2 (**4**) and 3 (**5a**), while the structures of **1** and the anion of **2** can be seen in ref 6 and also in Figure S1.[16] The principal bond lengths and bond angles for **4** and **5a** are given in Table IV. The complexes containing a $Mo(\mu\text{-}Cl)_3Mo$ core can be analyzed as having only weak Mo–Mo interactions. The actual bond distances, 2.746 (9) Å for **2** and 2.6896 (9) Å for **5a**, are indicative of substantially less than the triple bonds that might be anticipated for a bis(molybdenum(III)) complex. With use of the criteria of Cotton and Ucko,[21] the angles

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(21) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

subtended at the μ-Cl atoms (66–68°) approach the value expected (70.53°) for an idealized, undistorted confacial bioctahedron. The angles subtended at the Mo atoms are all close to 90°, regardless of whether they involve bridging or terminal ligand atoms. In sharp contrast to this situation, the complexes with a Mo(μ-Cl)$_2$(μ-thioether)Mo core possess all the features necessary for assigning a strong, Mo≡Mo triple bond. The actual bond lengths are short (2.470 (1) Å for **4**; 2.462 (2) Å for **1**), the angles subtended at the bridging ligand atoms are much more acute than 70.53°, and the L_{br}–Mo–L_{br} angles are correspondingly more obtuse than 90°. The other feature of note is the marked shortening of the Mo–S bonds for bridging thioethers as compared with the terminal thioethers. This is particularly evident in the structures of **1** and **4** wherein both types of ligation occur, and a difference of ca. 0.15 Å is seen in each case. The terminally bound thioethers in the complexes **2** and **5a** possess Mo–S bond lengths in the same range as their analogues in **1** and **4**, i.e. 2.50–2.55 Å. In contrast, the Mo–Cl bond lengths show the more normal behavior in that the terminal Mo–Cl distances are shorter than the Mo–Cl_{br} distances, by ca. 0.1 Å. Metal–halide bond length differences of this type have been observed in the isostructural, isoelectronic complexes $Mo_2Cl_9^{3-}$ (Cs^+ salt[22]) and $Mo_2Cl_8H^{3-}$.[23] Compounds **1** and **4** are closely analogous to $Ta_2Cl_6(Me_2S)_3$ and $Ta_2Cl_6(THT)_3$, whose structures were reported by Cotton and Najjar.[24] These d^2–d^2 complexes, however, have Ta=Ta bond lengths of 2.691 (1) and 2.681 (1) Å, respectively, which also influences the bond angles subtended at the metal centers and the μ-L atoms as discussed above.

^{1}H NMR and Magnetochemical Studies of the $Mo_2Cl_6(Me_2S)_3$ Complexes. The spectra of analogous dimethyl sulfide and tetrahydrothiophene complexes show the same general features, but since the former provide a much simpler set of proton spectra, these will be used to illustrate the unusual aspects of the solution chemistry of these complexes. ^{1}H NMR data for the THT complexes at room temperature are given in the Experimental Section.

The compounds with Mo(μ-Cl)$_2$(μ-thioether)Mo cores (and short Mo–Mo distances) are clearly diamagnetic and give sharp, predictable ^{1}H NMR spectra. Thus, **1** gives a spectrum indicative of C_{2v} symmetry in solution, with singlets at δ = 2.40 and 3.32 with intensities in a 2:1 ratio. The higher field signal is due to the terminal methyl sulfide ligands, and the lower field signal, to the μ-Me_2S ligand. The chemical shifts of these signals are not temperature dependent, but they do display a slight solvent dependence (CD_2Cl_2: μ-Me_2S, δ = 3.38; Me_2S_{term}, δ = 2.47 at 23 °C. $CDCl_3$: μ-Me_2S, δ = 3.43; Me_2S_{term}, δ = 2.49 ppm). These spectral data are almost identical with those reported for the analogous niobium complex, $(Me_2S)ClNb(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)NbCl_2(Me_2S)$.[25,26]

The unsymmetrical distributions of the three thioethers in terminal positions of M_2Cl_6(thioether)$_3$ complexes leads to the existence of two types of isomer, as shown schematically in Figure 1. The meso (C_s) isomer, **3a**, is also depicted in a Newman projection in Figure 4 to illustrate the expected types of methyl environment (x, y, z). At room temperature rapid inversion of the sulfur atom of terminally coordinated thioethers usually results in the alkyl groups becoming magnetically equivalent.[27] In this instance the y and z methyl groups appear as only one broad resonance (δ = 0.14 ppm, 12 H) at 23 °C, as shown in Figure 4. The protons of the x methyl groups lie to slightly higher field (δ = −0.03 ppm, 6 H). Lowering of the temperature of the probe resulted in the series of spectra shown in Figure 4. In the −80 °C spectrum three broad, overlapping singlets of equal intensity appear, which are indicative of the freezing out of the inversion process that rendered the y and z protons equivalent at room temperature. With the method of Hogeveen and Kellogg[28] (assuming a coalescence temperature of −65 °C and a peak separation of 20 Hz), the barrier to inversion at the sulfur atoms of the nonunique Me_2S ligands was computed to be 43 ± 3 kJ mol^{-1}. Such a value seems to be fairly typical for terminally coordinated, simple thioethers.[29-31] The spectrum of the anion of **2** exhibited similar behavior with respect to inversion at the terminal thioether's sulfur atom. At room temperature the spectrum consists of a singlet in the region for the methyl resonances (δ = −0.38 ppm, CD_2Cl_2), and this is split into a doublet below −70 °C. The barrier to inversion at sulfur was calculated to be 43 ± 3 kJ mol^{-1}, on the basis of a coalescence temperature of −70 °C and a signal separation of 13 Hz.[28] The second type of isomer of $Cl_2(Me_2S)Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$, the C_1 enantiomeric pair, **3b**, was never isolated in a pure form, but was always contaminated with **3a**. Its presence in the mixture of compounds produced in the original synthesis (see Experimental Section) was deduced from the ^{1}H NMR spectrum of the second fraction of solid to be precipitated. This fraction contained none of the diamagnetic product **1**. The C_1 isomers would be expected to display three proton resonances at room temperature, corresponding to the three nonidentical methyl sulfide ligands. At low temperatures these would split, as observed for **3a** and as discussed above. Thus, a mixture of **3a** and **3b** would be expected to display five resonances at ambient temperature. In practice these five lines are not fully resolved, since the antiferromagnetic nature of these isomers leads to broad lines in the NMR spectrum. At the most, three broad, overlapping lines were seen, and their relative intensities varied from sample to sample. The total width of this multiplet was ~50 Hz, and it was centered at δ ~ 0.10 ppm at 22 °C. At low temperatures (−80 °C) the ^{1}H NMR spectrum of these mixtures of **3a** and **3b** appeared as broad multiplets (four to six lines could be identified, depending on the sample) centered at ~1.37 ppm. All nine possible resonances were never resolved under the conditions used.

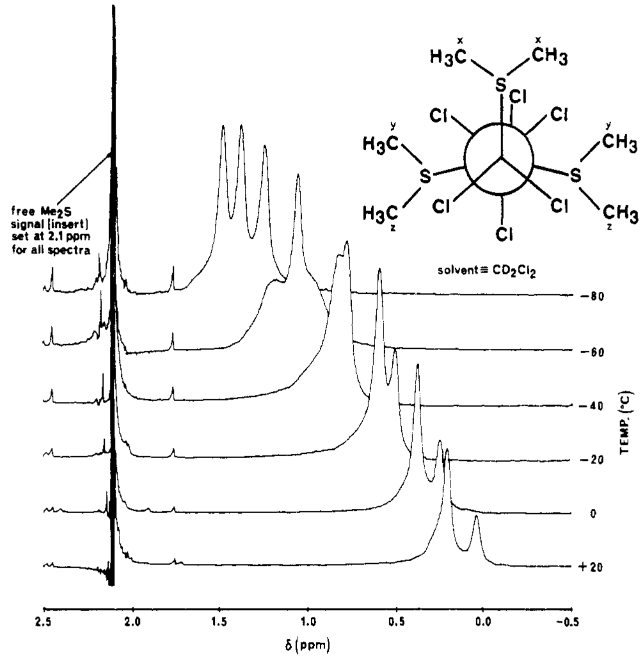

Figure 4. 200-MHz ^{1}H NMR spectra of the complex *meso*-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$ (**3a**) recorded between +20 and −80 °C in CD_2Cl_2 solution (insert contents = CD_2Cl_2 + Me_2S).

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Table V. Magnetochemical Data for the Complex *meso*-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(SMe_2)_2$[a]

T, K	82	100	119	138	157	177	196	215	234	253	273	292
$10^4\chi$, cgsu	1.89	3.05	3.67	3.97	4.09	4.39	4.39	4.22	4.34	5.25	4.52	4.52
μ_{obs}, μ_B	0.35	0.49	0.59	0.66	0.71	0.79	0.83	0.85	0.90	1.03	0.99	1.02
μ_{calc}, μ_B	0.38	0.44	0.50	0.58	0.63	0.72	0.78	0.88	0.93	1.00	1.08	1.15

[a] $J = -420$ cm^{-1}; μ_{obs} and μ_{calc} per Mo atom.

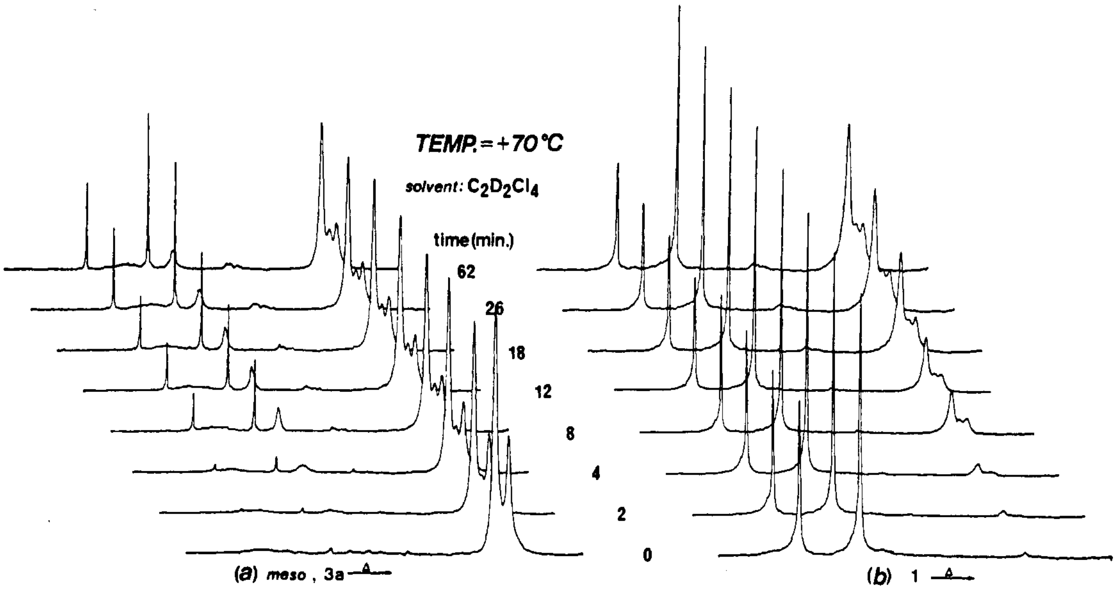

Figure 5. 200-MHz ^1H NMR spectra, showing the interconversion of, and the equilibrium between, the diamagnetic and antiferromagnetic isomers of $Mo_2Cl_6(SMe_2)_3$. *meso*, **3a** ≡ *meso*-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$; **1** ≡ $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$.

The most striking feature of the spectra displayed in Figure 4 is the temperature dependence of the chemical shifts of the coordinated methyl sulfide ligands. As the temperature is lowered, the resonances move toward more "normal" spectral positions, thus suggesting that the paramagnetism of this compound decreases with decreasing temperature, i.e. the compound displays antiferromagnetic behavior. Similar behavior was observed for compounds **2** and **5a**, and this is shown quantitatively for **2** in Figure S2.[16] It was therefore of interest to undertake a study of the temperature dependence of the magnetic susceptibility of one of the $Mo(\mu\text{-}Cl)_3Mo$-containing complexes to try to quantify this behavior. This was done on **3a**, *meso*-$(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2$, and the data are given in Table V. The magnetic moment per molybdenum atom shows a decrease from 1.02 at 292 K to 0.35 T A m^{-1} at 82 K, and the magnetic susceptibility shows a corresponding decrease as the temperature is lowered. Measurements were taken at three field strengths and on three samples. The results show that the compound is indeed antiferromagnetic, as predicted from the ^1H NMR data. Therefore, the six 4d electrons are not fully paired in metal–metal bonds. The values of the magnetic moments calculated by the Bleaney–Bowers treatment,[32] using $g = 2.0$, $J = -420$ cm^{-1}, and $N\alpha = 2.10 \times 10^{-4}$ cgsu, are shown in Table V. This equation assumes the compound only has singlet and triplet spin states, but we feel this simplification is justified as, with such a large J value, any quintet or septet spin states would be unlikely to be populated at the temperatures used in the experiment. It must be remembered, however, that the above treatment does not distinguish between simple antiferromagnetism and antiferromagnetism combined with a single or double Mo–Mo bond (which is the likely situation in this compound).

As the susceptibility of **3a** is so low, its measurement is less precise than in most magnetochemical studies; the paramagnetism barely outweighs the diamagnetism of the sample holder, and hence and estimated error of ca. 30% should be applied to the magnetic moment values. Hence, we believe it would be unjustifiable to attempt best fit calculations, and the parameters mentioned above should be taken as illustrating the applicability of the Bleaney–Bowers treatment to these data rather than as accurately calculated values of g, J, and $N\alpha$.

There is particular difficulty in selecting a suitable value of $N\alpha$, the second-order susceptibility for this complex, since few relevant studies have been reported on Mo(III) complexes. The most useful data are on the various salts of the $Mo_2Cl_9^{3-}$ ion, which show J values from −240 to −560 cm^{-1}, and their $N\alpha$ values do not exceed 2.10×10^{-4} cgsu.[33] A greater range of values for the $N\alpha$ parameter, from 10^{-4} to 4.07×10^{-4} cgsu, was taken for amino acid (L) complexes of the type $[Mo_2O(C_2O_4)L_2(H_2O)_4]$.[34]

As a final probe of the magnetic properties of **2** and **3a**, their ESR spectra were recorded.[35] **3a** was examined as a powder at 295 and 77 K and as a frozen glass at 77 K, with both X- and Q-band frequencies. In each case the spectrum consisted of a broad, asymmetric resonance, $g = 1.94$. **2** yielded a similar spectrum, $g = 1.95$ (X-band frequency) at 77 and 295 K, both as a frozen glass (CH_2Cl_2) and as a powder. Thus, all physical properties of the complexes with a $Mo(\mu\text{-}Cl)_3Mo$ core point to the same interpretation, namely that the two metal centers are antiferromagnetically coupled. This point is examined again in the final discussion.

Interconversion of the $Mo_2Cl_6(Me_2S)_3$ Isomers. The ^1H NMR solution spectra of various individual isomers revealed that at temperatures about ca. 323 K there are isomerization reactions. Hence, we attempted to quantify these observations. This proved to be impracticable due to the broadness of the peaks arising from the antiferromagnetic isomers and the slow precipitation of an unidentified solid from solution. (This was accompanied by the release of small amounts of free dimethyl sulfide, especially when the starting material was **3a**.) Nevertheless some significant observations were made about these processes. A synopsis of the reactions is recorded in the time-dependent spectra (Figure 5) of solutions of the meso isomer **3a** and the diamagnetic μ-Me_2S isomer **1**, in $C_2D_2Cl_4$ solution at 343 K. It is clear that the systems

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approach an equilibrium concentration of the antiferromagnetic and diamagnetic isomers after ca. 1 h, as seen by the similarity of the spectra derived from both isomers. The final spectra are not merely superpositions of the initial spectra of **1** and **3a** but show signs of the presence of a second antiferromagnetic isomer, which we assign as **3b**, whose spectrum overlaps that of **3a**. **3a** always appears to be present in a greater concentration than **3b**, and there is not simply a statistical mixture. It is not feasible to determine the absolute concentrations of each of these species. The process of interconversion was not affected by the presence of free Me_2S, and the rates were (qualitatively) independent of the initial concentrations of the pure isomers. Hence, we conclude that the process of interconversion is intramolecular, likely involving exchange between bridging and terminal ligands, a process that has been observed previously.[19] This type of reaction may well have implications for the potential catalytic properties of these thioether complexes.

Discussion

The isomeric forms of the complexes of general formula $Mo_2Cl_6(\text{thioether})_3$ (thioether = dimethyl sulfide, tetrahydrothiophene), as described above, add to the increasing inventory of confacial bioctahedral complexes of Mo(III) and W(III). The structural characterization of syn and gauche forms of the $[Mo_2Cl_7(PMe_3)_2]^-$ anion was recently reported by Cotton and Luck.[4] The interconversion of these two isomers was found to involve dissociation of phosphine, and the statistically expected ratio of the two forms is achieved at equilibrium in solution. The Mo–Mo bond lengths in the anions are comparable (2.69–2.76 Å) to those observed in the thioether complexes with $Mo(\mu\text{-}Cl)_3Mo$ cores reported here. On the basis of NMR properties, the phosphine complexes also exhibited a degree of paramagnetism. An analogous iodo complex, *syn*-$[Mo_2I_7(PMe_3)_2]^-$, was previously reported by Cotton and Poli[35] to possess an even longer Mo–Mo separation (>3.0 Å) and to be more paramagnetic. The 300 K value of χ_M' was reported as 1409×10^{-6} cgsu, with μ_{eff} of 1.83 μ_B per dimer (1.29 μ_B per monomer) for the compound $[NMe_4][Mo_2I_7(PMe_3)_2]\cdot 2THF$. This compound was also observed, on the basis of VT NMR data, to have a temperature-dependent magnetic behavior, similar to that observed in this work. However, this iodo complex was not subjected to a full variable-temperature magnetic study.

It is also relevant to consider the recent reports of Chisholm and co-workers on binuclear tungsten(III) complexes. The anionic species $[W_2Cl_7(THF)_2]^-$ was structurally characterized[2] and possesses a very short W–W bond distance (2.4028 (15) Å). It is diamagnetic. The THF ligands are terminally bound and in the solid state occupy syn positions. This compound was found to be a good precursor to other bis(tungsten(III)) complexes, including the edge-sharing bioctahedral complex $W_2Cl_6(PEt_3)_4$. Of particular interest is the equilbrium between this latter complex and the face-shared bioctahedral compound $W_2Cl_6(PEt_3)_3$.[3]

As far as thioether complexes of molybdenum are concerned, there is one tetrahydrothiophene complex reported by Richards and co-workers[36] that is of direct relevance to the structures reported herein. The compound has the structural formula $(THT)Cl_3Mo(\mu\text{-}S_2)(\mu\text{-}THT)MoCl_3(THT)$. It has been described as possessing two approximately pentagonally bipyramidally coordinated Mo(IV) centers, sharing a common face. The Mo–Mo bond length is 2.769 Å, and the Mo–S bonds to terminal thioethers are, as in our structures, significantly longer than those to the bridging THT ligands.

As mentioned earlier, one of the most attractive aspects of the thioether complexes of early transition metals in low oxidation states is their potential reactivity, as demonstrated by Cotton and Hall for the $Nb_2X_6(THT)_3$ complexes and their tantalum analogues.[7,8] The recent report by Green and co-workers on the reactivity of $NaW_2Cl_7(THF)_5$ with alkynes[5] clearly demonstrates that labile confacial bioctahedral complexes may, in general, deserve further study for their potential catalytic properties. The isomeric $Mo_2Cl_6(\text{thioether})_3$ complexes are particularly attractive in this regard, since two different structures are available, with their attendant electronic structural differences, as shown by their different magnetic properties. Preliminary investigations on their reactivity toward alkynes support this expectation.

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Supplementary Material Available: Figures S1 and S2, showing annotated ORTEP plots of compound **1** and the anion of **2** and a plot of the temperature dependence of the ^1H δ values for the Me_2S resonances in the anion of **2**, and Tables S1–S7, listing experimental crystallographic parameters, anisotropic thermal parameters for all non-hydrogen atoms, positional and isotropic thermal parameters for all hydrogen atoms, and complete bond lengths and angles (12 pages); listings of observed and calculated structure factors for compounds **4** and **5a** (120 pages). Ordering information is given on any current masthead page.

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