

## Synthesis and Characterization of Novel Molybdenum(III) Confacial Bioctahedral Complexes: X-Ray Crystal Structures of $[\text{Ph}_4\text{P}][(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]$ and $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{MoCl}_2(\text{SMe}_2)$

P. Michael Boorman,\* Kelly J. Moynihan, and Richard T. Oakley

Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada

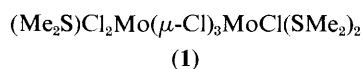
The reaction of  $\text{Et}_3\text{SiH}$  with  $\text{MoCl}_4(\text{Me}_2\text{S})_2$  produces a series of isomeric molybdenum(III) complexes with the general formula  $\text{Mo}_2\text{Cl}_6(\text{Me}_2\text{S})_3$ ; X-ray crystallographic results and/or  $^1\text{H}$  n.m.r. and analytical data establish the existence of the antiferromagnetic species,  $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}(\text{SMe}_2)_2$  (**1**) [*meso*- and (+), (-)-forms], its chloro-anionic derivative,  $[\text{Ph}_4\text{P}][(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]$  (**2**), and the diamagnetic complex,  $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{MoCl}_2(\text{SMe}_2)$  (**3**).

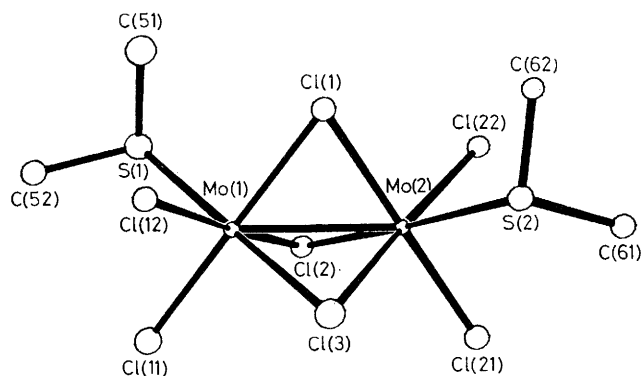
A recent theoretical analysis of the electronic and structural aspects of complexes possessing confacial bioctahedral frameworks by Hoffmann and Summerville has shown that the nature of the metal-metal interaction in such compounds is influenced by the d-electron configuration(s) of the metal centres and the characteristics of the bridging and terminal ligands.<sup>1</sup> Of the ligand effects, those involving the bridging groups are of greater importance with respect to metal-metal bonding. The magnitude of the bridging ligand-based effects has, however, been difficult to quantify systematically since few isonuclear and isoelectronic confacial bioctahedral species differing only in the identity of one bridging moiety have been structurally characterized. We report here the X-ray crystal structures of two molybdenum(III) dinuclear complexes which illustrate how profound structural changes can occur when one bridging ligand is replaced by another.

The treatment of  $\text{MoCl}_4(\text{Me}_2\text{S})_2$  [most easily prepared from  $\text{MoCl}_4(\text{thf})_2^2$  (thf = tetrahydrofuran) and  $\text{Me}_2\text{S}$  in  $\text{CH}_2\text{Cl}_2$ ] with an excess of  $\text{Et}_3\text{SiH}$  in  $\text{CH}_2\text{Cl}_2$  produces a mixture of isomeric  $\text{Mo}^{\text{III}}$  complexes with the general formula

$\text{Mo}_2\text{Cl}_6(\text{Me}_2\text{S})_3$ . In contrast, the major tungsten-containing product obtained from the reaction between  $\text{WCl}_4(\text{Me}_2\text{S})_2$  and  $\text{Et}_3\text{SiH}$  has been shown to be a  $\mu$ -hydrido-bis( $\mu$ -dimethyl sulphide)-ditungsten(III) complex containing a W-W triple bond.<sup>3</sup>

The first  $\text{Mo}_2\text{Cl}_6(\text{Me}_2\text{S})_3$  isomer that was isolated from the reaction mixture has been shown analytically and spectroscopically to be (**1**). Since each metal centre in this species possesses different terminal ligation, it follows that the complex (**1**) could potentially exhibit a number of stereochemistries.  $^1\text{H}$  N.m.r. studies have shown that (**1**) does exist as a mixture of stereoisomers [(+), (-)-pair and a *meso*-complex], and that at temperatures above room temperature, these stereoisomers can be easily interconverted. Complexes of the type  $\text{LCl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2$  (L = thf,  $\text{PEtPh}_2$ , dioxan) have been previously reported but not structurally characterized.<sup>4-6</sup>

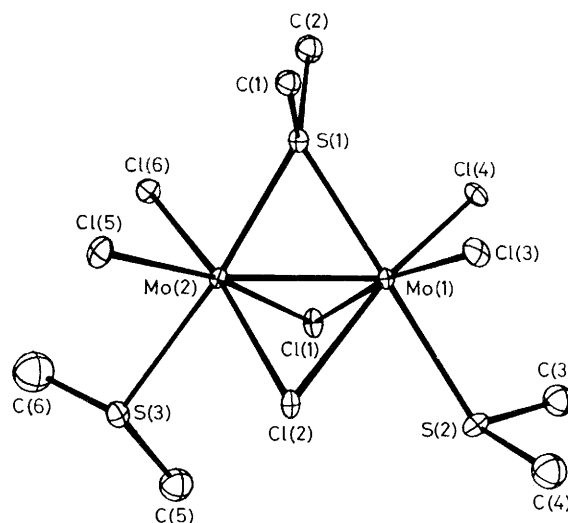




**Figure 1.** ORTEP drawing of the structure of the  $[(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]^-$  anion (**2**) showing the atomic numbering scheme. Important bond lengths and angles: Mo(1)–Mo(2) 2.746(9), Mo(1)–Cl(1) 2.47(1), Mo(1)–Cl(2) 2.45(1), Mo(1)–Cl(3) 2.43(2), Mo(1)–Cl(11) 2.37(1), Mo(1)–Cl(12) 2.38(1), Mo(1)–S(1) 2.51(2), Mo(2)–Cl(1) 2.46(2), Mo(2)–Cl(2) 2.43(2), Mo(2)–Cl(3) 2.46(1), Mo(2)–Cl(21) 2.36(2), Mo(2)–Cl(22) 2.40(1), and Mo(2)–S(2) 2.54(2) Å;  $\angle$  Mo(1)–Cl(1)–Mo(2) 67.8(4),  $\angle$  Mo(1)–Cl(2)–Mo(2) 68.5(3), and  $\angle$  Mo(1)–Cl(3)–Mo(2) 68.3(4)°.

One of the terminal dimethyl sulphide groups in (**1**) is labile, and the reaction of (**1**) [(+), (–) and/or *meso*] with an excess of  $\text{Cl}^-$  in  $\text{CH}_2\text{Cl}_2$  yields the  $[(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]^-$  anion, (**2**). The X-ray crystal structure†‡ of  $[\text{Ph}_4\text{P}][(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]$  has been determined. The ORTEP view of the chloro-anion (**2**) (Figure 1) shows that it possesses a slightly distorted confacial biotetrahedral framework<sup>1,7</sup> with a weak metal–metal interaction {Mo–Mo = 2.746(9) Å;  $[\text{Mo}-(\mu\text{-Cl})\text{-Mo}]_{\text{av}} = 68.1(4)^\circ$ }. The positions of the two  $\text{Me}_2\text{S}$  ligands in (**2**) impart approximate  $C_2$  symmetry to the anion. The length of the Mo–Mo vector in (**2**) is 0.1 Å longer than that in the related isoelectronic  $\text{Mo}_2\text{Cl}_9^{3-}$  ion,<sup>8</sup> and this bond lengthening (and the consequent increase in the values of the angles subtended at the bridging atoms) in (**2**) is likely to be due to the fact that  $\text{Me}_2\text{S}$  is a better  $\pi$ -acceptor ligand than Cl. Hoffmann and Summerville have shown that  $\pi$ -acceptor terminal ligands have the effect of perturbing certain metal-centred orbitals in a confacial biotetrahedral complex so as to weaken the interaction between the metal atoms.<sup>1</sup> Variable temperature  $^1\text{H}$  n.m.r. studies of (**1**) and its chloro-anionic derivative (**2**) have shown that the molybdenum atoms in these complexes are antiferromagnetically coupled.

The second major  $\text{Mo}_2\text{Cl}_6(\text{SMe}_2)_3$  isomer isolated from the initial reaction mixture has been shown analytically,



**Figure 2.** ORTEP drawing of the structure of  $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{MoCl}_2(\text{SMe}_2)$  (**3**) showing the atomic numbering scheme. Important bond lengths and angles: Mo(1)–Mo(2) 2.462(2), Mo(1)–S(1) 2.400(4), Mo(1)–Cl(1) 2.480(5), Mo(1)–Cl(2) 2.486(4), Mo(1)–S(2) 2.545(4), Mo(1)–Cl(3) 2.369(5), Mo(1)–Cl(4) 2.365(4), Mo(2)–S(1) 2.405(5), Mo(2)–Cl(1) 2.455(4), Mo(2)–Cl(2) 2.474(4), Mo(2)–S(3) 2.561(5), Mo(2)–Cl(5) 2.372(4), and Mo(2)–Cl(6) 2.379(5) Å;  $\angle$  Mo(1)–S(1)–Mo(2) 61.6(1),  $\angle$  Mo(1)–Cl(1)–Mo(2) 59.9(1), and  $\angle$  Mo(1)–Cl(2)–Mo(2) 59.5(1)°.

spectroscopically, and crystallographically‡§ to be  $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{MoCl}_2(\text{SMe}_2)$  (**3**). The ORTEP view of this diamagnetic compound (Figure 2) shows that it possesses a distorted confacial biotetrahedral structure with approximate  $C_{2v}$  symmetry. Compound (**3**) is the first example of a dinuclear molybdenum complex that contains a bridging simple dialkyl sulphide ligand.<sup>9</sup> A comparison of the structural parameters of (**2**) and (**3**) shows that the simple replacement of a  $\mu\text{-Cl}$  by a  $\mu\text{-Me}_2\text{S}$  ligand in these confacial biotetrahedral complexes has a dramatic effect upon the Mo–Mo contact. The length of the metal–metal vector [Mo–Mo = 2.462(2) Å] and the very acute angles subtended at the bridging atoms  $\{[\text{Mo}-(\mu\text{-X})\text{-Mo}]_{\text{av}} = 60.3(1)^\circ\}$  in (**3**) suggest that a formal Mo–Mo triple bond exists between the metal centres.<sup>1,7</sup> Similar values have been reported for the isoelectronic  $[\text{Cl}_3\text{Mo}(\mu\text{-H})(\mu\text{-Cl})_2\text{MoCl}_3]^{3-}$  anion in which a metal–metal triple bond has been proposed to exist between the molybdenum atoms.<sup>10</sup> The structure of (**3**) is very similar to that of the recently reported analogous diamagnetic tantalum compound,  $(\text{Me}_2\text{S})\text{Cl}_2\text{Ta}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{TaCl}_2(\text{SMe}_2)$ .<sup>11</sup> The tantalum complex ( $d^2\text{-}d^2$ ) possesses a metal–metal double bond and consequently the values for the metal–metal bond length [Ta–Ta = 2.691(1) Å] and the M–( $\mu\text{-X}$ )–M bond angles  $\{[\text{Ta}-(\mu\text{-Cl})\text{-Ta}]_{\text{av}} = 65.2(2)$  and  $\text{Ta}-(\mu\text{-S})\text{-Ta} = 68.9(2)^\circ\}$  are greater than those in (**3**) ( $d^3\text{-}d^3$ ). The  $^1\text{H}$  n.m.r. spectrum of (**3**) is virtually identical with that of the analogous diamagnetic niobium complex,  $(\text{Me}_2\text{S})\text{Cl}_2\text{Nb}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{NbCl}_2(\text{SMe}_2)$ ,<sup>12,13</sup> and shows no temperature dependence in the range  $-90$  to  $+30^\circ\text{C}$ . At

† *Crystal Data:*  $[\text{Ph}_4\text{P}][(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_2(\text{SMe}_2)]$ ,  $\text{C}_{28}\text{H}_{32}\text{Cl}_7\text{Mo}_2\text{PS}_2$ ,  $M = 903.71$ , triclinic, space group  $P1$ , [cell constants at  $-100(5)^\circ\text{C}$ ]  $a = 10.704(2)$ ,  $b = 12.641(3)$ ,  $c = 16.254(2)$  Å,  $\alpha = 63.12(2)$ ,  $\beta = 65.51(1)$ ,  $\gamma = 69.67(2)^\circ$ ,  $U = 1750(2)$  Å<sup>3</sup>,  $Z = 2$ . The structure was solved by direct methods followed by conventional difference Fourier syntheses and refined by full-matrix least-squares techniques (phenyl rings were treated as rigid bodies) using absorption-corrected data collected at  $-100(5)^\circ\text{C}$ . Final agreement factors:  $R = 0.054$ ,  $R_w = 0.055$ .

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ *Crystal Data:*  $(\text{Me}_2\text{S})\text{Cl}_2\text{Mo}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{MoCl}_2(\text{SMe}_2)$ ,  $\text{C}_6\text{H}_{18}\text{Cl}_6\text{Mo}_2\text{S}_3$ ,  $M = 590.99$ , monoclinic, space group  $P2_1/n$ , [cell constants at  $-100(5)^\circ\text{C}$ ]  $a = 8.213(4)$ ,  $b = 20.956(3)$ ,  $c = 10.733(5)$  Å,  $\beta = 97.32(2)^\circ$ ,  $U = 1832(1)$  Å<sup>3</sup>,  $Z = 4$ . The structure was solved by the heavy-atom method followed by conventional difference Fourier syntheses and refined by full-matrix least-squares techniques using absorption-corrected data collected at  $-100(5)^\circ\text{C}$ . Final agreement factors:  $R = 0.057$ ,  $R_w = 0.069$ .

elevated temperatures ( $\geq +50$  °C), the isomers (1) [(+), (-) and *meso*] and (3) can be easily interconverted.

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