

Note

Desulfurization of bibenzyl trisulfide by $[\text{CpMo}(\text{CO})_3]_2$: Formation and isolation of thiolato-bridged dimolybdenum complexes of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$, $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ and $[\text{CpMo}(\text{SBz})\text{S}]_2$ ($\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$, $\text{Bz} = \text{PhCH}_2\text{-}$). Crystal structures of two polymorphs of $[\text{CpMo}(\text{SBz})\text{S}]_2$

Richard C.S. Wong ^{*}, Mei Lee Ooi, Guan Huat Tan, Seik Weng Ng*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Received 27 July 2006; received in revised form 12 February 2007; accepted 15 February 2007

Available online 21 February 2007

Abstract

The reaction of $[\text{CpMo}(\text{CO})_3]_2$ (**1**) with a molar equivalent of Bz_2S_3 at 60 °C for 3.5 h has led to the isolation of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$ (**2**), $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**) and $[\text{CpMo}(\text{SBz})\text{S}]_2$ (**4**) in 16.9%, 3.1% and 61.1% yields, respectively, as main products. Thermolytic studies showed that **2** underwent stepwise decarbonylation to give **3** and **4**. All the three products of **2**, **3** and **4** were thiolato-bridged dimolybdenum complexes with bond orders of zero, one and two for **2**, **3** and **4**, respectively. In addition, both **3** and **4** have one and two S atoms bridged in a $\mu\text{-}\eta^2$ -mode, respectively. The structures of **2** and **3** have been reported previously. The totally decarbonylated **4** was isolated as polymorphs, **4a** and **4b**, which have been characterized by elemental, spectral analyses and structurally determined.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dimolybdenum complexes; Bibenzyl trisulfide; Polymorphs; Thermolytic studies; Desulfurization**1. Introduction**

Despite several decades of research work on the chemistry of transition metal thiolate compounds, the area still offer interesting new findings and prospects. Basically, the important features of these compounds lay in their wealth of bonding, structural and reactivity properties [1,2]. Transition metal thiolate complexes have generated a lot of interest due to their importance in catalytic processes such as desulfurization [3–7] and involvement in a large number of biological systems [8–11]. Much attention has been focused especially on the triply bonded complexes $[(\eta^5\text{-Cp})\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), which have displayed interesting chemistry due to the high reactivity and versatility of the metal–metal triple bond which are able to exhibit

a variety of addition [12,13] and substitution [14,15] type reactions. Sulfur donor ligands such as thiolato (SR^-) [16,17], thioether (SR_2) [18] and hydrosulfido (SH^-) [19] especially have been known to serve as bridging and stabilizing ligands for many of these transition metal complexes. Among the earliest examples of such thiolato-bridged cyclopentadienyl complexes were $[\text{CpM}(\text{CO})_2(\mu\text{-SR})]_2$ ($\text{M} = \text{Mo}$, $\text{R} = \text{Me}$ [20], Ph [21], Bu^t , $p\text{-tolyl}$ [22] and $\text{M} = \text{Cr}$, $\text{R} = \text{Ph}$ [23]), which feature a centered M_2S_2 ring but without any metal–metal bonds. All of these complexes underwent decarbonylation readily on heating to give doubly bonded $[\text{CpM}(\text{CO})(\mu\text{-SR})]_2$. In a preliminary paper, we reported the facile reaction of $[\text{CpCr}(\text{CO})_3]_2$ towards Bz_2S_3 which proceeded at ambient temperature leading to thiolate-bridged metal complexes as main products [24]. As part of our ongoing investigation, we wish to report herein a comparative study of the reactivity of $[\text{CpMo}(\text{CO})_3]_2$ towards Bz_2S_3 .

^{*} Corresponding author. Tel.: +60 379674260; fax: +60 379674193.E-mail address: richard@um.edu.my (R.C.S. Wong).

2. Experimental

2.1. General procedures

All experiments were carried out under nitrogen using Schlenk techniques and further manipulation of complexes were performed inside a dry-box equipped with a HE-493 dri-train under argon atmosphere. ^1H and ^{13}C NMR spectra were measured on a JEOL Lambda FT 400 MHz spectrometer, and chemical shifts referenced to residual C_6H_6 in benzene- d_6 . IR spectra in Nujol mulls were measured in the range $4000\text{--}400\text{ cm}^{-1}$ by means of a Perkin–Elmer 2000 FTIR spectrophotometer. Elemental analyses were performed by the Chemical, Molecular and Materials Analysis Centre (CMMAC), National University of Singapore.

$[\text{CpMo}(\text{CO})_3]_2$ was synthesized using $\text{Mo}(\text{CO})_6$ purchased from Fluka Ltd. according to Manning's method [25]. Bz_2S_3 was purchased from Sigma–Aldrich Chemical Company and was used without any purification. Silica gel (Merck Kieselgel 60, 35–70 mesh) and Celite (Fluka AG) were dried at 140°C overnight before chromatographic use. All solvents were distilled with sodium and benzophenone under nitrogen prior to use.

2.2. Reaction of $[\text{CpMo}(\text{CO})_3]_2$ (**1**) with Bz_2S_3

To a reddish purple solution of $[\text{CpMo}(\text{CO})_3]_2$ (200 mg, 0.41 mmol) in toluene (ca. 20 mL) was added Bz_2S_3 (114 mg, 0.41 mmol). The reaction mixture was stirred under nitrogen at 60°C for 3.5 h. The resultant reddish brown solution was filtered through a disk of Celite ($1 \times 1.5\text{ cm}$) and concentrated to ca. 2–3 mL, and then loaded onto a silica gel column ($10 \times 1.5\text{ cm}$) which was prepared in *n*-hexane. The following fractions were eluted:

- (i) A reddish brown fraction in a 2:1 *n*-hexane/toluene mixture (90 mL) which upon concentration to dryness under vacuo gave dark brown crystalline solids of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$ (**2**) [26] (46 mg, 0.067 mmol, 16.3% yield). ^1H NMR (C_6D_6): (C_6H_5) 7.72–7.03 (m, 10H); (C_5H_5) 4.61 (s, 5H); (CH_2) 3.69 (s, 2H). ^{13}C NMR (C_6D_6): (CH_2) 38.85; (C_5H_5) 96.67, 96.72, 96.76, 96.79, ($\text{S}-\text{CH}_2-\text{C}_6\text{H}_5$) 127.72, 128.73, 130.32, 141.15; (CO) 256.67. IR: $\nu(\text{CO})$ at 1944vs, 1918sh, 1849vs, 1831sh cm^{-1} ; other bands, 1067vw, 1029vw, 1009w, 842w, 808m, 700m cm^{-1} (nujol). Anal. Calc. for $\text{C}_{28}\text{H}_{24}\text{Mo}_2\text{O}_4\text{S}_2$: C, 49.4; H, 3.5; Mo, 28.2; S, 9.4. Found: C, 49.5; H, 3.6; Mo, 28.5; S, 9.3%.
- (ii) A pink fraction in a 4:1 toluene/ether mixture (30 mL) which upon concentration to dryness under vacuo gave fine dark pink crystalline solids of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4a**) (53 mg, 0.084 mmol, 21.0% yield). ^1H NMR (C_6D_6): (C_6H_5) 7.72–7.01 (m, 10H); (C_5H_5) 5.89 (s, 5H); (CH_2) 2.72 (s, 2H). ^{13}C NMR (C_6D_6): (CH_2) 38.8; (C_5H_5) 98.07, 98.14, 98.19, 98.22; ($\text{S}-\text{CH}_2-\text{C}_6\text{H}_5$) 129.62, 129.79, 142.26. IR: ν at 1667m, 1599w, 1317w, 1277m, 1008w,

808m, 698s cm^{-1} (nujol). Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{Mo}_2\text{S}_4$: C, 45.6; H, 3.8; Mo, 30.4; S, 20.3. Found: C, 45.6; H, 3.4; Mo, 30.7; S, 19.8%.

- (iii) A brownish pink fraction in a 2:1 toluene/ether mixture (25 mL) which gave fine dark pink crystalline solids of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4b**) (102 mg, 0.161 mmol, 40.3% yield) when concentrate to dryness. ^1H NMR (C_6D_6): (C_6H_5) 7.72–6.89 (m, 10H); (C_5H_5) 5.84 (s, 5H); (CH_2) 2.78 (s, 2H). ^{13}C NMR (C_6D_6): (CH_2) 41.57; (C_5H_5) 97.95; ($\text{S}-\text{CH}_2-\text{C}_6\text{H}_5$) 129.37, 130.32, 142.05. IR: ν at 1667m, 1599w, 1317w, 1276m, 1011w, 800m, 698s cm^{-1} (nujol).
- (iv) A pinkish brown fraction in ether (7 mL) which upon concentration to dryness under vacuo gave pinkish brown crystalline solids of $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**) [27] (8 mg, 0.012 mmol, 2.9% yield). ^1H NMR (C_6D_6): (C_6H_5) 7.42–7.01 (m, 10H); (C_5H_5) 4.83 (s, 5H); (CH_2) 4.02 (s, 2H). ^{13}C NMR (C_6D_6): (CH_2) 49.37; (C_5H_5) 90.38, 90.71, 91.03, 91.24, 91.56; ($\text{S}-\text{CH}_2-\text{C}_6\text{H}_5$) 128.74, 143.10; (CO) 244.10. IR: $\nu(\text{CO})$ at 1925vs, 1869s, 1846sh cm^{-1} ; other bands, 1061vw, 1031vw, 1011vw, 813m, 760m, 700m cm^{-1} (nujol). Anal. Calc. for $\text{C}_{26}\text{H}_{24}\text{Mo}_2\text{O}_2\text{S}_2$: C, 47.6; H, 3.7; Mo, 29.3; S, 14.6. Found: C, 47.5; H, 3.8; Mo, 30.2; S, 14.9%. A dark brown band remained uneluted on the top of the column.

2.3. Thermolysis of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$ (**2**)

A stirred reddish brown solution of **2** (100 mg, 0.147 mmol) in toluene (15 mL) was maintained at 60°C for ca. 14.5 h. The resultant dark yellowish brown solution was filtered through Celite (1 cm disk), concentrated (ca. 2 mL) and then loaded onto a silica gel column ($1.5 \times 10\text{ cm}$) prepared in *n*-hexane. Two fractions were eluted:

- (i) A deep pink fraction in a 2:1 toluene/ether mixture (20 mL) which when concentrated to dryness gave deep pink crystalline solids of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) (15 mg, 0.024 mmol, 16.3% yield).
- (ii) A pinkish brown fraction in ether (15 mL) which when concentrated to dryness gave dark reddish brown crystalline solids of **3** (25 mg, 0.038 mmol, 25.9% yield).

2.4. Thermolysis of $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**)

A pinkish brown solution of **3** (100 mg, 0.152 mmol) in toluene (15 mL) was maintained at 110°C for 18 h. The resultant dark yellowish brown solution was filtered through Celite (1 cm disk), concentrated (ca. 2 mL) and then loaded onto a silica gel column ($1.5 \times 10\text{ cm}$) prepared in *n*-hexane–toluene (1:1). Only one fraction was eluted as a pink solution in 2:1 toluene/ether mixture (35 mL) which

when concentrated to dryness gave deep pink crystalline solids of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) (24 mg, 0.038 mmol, 25.0% yield). A dark brown layer remained uneluted at the top rim of the column.

2.5. NMR tube reactions

2.5.1. Cothermolysis of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$ (**2**) with Bz_2S_3

A reddish brown solution of **2** (20 mg, 0.029 mmol) in C_6D_6 (0.6 mL) placed in a 5 mm NMR tube was heated with an equivalent of Bz_2S_3 (8 mg, 0.029 mmol) at 60 °C for 9.5 h. Its ^1H NMR spectrum showed that the resultant yellowish brown solution consists of $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**) (31% yield) and $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) (49% yield) together with some uncharacterized dark brown precipitates.

2.5.2. Cothermolysis of $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**) with Bz_2S_3

A pinkish brown solution of **3** (20 mg, 0.030 mmol) in d_8 -toluene (0.6 mL) in a 5 mm NMR tube was heated with an equivalent of Bz_2S_3 (8 mg, 0.030 mmol) at 110 °C for 15 h. Its ^1H NMR spectrum showed that the resultant solution consists of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) (47% yield) together with some uncharacterized dark brown precipitates.

3. Results and discussion

3.1. Synthetic pathways

The reaction of $[\text{CpMo}(\text{CO})_3]_2$ (**1**) with an equimolar of Bz_2S_3 at 60 °C for 3.5 h has led to the isolation of $[\text{CpMo}$

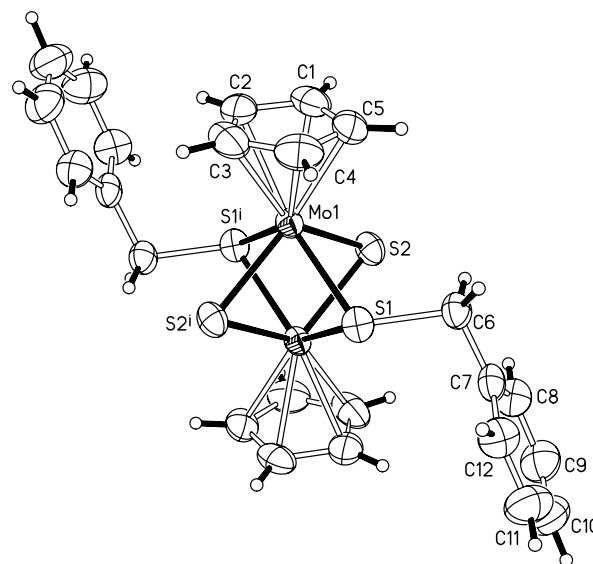
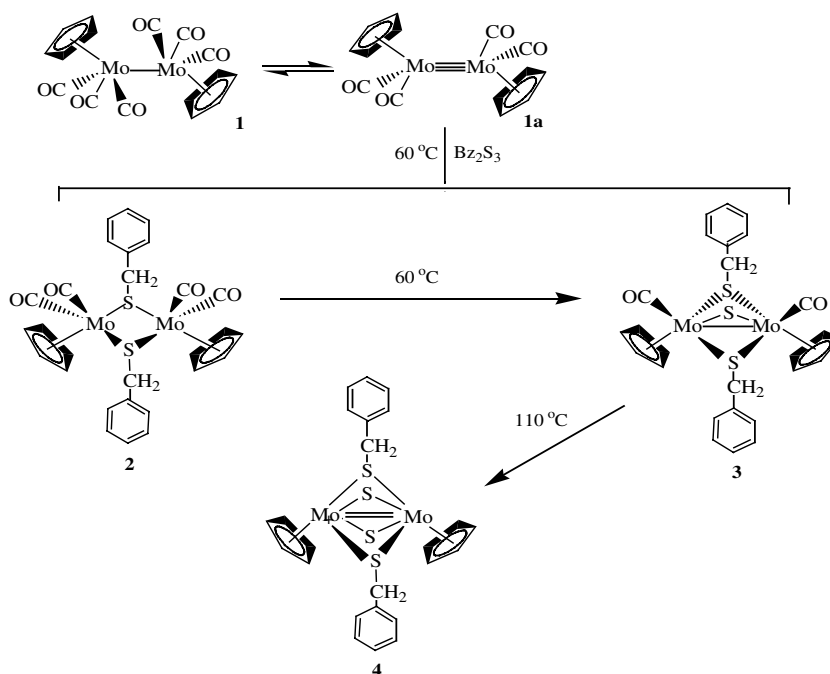


Fig. 1. ORTEP plot of the monoclinic modification of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{S})(\text{SCH}_2\text{C}_6\text{H}_5)]_2$ (**4a**); the molecule lies on a center-of-inversion in the crystal structure.

$(\text{CO})_2(\text{SBz})]_2$ (**2**), $[\text{CpMo}(\text{CO})(\text{SBz})]_2\text{S}$ (**3**) and $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) in 16.3%, 2.9% and 61.3% yields, respectively. Thermolysis of $[\text{CpMo}(\text{CO})_2(\text{SBz})]_2$ (**2**) at 60 °C for 14.5 h has resulted in the isolation of **3** and **4** in 25.9% and 16.3% yields, respectively. Prolonged thermolysis of **3** at an elevated temperature of 110 °C for 18 h resulted in the isolation of $[\text{CpMo}(\text{SBz})(\text{S})]_2$ (**4**) in 25.0% yield. NMR tube reaction study of **2** under similar thermo-



Scheme 1. Proposed synthetic pathway for the reaction of $[\text{CpMo}(\text{CO})_3]_2$ (**1**) with Bz_2S_3 .

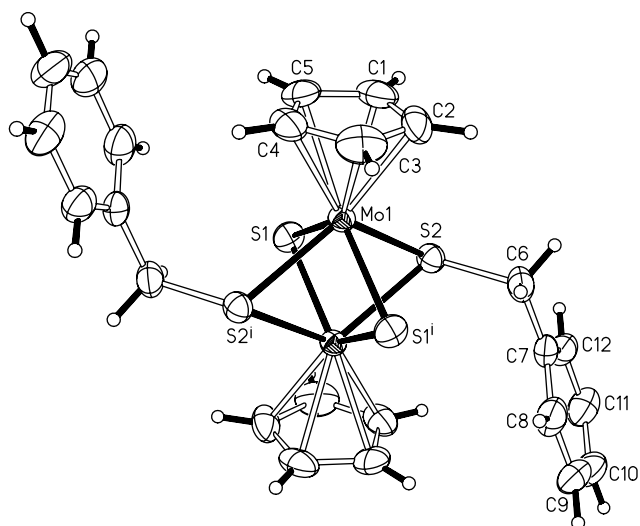


Fig. 2. ORTEP plot of the orthorhombic modification of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{S})(\text{SCH}_2\text{C}_6\text{H}_5)_2]_2$ (**4b**); the molecule lies on a center-of-inversion in the crystal structure.

lytic condition, but in the presence of Bz_2S_3 , gave higher yields of **3** (31%) and **4** (49%). Likewise, thermolysis of **3** in the presence of Bz_2S_3 also resulted in higher yield of **4** (47%).

A major consequence of reactions involving organic disulfides (RSSR) is the susceptibility of their S–S linkage to be cleaved by nucleophilic, electrophilic or radical processes [28a,28b,28c]. The closely related organic trisulfides (RSSSR) having two adjacent sulfur–sulfur bonds as in Bz_2S_3 is expected to undergo similar desulfurization process as well. According to Harpp et al. [29], the central sulfur atom being bonded to two soft sulfur atoms, would be a softer acceptor than a terminal sulfur atom that is bonded to a carbon atom hence the desulfurization process is targeted towards the central sulfur. For this reaction, it is postulated that the coordination of the thiobenzyl moiety from the desulfurized Bz_2S_3 has led to the formation of the thiolate-bridged dimer $[\text{CpMo}(\text{CO})_2(\text{SBz})_2]$ (**2**) which was observed previously in a similar reaction with the Cr analogue [24]. Initial isolation of **2** which underwent stepwise decarbonylation to yield $[\text{CpMo}(\text{CO})(\text{SBz})_2\text{S}]$ (**3**) and finally to the completely decarbonylated $[\text{CpMo}(\text{SBz})(\text{S})_2]$ (**4**) after prolonged thermolysis indicates that **2** is a primary product (Scheme 1). The partial decarbonylation of **2** results in the loss of two carbonyl ligands but proceeds with a formal insertion of an S(0) atom (presumably from the desulfurized Bz_2S_3) across the singly-bonded Mo center to form the $\text{Mo}-(\mu_2\text{-S})\text{-Mo}$ bridged complex **3**. Finally, **3** succumbed to complete decarbonylation, coupled with concomitant sulfur insertions ultimately gave rise to the mixed quadruply thiolato-bridged complex **4**. A different synthetic route reported by Franz et al. [30] involves a two-step exchange of both the $\mu_2\text{-SH}$ groups from $[\text{CpMo}(\mu\text{-S})(\mu\text{-SH})_2]$ with benzylthiol to give the final dibenzyl substituted cluster similar to **4** which was character-

ized by NMR spectroscopy. As with the Cr analogue, $[\text{CpMo}(\text{CO})_3]_2$ (**1**) also demonstrates the ability to desulfurize trisulfides to disulfides and monosulfides in an effective manner.

3.2. Structural study

The reported structures of **2** and **3** [26,27] feature a *cis* arrangement of the carbonyl ligands similar to the chromium analogue $[\text{CpCr}(\text{CO})_2(\text{SBz})_2]_2$. Both have the same type of non-planar Mo_2S_2 ring system. The decarbonylated $[\text{CpMo}(\text{CO})(\text{SBz})_2\text{S}]$ (**3**) differs from **2** with an extra sulfide linkage in addition to the two benzylthiolate linkages. The $\text{Mo}(1)\cdots\text{Mo}(2)$ separation of 3.836 (3) Å of **2** is much longer than the normal Mo–Mo single bond found in related dinuclear complex **1** (3.235 Å) [31,32] indicates the absence of metal–metal bond between them.

$[\text{CpMo}(\text{SBz})_2]_2$ (**4**) can be obtained as two polymorphous species. Complex **4a** crystallizes in the space group *Pcba* of the orthorhombic system and **4b** in the space group *P2₁/c* of the monoclinic system. The ORTEP plots of **4a** and **4b** are presented in Figs. 1 and 2 respectively and define the atomic numbering scheme. Both compounds consist of a Mo_2S_4 framework with the geometry of the Mo atom described as pseudo-pentagonal bipyramidal and feature a nearly square-planar arrangement of the four sulfur atoms, perpendicular to the Mo–Mo bond and almost parallel to the two $(\eta^5\text{-C}_5\text{H}_5)$ planes. Their phenyl groups attached to the thiolato bridges are in an equatorial-axial configuration being *trans* to each other. The quadruply thiolato-bridged complex belongs to a well characterized group of structures which contain a $\text{Mo}_2(\mu\text{-S})_4$ residue such as $\text{Cp}_2^*\text{Mo}_2(\mu\text{-SCH}_3)_2(\mu\text{-S})_2$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) [33], $\text{Cp}_2^*\text{Mo}_2(\mu_2\text{-SCH}_3)_4$ [34], $\text{Cp}_2'\text{Mo}_2(\mu_2\text{-SCH}_3)_2(\mu_2\text{-S})_2$ ($\text{Cp}' = \eta^5\text{-methylcyclopentadienyl}$) [35] and $\text{Cp}_2''\text{Mo}_2(\mu_2\text{-SCH}_3)_4$ ($\text{Cp}'' = \eta^5\text{-ethyltetramethylcyclopentadienyl}$) [36]. In all these complexes, the formal +4 oxidation state of the Mo atoms would require the existence of a double bond between them, in accordance to the demands of the 18 e-rule. Both **4a** and **4b** with Mo–Mo bond lengths of 2.579(7) and 2.581(5) Å

Table 1
Comparison of Mo–Mo bonds and Mo–S bonds in complexes 1–4

Complex	Mo–Mo (Å)	Mo–S(sulfido) (Å)	Mo–S(thiolato) (Å)	Ref
1	3.235	–	–	[31,32]
2	–	–	2.512 (7) 2.521 (7)	[26]
3	2.802	2.437 (2)	2.460 (2) 2.452 (2)	[27]
4a	2.579 (7)	2.341 (1) 2.355 (1)	2.465 (1) 2.478 (1)	this work
4b	2.581 (5)	2.352 (1) 2.344 (1)	2.479 (1) 2.476 (1)	this work

Table 2
X-ray crystal data and structure refinement for **4a** and **4b**

Identification code	4a	4b
Empirical formula	C ₂₄ H ₂₄ Mo ₂ S ₂	C ₂₄ H ₂₄ Mo ₂ S ₂
Formula weight	632.55	632.55
Temperature (K)	223(2)	223(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	orthorhombic, <i>Pcba</i>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	12.084(1)	8.052(1)
<i>b</i> (Å)	7.834(1)	12.328(1)
<i>c</i> (Å)	12.563(1)	23.838(1)
α (°)	90	90
β (°)	98.542(1)	90
γ (°)	90	90
<i>V</i> , Volume (Å ³)	1176.1(2)	2366.3(1)
<i>Z</i> , Calculated density (Mg/m ³)	2, 1.786	4, 1.776
Absorption coefficient (mm ^{−1})	1.432	1.423
<i>F</i> (000)	632	1264
Crystal size (mm)	0.10 × 0.10 × 0.04	0.14 × 0.10 × 0.09
θ Range for data collection (°)	1.70–27.54	1.71–27.53
Limiting indices	−15 ≤ <i>h</i> ≤ 13, −10 ≤ <i>k</i> ≤ 10, −16 ≤ <i>l</i> ≤ 15	−9 ≤ <i>h</i> ≤ 10, −16 ≤ <i>k</i> ≤ 14, −24 ≤ <i>l</i> ≤ 30
Reflections collected/unique [<i>R</i> _{int}]	8009/2693 [0.0360]	15 518/2722 [0.0543]
Completeness to $\theta = 27.54$ (%)	100	100
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2693/0/136	2722/0/136
Goodness-of-fit on <i>F</i> ²	1.063	1.103
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.1036	<i>R</i> ₁ = 0.036, <i>wR</i> ₂ = 0.0753
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0559, <i>wR</i> ₂ = 0.1102	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.0816
Largest difference in peak and hole (e Å ^{−3})	1.302 and −0.388	0.506 and −0.364

compares very closely to Cp₂Mo₂(μ-SCH₃)₂(μ-S)₂ (2.573(1) Å) and Cp₂Mo₂(μ₂-SCH₃)₂(μ₂-S)₂ (2.582(1) Å) bond distances. The four S atoms are bonded in a μ-η²-mode. The Mo–S(thiolato) bond distances [average 2.472(1) Å] are significantly longer than the Mo–S(sulfido) distances

[average 2.348(1) Å] resulting in a more acute Mo1–S1–Mo1ⁱ angle and a comparison of the measured Mo–Mo and Mo–S bond lengths for complexes **1–4** is shown in Table 1. It is likely that these observations arise due to greater steric repulsions between the SBz group and an S substituent (Tables 2,3).

Table 3
Bond lengths (Å) and angles (°) for **4a** and **4b**

	4a	4b
<i>Bond lengths (Å)</i>		
Mo1–C1	2.339(4)	2.325(3)
Mo1–C2	2.346(5)	2.312(4)
Mo1–C3	2.348(5)	2.334(4)
Mo1–C4	2.327(4)	2.350(3)
Mo1–C5	2.315(4)	2.351(3)
Mo1–S1	2.465(1)	2.352(1)
Mo1–S1 ⁱ	2.478(1)	2.344(1)
Mo1–S2	2.341(1)	2.479(1)
Mo1–S2 ⁱ	2.355(1)	2.476(1)
Mo1–Mo1 ⁱ	2.579(2)	2.581(5)
<i>Bond angles (°)</i>		
S1–Mo1–S1 ⁱ	117.1(1)	113.3(1)
S1–Mo1–S2	77.3(1)	69.7(1)
S1–Mo1–S2 ⁱ	69.6(1)	76.8(1)
S1 ⁱ –Mo1–S2	69.6(1)	76.9(1)
S1 ⁱ –Mo1–S2 ⁱ	76.8(1)	69.9(1)
S2–Mo1–S2 ⁱ	113.4(1)	117.2(1)
Mo1–S1–Mo1 ⁱ	62.9(3)	66.7(2)
Mo1–S2–Mo1 ⁱ	66.6(3)	62.8(2)

Symmetry transformation: *i* = 1 − *x*, 1 − *y*, 1 − *z*.

Acknowledgements

The author acknowledges with thanks financial support from SAGA Grant 66-02-03-0044 from the Academy Of Sciences Malaysia.

Appendix A. Supplementary material

CCDC 293259, 615748 contains the supplementary crystallographic data for **4a** and **4b**. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2007.02.021](https://doi.org/10.1016/j.ica.2007.02.021).

References

- [1] P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121, and references cited therein.

- [2] I.G. Dance, *Polyhedron* 5 (1986) 1037, and references cited therein.
- [3] M. Hidai, Y. Mizobe, *Chem. Rev.* 95 (1995) 1115.
- [4] M. Rakowski Du Bois, *Chem. Rev.* 89 (1989) 1, and references cited therein.
- [5] O. Weisser, S. Landa, In *Sulfide Catalysts, Their Properties and Applications*, Pergamon, New York, 1973.
- [6] A.F. Browning, A.D. Bacon, C. White, *J. Mol. Catal.* 83 (1995) 1.
- [7] R. Vilar, R. Salcedo, R. Gavino, T. Ogawa, *Eur. Polym. J.* 31 (1995) 1135.
- [8] B. Krebs, G. Henkel, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 769, and references therein.
- [9] K. Osakada, Y. Kawaguchi, T. Yamamoto, *Organometallics* 14 (1995) 4542.
- [10] J.J. García, P.P. Maitlis, *J. Am. Chem. Soc.* 115 (1993) 12200.
- [11] M.N. Hughes, *The Inorganic Chemistry of Biological Processes*, NY, 1981.
- [12] M.D. Curtis, R.J. Klingler, *J. Organomet. Chem.* 161 (1978) 23.
- [13] M.D. Curtis, K.R. Han, W.M. Butler, *Inorg. Chem.* 19 (1980) 2096.
- [14] J. Wachter, A. Mitschler, J.G. Riess, *J. Am. Chem. Soc.* 103 (1981) 2121.
- [15] H. Brunner, W. Meier, J. Wachter, *J. Organomet. Chem.* 210 (1981) C23.
- [16] H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.* 14 (1975) 322.
- [17] F.Y. Petillon, P. Schollhammer, J. Talarmin, K.W. Muir, *Coord. Chem. Rev.* 178–180 (1998) 203–247.
- [18] S.G. Murray, F.R. Hartley, *Chem. Rev.* 81 (1981) 365.
- [19] S. Kuwata, M. Hidai, *Coord. Chem. Rev.* 213 (2001) 211–305.
- [20] P.M. Treichel, J.H. Morris, F.G.A. Stone, *J. Chem. Soc.* (1963) 720.
- [21] R. Havlin, G.R. Knox, *Z. Naturforsch. B* 21 (1966) 1108.
- [22] I.B. Benson, S.D. Killops, S.A.R. Knox, A.J. Welch, *J. Chem. Soc., Chem. Commun.* (1980) 1137–1139.
- [23] L.Y. Goh, M.S. Tay, T.C.W. Mak, R.J. Wang, *Organometallics* 11 (1992) 1711–1717.
- [24] R.C.S. Wong, M.L. Ooi, C.F. Chee, G.H. Tan, *Inorg. Chim. Acta* 358 (2005) 1269–1273.
- [25] R. Birdwhistell, P. Hackett, A.R. Manning, *J. Organomet. Chem.* 157 (1978) 239.
- [26] R.C.S. Wong, M.L. Ooi, K.M. Lo, S.W. Ng, *Acta Crystallogr., Sect. E* 60 (2004) m687.
- [27] R.C.S. Wong, M.L. Ooi, S.W. Ng, *Acta Crystallogr., Sect. E* 60 (2004) m690.
- [28] (a) J.L. Kice, in: A. Senning (Ed.), *Sulfur in Organic and Inorganic Chemistry*, vol. 1, Marcel Dekker, New York, 1971, p. 153;
(b) T. Nagno, K. Arakane, M. Hirobe, *Tetrahedron Lett.* 21 (1980) 5021;
(c) J. Cuomo, J.H. Merrifield, J.F.W. Keana, *J. Am. Chem. Soc.* 45 (1980) 4216.
- [29] D.N. Harpp, R.A. Smith, *J. Am. Chem. Soc.* 104 (1982) 6045.
- [30] J.A. Franz, J.C. Birnbaum, D.S. Kolwaite, J.C. Linehan, D.M. Camaioni, M. Dupuis, *J. Am. Chem. Soc.* 126 (2004) 6680.
- [31] F.C. Wilson, D.P. Shoemaker, *J. Chem. Phys.* 27 (1957) 809.
- [32] R.D. Adams, D.M. Collins, F.A. Cotton, *Inorg. Chem.* 13 (1974) 1086.
- [33] H. Brunner, W. Meier, J. Wachter, P. Weber, M.L. Ziegler, J.H. Enemark, C.G. Young, *J. Organomet. Chem.* 309 (1986) 313.
- [34] N.G. Connelly, L.F. Dahl, *J. Am. Chem. Soc.* 92 (1970) 7470.
- [35] M. Rakowski DuBois, M.C. VanDerveer, D.L. DuBois, R.C. Haltiwanger, W.K. Miller, *J. Am. Chem. Soc.* 102 (1980) 7456.
- [36] J.H. Shin, G. Parkin, *Polyhedron* 13 (1994) 1498.