

# Reactions of $\alpha,\omega$ -dithiolate ligands with bis(cyclopentadienyl)molybdenum dichloride; crystal structures of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\{\text{S}(\text{CH}_2)_n\text{S}\}$ ( $n = 2, 3$ ) and a layered hydrate, $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O}) \cdot 4.5\text{H}_2\text{O}$

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## Abstract

Reaction of bis(cyclopentadienyl)molybdenum dichloride **1** in ethanol with 1,3-propanedithiol **2** either in the presence of base or as its thallium derivative produces  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})]$  (**5**) containing a 6-membered ring with a chair conformation, structurally characterized by X-ray diffraction. However, reactions of compound **1** with 2,2'-thiodiethanethiol (**3**) or 2,2'-oxydiethanethiol (**4**) under the same conditions do not form complexes with 8-membered chelate rings but lead to thioether or ether bond cleavage, respectively, to yield as major products  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{X})]$  (**6**, X = S, or **7**, X = O), containing ligands which form 5-membered rings; crystal structures of **6** and **7** are reported and both contain chelating ligands with envelope conformations. Compound **7** readily incorporates water and the unusual crystal structure of the hydrate  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O}) \cdot 4.5\text{H}_2\text{O}$  comprises stacks of double layers of hydrated organometallic molecules of overall composition  $[\{\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O})\}_2 \cdot \text{H}_2\text{O}]_n$ , separated by layers of hydrogen-bonded water molecules, interconnected by H-bonds between  $\text{H}_2\text{O}$  molecules and O-atoms of the 2-thioethoxy ligand.

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## 1. Introduction

Bis(cyclopentadienyl)molybdenum thiolate complexes, and related tungsten derivatives, were first prepared in the 1960s [1] and a range of compounds of general formulae  $\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$  and  $\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})\text{X}$  ( $\text{M} = \text{Mo}^{\text{IV}}, \text{W}^{\text{IV}}$ ) have since been reported (e.g., see [2–5]). These compounds are relatively stable to hydrolysis and thermolysis but are useful precursors for synthetic transformations at the metal centre, since thiolate groups are easily replaced by other ligands, e.g., by carboxylate on reaction with carboxylic acid

[2]. Bond enthalpies  $E(\text{Mo-SR})$  of bis(cyclopentadienyl)molybdenum dithiolates, derived from calorimetric studies, are in the range 200–250  $\text{kJ mol}^{-1}$  with variations being partly attributed to steric effects of the group R, and these enthalpy values are reported to be ca. 100  $\text{kJ mol}^{-1}$  lower than for corresponding Mo–O or Mo–Cl bonds [6].

Interesting aspects of reactivity of the thiolate groups are their ready alkylation to form neutral thioether ligands, as in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{SRR}')\text{X}]^+$  [2,5,7], and their coordination to other transition metals [8–10] and heavy main-group metals [2,11] to form heteronuclear systems. The metal(IV) derivatives can be oxidized to V and VI oxidation states, as demonstrated electrochemically [4,12]; the higher oxidation state species are generally

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more stable when unsaturated dithiolene ligands are present [13,14], and the oxidative chemistry of some functionalized molybdocene–dithiolene derivatives has been reported [15–17]; nevertheless, simple molybdenum(VI) cations of formula  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2]^{2+}$  can be prepared by oxidations involving  $\text{AsF}_3$  [18]. Chemical oxidation by ferricenium salts followed by elimination of thio-radical is a pathway for the introduction of neutral 2-electron ligands [3,12], and more complex redox reactions form ligand-coupled products [19].

Crystal structures of the di-*t*-butyl and diphenyl compounds,  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$  ( $\text{R} = \text{Bu}^t$  [20],  $\text{Ph}$  [19]), have been reported, as have structures of several dithiolene derivatives,  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{dithiolene})$ , containing 1,2-arylenedithiolate [21] or 1,2-alkenedithiolate ligands [16,17]. The structures of a number of heterometallic compounds containing  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$  entities as metalloligands have also been determined [8b,9b,11,22].

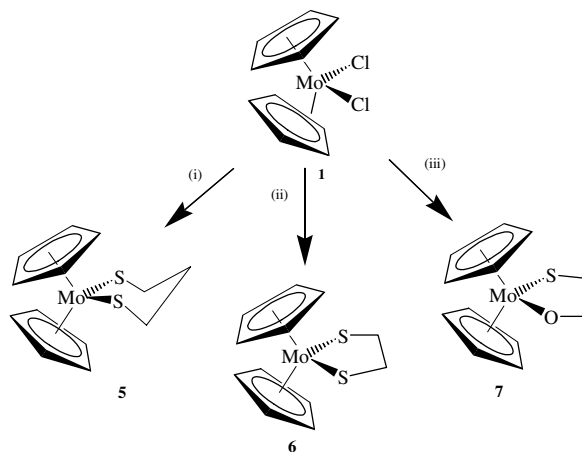
In recent years we have been studying cyclopentadienyl derivatives of the early transition metals with dithiolate ligands, including complexes of titanium [23], niobium [24,25] and tantalum [24].  $\alpha,\omega$ -Dithiolates form dithiometallacycles with interesting ring conformations and solid-state structures; rings containing additional thioether or ether linkages have potential for further coordination either to the existing metal [25] or, as a macrocyclic ligand, to an added metal centre. In this paper, we present synthetic, spectroscopic and structural investigations on bis(cyclopentadienyl)molybdenum thiolate complexes produced by reactions of  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  (**1**) with potentially chelating ligands, 1,3-propanedithiol (**2**), 2,2'-thiodiethanethiol (**3**), and 2,2'-oxydiethanethiolate (**4**). It should be noted that an electrochemically active tungsten complex,  $\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{SCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{S}\}$  containing a 14-membered  $\text{WS}_2\text{O}_3$  ring, has previously been prepared from  $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  and 3,6,9-trioxo-1,11-undecanedithiol but no evidence was obtained for its ability to act as metalloligand [4].

## 2. Results and discussion

### 2.1. Reaction of 1,3-propanedithiol

Reaction of bis(cyclopentadienyl)molybdenum dichloride (**1**) in ethanol either with an equimolar amount of 1,3-propanedithiol in the presence of 2 mol of sodium ethoxide or with the dithallium derivative of **2** at 80 °C gave the expected chelate complex  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SC}_3\text{H}_6\text{S})$  (**5**) in isolated yields of ca. 65%. The  $^1\text{H}$  NMR spectrum of **5** at ambient temperature showed two, second-order multiplet resonances (approximate triplet and quintet) assignable to an  $\text{A}_2\text{A}'_2\text{BB}'$  spin system of three adjacent methylene groups of a 6-membered ring lying on an apparent plane of symmetry,

probably resulting from rapid ring inversion, and one singlet resonance assignable to two equivalent  $\eta^5$ -cyclopentadienyl ligands. VT 400 MHz  $^1\text{H}$  NMR spectra of **5** recorded in  $\text{d}_2$ -dichloromethane at temperatures down to  $-80$  °C showed no change in these resonances.



(i)  $\text{MSCH}_2\text{CH}_2\text{CH}_2\text{SM}$ ; (ii)  $\text{MSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SM}$ ; (iii)  $\text{MSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SM}$ .  $\text{M} = \text{Na}$  or  $\text{Tl}$ ; reaction conditions: 1:1 dithiolate: $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  in ethanol,  $\sim 80^\circ\text{C}$ .

Crystallization of **5** from dichloromethane–light petroleum at  $-15$  °C produced crystals suitable for structure determination by X-ray diffraction (XRD). The molecular structure is depicted in Fig. 1 and important geometrical parameters are listed in Table 1. The overall coordination geometry around Mo in the complex is typical pseudo-tetrahedral. The dithiolate ligand is chelating, forming a 6-membered ring in a chair conformation with bond lengths  $\text{Mo}-\text{S}(1)$  and  $\text{Mo}-\text{S}(2)$  of 2.4816(3) and 2.4971(4) Å, respectively, and a bite angle  $\text{S}(1)-\text{Mo}-\text{S}(2)$  of  $87.599(11)^\circ$ . The  $\text{Mo}-\text{S}$  bond lengths lie within the range of  $\text{Mo}-\text{S}$  bonds previously reported for bis(cyclopentadienyl)molybdenum thiolates

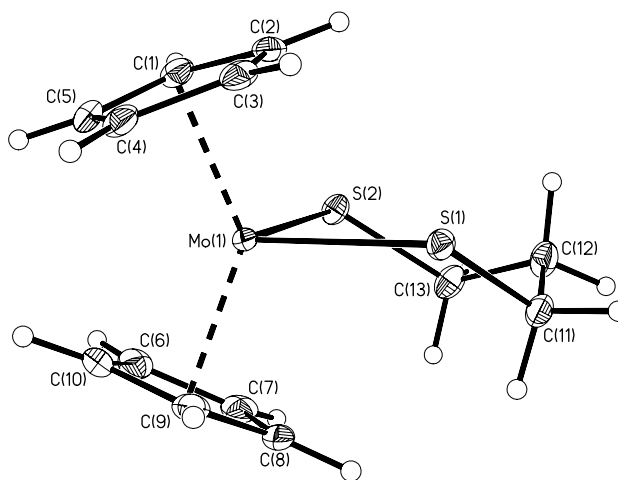


Fig. 1. Molecular structure of compound **5** (50% probability displacement ellipsoids).

Table 1  
Selected bond distances and angles for compounds **5**–**7**

Mo( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> S)		Mo( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (SCH <sub>2</sub> CH <sub>2</sub> S)		Mo( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (SCH <sub>2</sub> CH <sub>2</sub> O) · 4H <sub>2</sub> O	
<b>5</b>		<b>6</b>		<b>7</b>	
Mo(1)–S(1)	2.4816(3)	Mo(1)–S(1)	2.4624(4)	Mo(1)–S(1)	2.4681(15)
Mo(1)–S(2)	2.4971(4)	Mo(1)–S(2)	2.4623(4)	Mo(1)–O(1)	2.097(4)
Mo(1)–Cp(1)	1.9924(2)	Mo(1)–Cp(1)	1.99904(19)	Mo(1)–Cp(1)	1.9976(8)
Mo(1)–Cp(2)	1.98264(16)	Mo(1)–Cp(2)	1.9952(3)	Mo(1)–Cp(2)	1.9939(8)
S(1)–C(11)	1.8184(13)	S(1)–C(11)	1.8435(18)	S(1)–C(12)	1.822(6)
S(2)–C(13)	1.8128(12)	S(2)–C(12)	1.8297(19)	O(1)–C(11)	1.456(7)
		S(1)–C(11A) <sup>a</sup>	1.808(4)		
		S(2)–C(12A) <sup>a</sup>	1.859(4)		
S(1)–Mo(1)–S(2)	87.599(11)	S(1)–Mo(1)–S(2)	82.111(11)	S(1)–Mo(1)–O(1)	79.47(11)
S(1)–Mo(1)–Cp(1)	105.098(8)	S(1)–Mo(1)–Cp(1)	107.145(11)	S(1)–Mo(1)–Cp(1)	107.87(4)
S(2)–Mo(1)–Cp(1)	104.417(9)	S(2)–Mo(1)–Cp(1)	106.188(12)	O(1)–Mo(1)–Cp(1)	109.21(11)
S(1)–Mo(1)–Cp(2)	107.094(10)	S(1)–Mo(1)–Cp(2)	106.958(8)	S(1)–Mo(1)–Cp(2)	107.54(4)
S(2)–Mo(1)–Cp(2)	106.605(10)	S(2)–Mo(1)–Cp(2)	107.429(11)	O(1)–Mo(1)–Cp(2)	105.47(11)
Cp(1)–Mo(1)–Cp(2)	135.648(6)	Cp(1)–Mo(1)–Cp(2)	134.566(7)	Cp(1)–Mo(1)–Cp(2)	133.90(2)
Mo(1)–S(1)–C(11)	113.93(4)	Mo(1)–S(1)–C(11)	106.12(6)	Mo(1)–S(1)–C(12)	113.93(4)
Mo(1)–S(2)–C(13)	112.73(4)	Mo(1)–S(2)–C(12)	104.64(6)	Mo(1)–O(1)–C(11)	112.73(4)
		Mo(1)–S(1)–C(11A) <sup>a</sup>	104.52(13)		
		Mo(1)–S(2)–C(12A) <sup>a</sup>	105.69(14)		

Cp, centroid of cyclopentadienyl ring (Cp(1), C(1)–C(5); Cp(2), C(6)–C(10)).

<sup>a</sup> Parameters for minor conformer (30%).

(2.424–2.505 Å) [19]. The angle S(1)–Mo–S(2) is larger than reported for other molybdocene(IV) derivatives, with exception of the inorganic 5-membered tetrasulfur ring in Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(S<sub>4</sub>), 88.2° [26]; simple derivatives Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(SR)<sub>2</sub> have significantly more acute angles, 71–73° [19,20], and bite angles for complexes with planar 5-membered dithiolene rings are ca. 81–82° [16,17,21]. The crystal structure of the d<sup>1</sup> compound Nb( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(SC<sub>3</sub>H<sub>6</sub>S) has recently been determined [27] and it has a very similar geometry to **5**, containing a NbSC<sub>3</sub>S ring in a chair conformation with Nb–S.

In an early theoretical study [28], supported by structural data [29], Lauher and Hoffmann concluded that X–M–X angles in derivatives M( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>X<sub>2</sub> should increase as the d-electron occupation decreases: d<sup>2</sup> (ca. 76–82°), d<sup>1</sup> (ca. 85–88°), d<sup>0</sup> (ca. 94–97°). The large S–Mo–S angle for d<sup>2</sup> compound **5** and its similarity to the d<sup>1</sup> niobium analogue is presumably largely determined by the steric constraints of the 6-membered chelating ring and the optimum Mo–S bond lengths. However, it should be noted that the 1,3-propanedithiolate ligands in the d<sup>0</sup> species Nb( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(SC<sub>3</sub>H<sub>6</sub>S)<sub>2</sub> [25] and [Nb(SC<sub>3</sub>H<sub>6</sub>S)<sub>3</sub>]<sup>−</sup> [30] adopt a twist (skew-boat) conformation with shorter Nb–S bonds and smaller bite angles (83–86°). Also, in contrast to compound **5**, the structurally-characterized 1,3-propanedithiolate complex of d<sup>0</sup> bis(cyclopentadienyl)zirconium(IV), [Zr( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>( $\mu$ -SC<sub>3</sub>H<sub>6</sub>S)]<sub>2</sub>, is binuclear and contains a 12-membered open macrocycle in which the S–Zr–S angles are 99.87(5)° and 100.86(6)° and the mean Zr–S bond length is 2.504 Å [31]; this macrocyclic compound acts as a metalloligand and encapsulates Ag(I) cations in a pseudo-tetrahedral site.

In the solid-state structure, *axial* and *equatorial* hydrogens of the dithiolate ring of **5** are chemically and magnetically inequivalent, as are the hydrogens of the two cyclopentadienyl ligands, so that the <sup>1</sup>H NMR spectrum of a rigid system should be more complex than observed at −80 °C; such inequivalency is generally observed in NMR spectra of cyclohexane derivatives at low temperatures, with activation barriers to exchange of >40 kJ mol<sup>−1</sup> [32]. Therefore, unless the resonances of these hydrogen nuclei overlap, it appears that *axial/equatorial* interconversion in compound **5** must be fast on the NMR timescale with a low barrier to ring inversion. In contrast, the twist (skew-boat) forms of chelating 1,3-propanedithiolates in Nb( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(SC<sub>3</sub>H<sub>6</sub>S)<sub>2</sub> show typical coalescence behaviour of the methylene H-resonances in VT NMR spectra and the activation free energy for inversion has been calculated as ca. 43 kJ mol<sup>−1</sup> at 230 K [25].

## 2.2. Reactions of 2,2'-thiodiethanethiol and 2,2'-oxydiethanethiol

Reaction of **1** in ethanol either with an equimolar quantity of 2,2'-thiodiethanethiol (**3**) in the presence of two moles of sodium ethoxide or with the dithallium derivative of **3** at 80 °C gave a number of products, but chromatography on alumina separated the 1,2-ethanedithiolate compound, Mo( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>S) **6**, as the main species in ca. 70% isolated yield. Compound **6** results from thioether bond cleavage of the dithiol **3**, probably assisted by the Mo(IV) centre. The preferred formation of a stable 5-membered chelate ring

must be a driving force for this C–S bond-cleavage reaction, rather than production of the expected mononuclear compound with an 8-membered ring (which was not detected) or of higher nuclearity species with bridging ligands. (It is possible that the latter may be present, as well as terminal monodentate thiolates, in the minor products eluted after compound **6** from the chromatographic column; these impure products showed complex  $^1\text{H}$  NMR spectra and were uncharacterized.) The preparative reaction was repeated at lower temperatures: at 20 °C the reaction was too slow, giving negligible conversion; reactions at 30–40 °C or 50–60 °C, over 3 h, led to increased conversions but, as at 80 °C, compound **6** was the major product. In contrast, it should be noted that dithiol **3** reacts under similar conditions with  $\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_4$  to give  $\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2\{\mu\text{-(SCH}_2\text{CH}_2)_2\text{S}\}$  containing the uncleaved dithiol [25], but acting as a tridentate ligand; also, titanocene and zirconocene compounds containing the uncleaved ligand are known as mononuclear or binuclear species, e.g.,  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\mu\text{-(SCH}_2\text{CH}_2)_2\text{S}\}]_2$  [31a]. The isolated molybdenum product **6** has been previously prepared by direct reaction from 1,2-ethanedithiol but has not been structurally characterized [2,7].

The structure of **6** has been determined by XRD on a single crystal obtained from dichloromethane–light petroleum. There are two closely related conformations of this molecule in the crystal, in relative proportions 70% and 30%, differing only in minor aspects of the geometry of the chelate ring. Both have typical pseudo-tetrahedral geometry and the 5-membered rings adopt envelope conformations. In the major conformer, C(12) is 0.708(4) Å out of the S(2)MoS(1)C(11) plane (rms deviation of fitted atoms = 0.0488 Å); see Fig. 2 and Table 1 for important geometrical parameters. In the minor conformer, C(11A) is 0.698(8) Å out of the S(1)MoS(2)C(12A) plane (rms deviation = 0.0515 Å) and the other parameters are identical to those of the other form. Mo–S(1) and Mo–S(2) bond lengths are 2.4624(4) and 2.4623(4) Å, respectively, and the S(1)–Mo–S(2) angle is 82.111(11)°. The S–Mo–S angle is more acute than in compound **5** and in the range predicted range for  $d^2$  systems but is still greater than observed for compounds  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$  containing monodentate thiolate ligands and the angle may be largely determined by the geometry of the 5-membered ring. It should be noted that attempts to prepare the analogous  $d^1$  niobium compound  $\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{S})$  have been unsuccessful but structures of this species and the corresponding  $d^0$  cation have been proposed on the basis of Hartree–Fock/ECP calculations [27]: in the  $d^1$  species the S–Nb–S angle is calculated to be 82.1°, similar to that of the  $d^2$  molybdenum compound **6**, but the ethanedithiolate chelate prefers a twist rather than an envelope conformation. The  $^1\text{H}$  NMR spectrum of

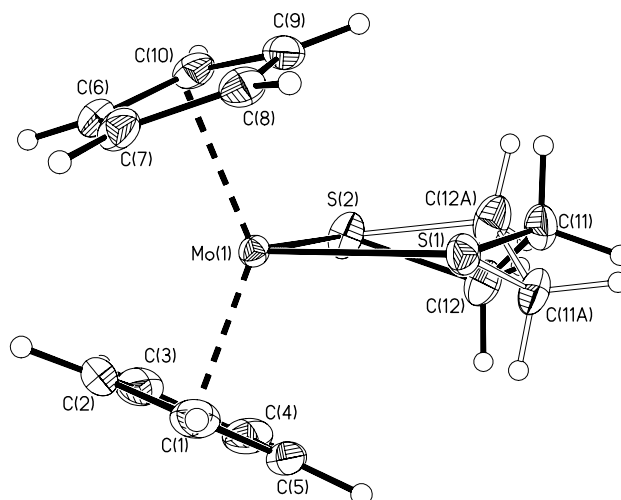


Fig. 2. Molecular structure of compound **6** {50% probability displacement ellipsoids; C(11A) and C(12A) from minor conformer (30%)}.

compound **6** in solution shows a singlet resonance for the four methylene-hydrogens of the dithiolate ligands, even at low temperatures, and this is consistent with facile 5-membered ring inversion and low energy barriers between ring conformations (cf. [7]). It is also of interest that the zirconocene–ethanedithiolate derivative has only been isolated and structurally characterized as binuclear  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-SCH}_2\text{CH}_2\text{S})]_2$  with unsymmetrical thiolate bridges [31b].

Reaction of **1** in ethanol with an equimolar quantity of the sodium or thallium derivative of 2,2'-oxydiethanethiolate (**4**), under similar conditions to those described for reactions with dithiol **3**, gave  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O})$  **7** as the main product, obtained after chromatography. Again, the ligand has been cleaved; in this case C–O rather than C–S bond cleavage has occurred to produce an O, S-chelate. This reaction is also probably assisted by the Mo(IV) centre and facilitated by the formation of a stable 5-membered metallocycle. The product has not been previously reported but the tungsten analogue,  $\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O})$ , has been mentioned, without details, as a by-product in reactions of 2-hydroxyethanethiol [4]. Compound **7** was characterized by  $^1\text{H}$  NMR (including two triplet resonances, 1.98 and 3.58 ppm, for the two methylene groups, consistent with a rapid inversion of the chelate ring) and by XRD, although the crystals readily incorporated water molecules which may be introduced via the ethanol solvent and/or during chromatography.

In contrast to the above reaction, we found that equimolar amounts of compound **1** with sodium or thallium derivatives of 3,6-dioxa-1,8-octanedithiol under similar reaction conditions to those employed for dithiol **4** yielded neither the cleavage product **7** nor



$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\{\text{SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{S}\}$ , containing an 11-membered macrocycle; products obtained, after chromatography using dichloromethane-ethanol mixtures as eluent, were oils which included the 1:2 compound  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\{\text{SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{SH}\}_2$  with monodentate ligands, but not isolated in pure form. Although C–O bond cleavage of the 3,6-dioxa-1,8-octanedithiol chain to form the 5-membered  $\text{SCH}_2\text{CH}_2\text{O}$  chelate ligand, as observed for the shorter 3-oxa-1,5-pentanedithiol system **4**, appears to be feasible, the absence of this reaction may be attributable to steric hindrance of the longer ligand to a metal-assisted mechanism. It is also of interest that reaction of  $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  with the even longer dithiolate, 3,6,9-trioxa-1,11-undecanedithiolate, has previously been reported to give the tungsten complex  $\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{SCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{S}\}$  containing a 14-membered ring, albeit in only 10% yield [4].

The tendency of compound **7** to hydration is particularly notable in the production of single crystals of stoichiometry  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O}) \cdot (4.5\text{H}_2\text{O})$  from a sample that had been exposed to water during chromatography and these were structurally characterized by XRD. The hydrate exhibits an interesting layer structure in the crystalline state. The molecular unit  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O})$  occurs as a single conformer with a similar structure to that of compound **6** in which the chelate ring adopts an envelope conformation with C(11) displaced 0.585(9) Å out of the O(1)Mo(1)S(1)C(12) plane (rms deviation of fitted atoms = 0.0124 Å); see Fig. 3 and Table 1 for important geometric parameters. The Mo–S and Mo–O distances are 2.4681(15) and 2.097(4) Å, respectively, and the O–Mo–S angle of 79.47(11)° is slightly more acute than the corresponding S–Mo–S angle of **6** but within the expected range. In the lattice, two molecules

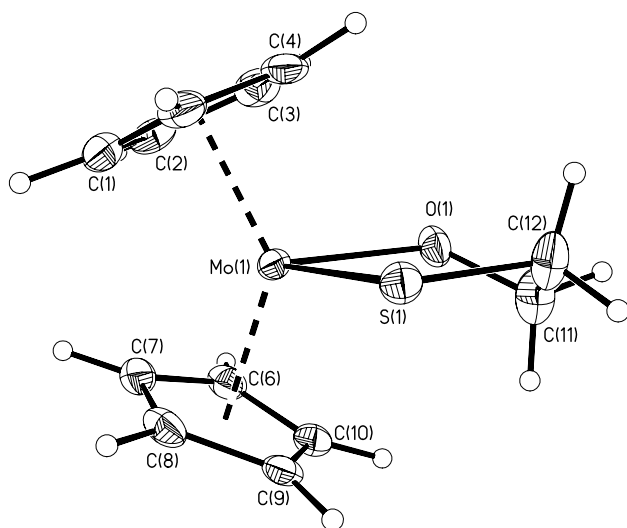


Fig. 3. Molecular structure of compound **7** (50% probability displacement ellipsoids).

of **7** are connected by a single water molecule (13S) hydrogen-bonded to the S-atoms {H(13S)··S(1) 2.35(2) Å; O(13S)··S(1) 3.227(4) Å; O(13S)–H(13S)–S(1) 169(7)°} and this water also interacts (weakly) with cyclopentadienyl C–H groups on these and two other molecules of the complex (O(13S)··H distances 2.561 and 2.377 Å); this generates a double layer of interconnected organometallic molecules lying with O-atoms of the chelating ligand pointing outwards (see Fig. 4(a)). The other water molecules occupy a second layer in the structure. Within this second layer there are four differing water molecules: two molecules lie at the periphery and are hydrogen-bonded to O(1) atoms of the organometallic as well as to the other waters; the other two molecules are in the centre of the layer and all are interconnected by H-bonds. Overall, the lattice contains alternating double layers of molybdenum complex and layers of water molecules (see Fig. 4(b)), and bears some resemblance to the

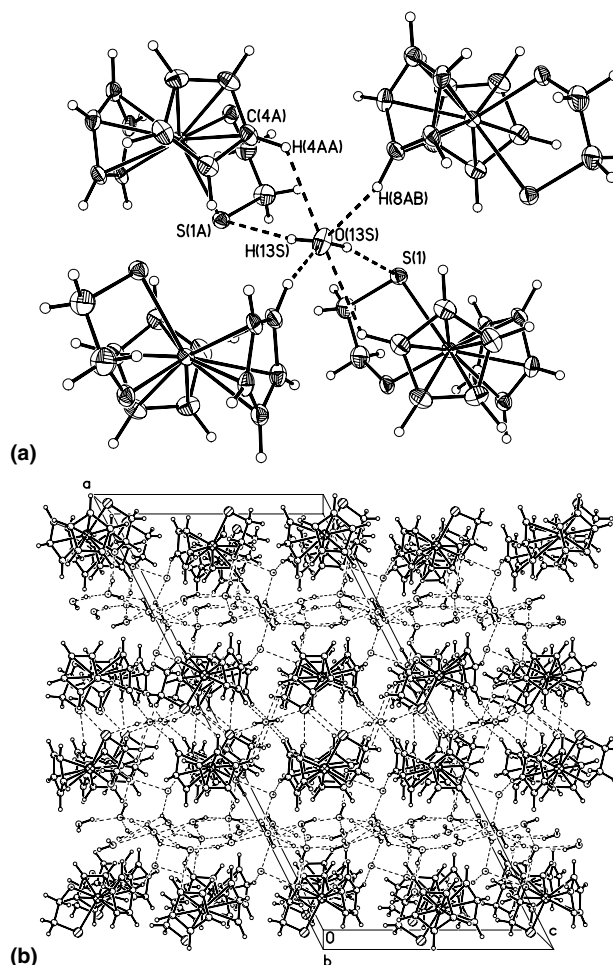


Fig. 4. Crystal structure of compound **7**: (a) environment around water (13S) enclosed by organometallic molecules; (b) extended structure showing alternating double layers of organometallic complexes and layers of other water molecules.

structures of clay-type minerals. This arrangement is unusual for an organometallic compound, and unprecedented for thiolate derivatives of early transition metals which are generally readily susceptible to hydrolysis.

### 3. Conclusions

Reactions of bis(cyclopentadienyl)molybdenum dichloride **1** with 1,3-propanedithiol derivatives give the expected dithiolate complex **5** containing a 6-membered chelating ring with a chair conformation. However, reactions involving the longer dithiols, 2,2'-thiodiethanethiol **3** or 2,2'-oxydiethanethiol **4**, under similar, relatively mild conditions do not produce dithiolate complexes with 8-membered rings but lead to cleavage of thioether or ether bonds of the ligands form complexes **6** and **7**, respectively, containing 5-membered rings. These apparently facile cleavages to form more stable chelates are probably assisted by the Mo(IV) metal centre; on the other hand, 3,6-dioxa-1,8-octanedithiol, in which dithiol **4** is extended by insertion of an additional ethylenoxy link, showed no evidence for a related cleavage to produce the complex  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{CH}_2\text{O})$  **7** and this may be attributed to the steric effect of the longer chain. Complex **7** in the solid-state readily includes water and a highly hydrated form of stoichiometric formula  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_2\text{-CH}_2\text{O}) \cdot 4.5\text{H}_2\text{O}$  has a novel crystal structure containing alternating layers of organometallic and water molecules.

### 4. Experimental

#### 4.1. General

Reactions and operations were conducted under an atmosphere of nitrogen gas, using Schlenk techniques. Although petroleum ether and dichloromethane were dried and freshly distilled before use, reagent-grade ethanol and methanol were used as supplied and probably contained some water. Light petroleum ether had a boiling range of 60–80 °C.  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$  was prepared by a literature method [33]. 1,3-Propanedithiol, 2,2'-thiodiethanethiol, 2,2'-oxydiethanethiol, 3,6-dioxa-1,8-octanedithiol and thallium(I) acetate were obtained commercially (Aldrich) and used as supplied; thallium dithiolates were obtained as precipitates by reaction of excess thallium(I) acetate with the appropriate dithiol in methanol. The  $^1\text{H}$  NMR spectra were recorded on a Bruker AC 200 spectrometer (at ca. 17 °C) and, in some cases, on a DPX 400 spectrometer (at variable temperatures, as stated) using  $\text{SiMe}_4$  as internal reference. Elemental analyses were carried out at Heriot-Watt University.

#### 4.2. Synthesis and characterization

##### 4.2.1. General procedure from dithiol and sodium ethoxide

A solution of the appropriate dithiol, **2**, **3** or **4** (1.35 mmol) in ethanol (20 cm<sup>3</sup>), which contained sodium ethoxide formed by prior reaction with sodium metal (0.064 g; 2.8 mmol), was added dropwise to a stirred suspension of bis(cyclopentadienyl)molybdenum dichloride **1** (0.400 g, 1.35 mmol) in boiling ethanol (30 cm<sup>3</sup>). The combined mixture was then heated under reflux for a further 30 min. After cooling, the solvent was removed in vacuo and the solid product was purified by column chromatography on neutral alumina using dichloromethane:ethanol (10:1) as eluent. (In one reaction of dithiol **4**, from which the hydrated product subjected to XRD analysis was obtained, water (2 cm<sup>3</sup>) was added to the column to accelerate the chromatography after a clear separation of the red product-band had been developed using dichloromethane; final elution was achieved with dichloromethane.) The main band was eluted, collected and the product recrystallized from dichloromethane-light petroleum to a yield brown/red crystalline solid.

##### 4.2.2. General procedure from thallium dithiolate

The thallium derivative of the appropriate dithiol, **2**, **3** or **4** (1.35 mmol) suspended in ethanol (20 cm<sup>3</sup>) was added to a stirred suspension of bis(cyclopentadienyl)molybdenum dichloride **1** (0.400 g, 1.35 mmol) in ethanol (30 cm<sup>3</sup>). The stirred mixture was then heated under reflux for for 30 min. After cooling, the solvent was removed under vacuum and the soluble product was extracted from the resulting solid with dichloromethane. Chromatography and recrystallization of this product, as described above, afforded the same brown/red solid.

##### 4.2.3. $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SC}_3\text{H}_6\text{S})$ (**5**)

Brown crystalline solid, ca. 65%. Found: C, 46.41; H, 4.81%;  $\text{C}_{13}\text{H}_{16}\text{MoS}_2$  requires C, 46.98; H, 4.85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  2.04 {m (2nd order ~ quin), 2H,  $\text{SCH}_2\text{CH}_2$ }, 2.28 {m (2nd order ~ t, 6.0 Hz) 4H,  $\text{SCH}_2$ }, 5.10 (s, 10H,  $\text{C}_5\text{H}_5$ ).

##### 4.2.4. $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SC}_2\text{H}_4\text{S})$ (**6**)

Red crystalline solid, ca. 70%. Found: C, 44.95; H, 4.46%;  $\text{C}_{12}\text{H}_{14}\text{MoS}_2$  requires C, 45.28; H, 4.43%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  2.37 (s, 4H,  $\text{SCH}_2$ ), 5.12 (s, 10H,  $\text{C}_5\text{H}_5$ ).

##### 4.2.5. $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SC}_2\text{H}_4\text{O})$ (**7**)

Red crystalline solid, ca. 70%. Found: C, 45.85; H, 4.49%;  $\text{C}_{12}\text{H}_{14}\text{MoOS} \cdot 0.5\text{H}_2\text{O}$  requires C, 46.31; H, 4.86%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  1.98 (t, 5.4 Hz, 2H,  $\text{SCH}_2$ ), 3.58 (t, 5.4 Hz, 2H,  $\text{OCH}_2$ ), 5.28 (s, 10H,  $\text{C}_5\text{H}_5$ ); also,  $\delta$  1.6 (variable,  $\text{H}_2\text{O}$ ).

Table 2  
Crystal and structure refinement data for compounds 5–7

	5	6	7 · 4.5H <sub>2</sub> O
Empirical formula	C <sub>13</sub> H <sub>16</sub> MoS <sub>2</sub>	C <sub>12</sub> H <sub>14</sub> MoS <sub>2</sub>	C <sub>12</sub> H <sub>23</sub> MoO <sub>5.5</sub> S
Formula weight	332.32	318.29	383.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	7.7601(8)	7.5867(10)	31.419(13)
<i>b</i> (Å)	13.7648(14)	13.0582(18)	7.686(3)
<i>c</i> (Å)	11.6815(12)	11.8446(15)	14.200(6)
$\beta$ (°)	94.245(5)	95.664(6)	116.87
Volume (Å <sup>3</sup> )	1244.4(2)	1167.7(3)	3059(2)
<i>Z</i>	4	4	8
Absorption coefficient (mm <sup>-1</sup> )	1.358	1.442	1.010
<i>F</i> (000)	672	640	1576
Crystal size (mm <sup>3</sup> )	0.42 × 0.30 × 0.12	0.35 × 0.28 × 0.15	0.38 × 0.28 × 0.15
$\theta$ Range for data collection (°)	2.96–36.46	2.33–37.39	2.75–30.55
Reflections collected	16233	63304	11078
Independent reflections [ <i>R</i> <sub>int</sub> ]	5889 [0.0220]	5710 [0.0287]	4126 [0.0855]
Data/restraints/parameters	5889/0/145	5710/0/155	4126/7/198
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.064	0.947
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0225, <i>wR</i> <sub>2</sub> = 0.0531	<i>R</i> <sub>1</sub> = 0.0215, <i>wR</i> <sub>2</sub> = 0.0534	<i>R</i> <sub>1</sub> = 0.0619, <i>wR</i> <sub>2</sub> = 0.1417
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0306, <i>wR</i> <sub>2</sub> = 0.0553	<i>R</i> <sub>1</sub> = 0.0270, <i>wR</i> <sub>2</sub> = 0.0548	<i>R</i> <sub>1</sub> = 0.0957, <i>wR</i> <sub>2</sub> = 0.1480

#### 4.3. X-ray data collection and crystal structure determination

Single crystals of compounds 5–7 were grown by slow diffusion of light petroleum into solutions of the compound in dichloromethane at –15 °C. For X-ray data collection, single crystals in Paratone-N oil were mounted on a glass fibre and intensity data were collected on a Bruker Nonius X8 Apex diffractometer at 100(2)K, cooled by an Oxford Cryosystems Cryostream, using graphite-monochromated Mo K $\alpha$  radiation (0.71073 Å). All structures were solved using direct methods, refined using full-matrix least squares against *F*<sup>2</sup> (SHELXTL) [34] and corrected for absorption by using symmetry related measurements (SADABS). Further details are given in Table 2.

Hydrogen atom positions were calculated and constrained to idealised geometries during refinement, except water hydrogen atoms which were located in the difference map and subject to restrained O–H distances. [0.89(2) Å]. No H atoms were located for water molecule O15S.

#### 5. Supplementary material

Crystallographic information files (CIF) have been deposited with Cambridge Crystallographic Data Centre: CCDC reference numbers 241347, 241348 and 241349 for 5, 6 and 7, respectively. Copies of this information can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 3336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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