

Note

# Reduction of $[\text{Cp}_2^*\text{Mo}_2\text{O}_5]$ by mercaptopropionic acid in an aqueous medium. Isolation and characterization of a dinuclear oxo- and 3-sulfido-propionato(2-)-bridged molybdenum(IV) compound

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## Abstract

Reaction of  $\text{Cp}_2^*\text{Mo}_2\text{O}_5$  with  $\text{HSCH}_2\text{CH}_2\text{COOH}$  in acidic (by  $\text{CF}_3\text{COOH}$ ) 50:50 MeOH– $\text{H}_2\text{O}$  solvent at room temperature yields compound  $\text{Cp}_2^*\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)_2$ , a dinuclear diamagnetic  $\text{Mo}^{\text{IV}}$  compound with a two-leg-sharing bis(four-legged piano stool) structure and a Mo–Mo distance of 2.6833(6) Å. A reaction monitoring by ESI MS shows the formation of an intermediate 18 mass units heavier, interpreted as a dihydroxo analogue. Electrochemistry shows a reversible, pH independent oxidation process and an irreversible, pH-dependent reduction process. Contrary to a recently published analogous reaction with the closely related  $\text{HSCH}_2\text{COOH}$  substrate, this process does not lead to C–S bond cleavage.

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## 1. Introduction

Aqueous organometallic chemistry is attracting growing interest because of its “green” impact [1–3] and because of its potential in catalytic [4,5] and biomedical applications [6]. Although this area is widely explored for low-valent systems, usually upon appending hydrophilic functionalities to the ligand periphery in order to increase solubility in an aqueous environment [7–9], studies of high oxidation organometallics are still rather scarce [10]. For redox-active metals, these studies are particularly interesting as they may open the way to electrocatalytic applications [10].

In a recent contribution [11], we have reported the result of the interaction between compound  $[\text{Cp}_2^*\text{Mo}_2\text{O}_5]$  and

mercaptopropionic (or thioglycolic) acid,  $\text{HSCH}_2\text{COOH}$ , which resulted in the isolation and characterization of the dinuclear  $\text{Mo}^{\text{IV}}$  product  $[\text{Cp}_2^*\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{COO})_2]$ . In this reaction, the mercaptopropionic acid exerts three simultaneous functions: reducing agent, ligand, and substrate for the reductive cleavage of the S–C bond (leading to the incorporation of the sulfur atom in the isolated product as a bridging sulfido ligand). This phenomenon, which is common to other Mo-mediated C–S bond cleavage reactions [12–17], mimics a step of the hydrodesulfurization process, which is in fact typically catalyzed by molybdenum–sulfur compounds [18–21]. We were interested in probing the generality of this reaction and proceeded to explore the reaction with mercaptopropionic acid,  $\text{HSCH}_2\text{CH}_2\text{COOH}$ , which contains an additional methylene unit between the acid and the mercapto functions relative to mercaptopropionic acid. The outcome of this reaction, which is unexpectedly

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different from that of the lighter analogue, is reported and discussed in this contribution.

## 2. Experimental

### 2.1. General procedures

All preparations and manipulations were carried out with Schlenk techniques under an oxygen-free argon atmosphere. All glassware was oven-dried at 120 °C. Solvents were dried by standard procedures and distilled under dinitrogen prior to use. <sup>1</sup>H NMR spectra were recorded on a Bruker AM 250, operating at 250 MHz. Chemical shifts are expressed in ppm downfield from Me<sub>4</sub>Si. Coupling constants are given in Hertz. The 2D-COSY spectrum were recorded on a Bruker Avance 500, operating at 500 MHz. Mass spectra were recorded with a Finnigan (San Francisco, USA) LCQ quadrupole ion-trap mass spectrometer equipped with an electrospray-ionization (ESI) interface. The ESI was operated in the positive-ion mode with a spray voltage of 4.0 kV, a capillary voltage of 5.5 V, and a source temperature of 100 °C. Mass spectra were obtained by scanning the mass analyzer from *m/z* 100 to 2000 with a total of 3 microscans. The maximum injection time into the ion trap was 25 ms. The analyzer was operated at a background pressure of  $2 \times 10^{-5}$  Torr. The compounds were isolated in the ion trap with isolation width of 15 *m/z* units and were activated by using increased collision energy to obtain the sequential product-ion fragmentation by collision-energy-dissociation [22,23]. The starting compound, [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>O<sub>5</sub>], was prepared as described in the literature [24]. The 3-mercaptopropionic acid (99%, ACROS) and the trifluoroacetic acid (99%, ACROS) were used as received. Cyclic voltammograms were recorded with an EG& G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software. The electrochemical cell was fitted with an Ag–AgCl(KCl sat) reference electrode, a platinum disk working electrode for aprotic solvents or glassy carbon disk electrode for H<sub>2</sub>O–MeOH solution, and a platinum wire counter-electrode. [Bu<sub>4</sub>N]PF<sub>6</sub> (ca. 0.1 M) was used as supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub> whereas NH<sub>4</sub>Ac (0.1 M) was used as a supporting electrolyte in addition to buffer solutions at different pH in MeOH–H<sub>2</sub>O. All potentials are reported relative to the ferrocene standard, which was added to each solution and measured at the end of the experiments. EPR measurements were carried out at the X-band microwave frequency on a Bruker ESP300 spectrometer. The spectrometer frequency was calibrated with diphenylpicrylhydrazyl (DPPH, *g* = 2.0037).

### 2.2. Preparation of [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>](μ-O)

HSCH<sub>2</sub>CH<sub>2</sub>COOH (0.392 g, 3.69 mmol) and nine drops of CF<sub>3</sub>COOH were added to a solution of Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>O<sub>5</sub> (0.200 g, 0.369 mmol) in MeOH:H<sub>2</sub>O (1:1, 5 ml), resulting in a color change from yellow to red–brown. After 3 h of

stirring, all solvents were removed in vacuum and the oily residue was washed with  $2 \times 5$  ml of oxygen-free distilled water and with  $2 \times 5$  ml of pentane. The resulting red–brown residue was extracted with THF, followed by addition of pentane to yield a brown precipitate which was filtered and isolated (0.127 g, 38% yield). The product is soluble in CH<sub>2</sub>Cl<sub>2</sub> and THF, insoluble in Et<sub>2</sub>O and saturated hydrocarbons. The NMR of the isolated product showed only the presence of the title compound, but the presence of a paramagnetic impurity, which could not be crystallized in pure form, was revealed by EPR spectroscopy in CDCl<sub>3</sub> (*g* = 1.97, *a*<sub>Mo</sub> = 41.6 G). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) revealed extensive overlap between the methylene protons of the ligand and those in a co-crystallized HOOCCH<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>COOH molecule (also revealed by the X-ray analysis on a single crystal). The assignment was aided by a 2D-COSY analysis (see Section 3). For the dinuclear Mo complex: δ 2.96 (m, 1H, H<sub>a</sub>), 2.65 (m, 1H, H<sub>b</sub>), 2.59 (m, 1H, H<sub>c</sub>), 1.93 (s, 15H, Cp<sup>\*</sup>), 1.87 (m, 1H, H<sub>d</sub>). For the disulfide by-product: δ 2.99 (t, *J* = 7.1 Hz), 2.81 (t, *J* = 7.2 Hz). Subsequent recrystallizations of the crude material did not completely remove the paramagnetic impurity (as shown by EPR spectroscopy), a possible reason for the imperfect analytical results: calculated for C<sub>32</sub>H<sub>48</sub>Mo<sub>2</sub>O<sub>9</sub>S<sub>4</sub> (896.86): C, 42.8; H, 5.4. Found: C, 42.1; H, 4.8%. A single crystal for the X-ray analysis was obtained by diffusion of a pentane layer into a brown CH<sub>2</sub>Cl<sub>2</sub> solution of the crude reaction product at room temperature.

### 2.3. X-ray diffraction study

A single crystal of the compound was mounted under inert perfluoropolyether on the tip of glass fibre and cooled in the cryostream of the Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the monochromatic Mo Kα radiation (*λ* = 0.71073). The structure was solved by direct methods (SIR97) [25] and refined by least-squares procedures on *F*<sup>2</sup> using SHELXL-97 [26]. All H atoms attached to carbon and oxygen (OH) were introduced in calculation in idealized positions and treated as riding on their parent atoms. The drawing of the molecules was realized with the help of ORTEP32 [27]. Crystal data and refinement parameters are shown in Table 1 and selected bond distances and bond angles in Table 2.

## 3. Results and discussion

The reaction between Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>O<sub>5</sub> and HSCH<sub>2</sub>CH<sub>2</sub>COOH qualitatively appeared to follow the same course as the previously described reaction with the related substrate HSCH<sub>2</sub>COOH [11], under identical experimental conditions (room temperature in a 1:1 H<sub>2</sub>O–MeOH mixture, acidified with CF<sub>3</sub>COOH), as suggested by the colour change and the <sup>1</sup>H NMR spectrum of the final product. However, crystallization of the product and

Table 1  
Selected crystallographic and refinement parameters for compound  
[Cp<sub>2</sub>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>] · (HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>COOH)

Empirical formula	C <sub>32</sub> H <sub>48</sub> Mo <sub>2</sub> O <sub>9</sub> S <sub>4</sub>
Formula weight	896.82
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 8.6819(9) Å, <i>α</i> = 85.526(7)° <i>b</i> = 14.2934(12) Å, <i>β</i> = 73.494(8)° <i>c</i> = 15.8121(14) Å, <i>γ</i> = 86.910(7)°
Volume	1874.6(3) Å <sup>3</sup>
Z	2
Density (calculated)	1.589 Mg/m <sup>3</sup>
Absorption coefficient	0.941 mm <sup>-1</sup>
<i>F</i> (000)	920
Crystal size	0.42 × 0.11 × 0.063 mm <sup>3</sup>
Theta range for data collection	2.85–30.44°
Index ranges	−12 ≤ <i>h</i> ≤ 12, −20 ≤ <i>k</i> ≤ 20, −22 ≤ <i>l</i> ≤ 19
Reflections collected	19 719
Independent reflections	11 259 [ <i>R</i> <sub>int</sub> = 0.0477]
Completeness to theta = 30.40°	98.1%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.9149 and 0.7873
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	11 259/0/435
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.931
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0464, <i>wR</i> <sub>2</sub> = 0.1016
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0948, <i>wR</i> <sub>2</sub> = 0.1325
Largest differences in peak and hole	1.076 and −1.228 e Å <sup>-3</sup>

determination of its molecular structure by single crystal X-ray diffraction yielded a surprising result: the product corresponds to the formulation [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>-

CH<sub>2</sub>COO)<sub>2</sub>] and therefore features an oxo bridge, whereas the analogous reaction with the mercaptoacetic acid yielded the sulfur bridged derivative, [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-S)(μ-SCH<sub>2</sub>COO)<sub>2</sub>] [11].

A reaction monitoring by electrospray mass spectrometry revealed that, in fact, the primary reaction product has a molecular mass 18 units greater (*m/z* = 704.7). The isotopic envelope corresponding to this intermediate decreases as the reaction progresses, accompanied by the increase of the product isotopic envelope (*m/z* = 687.0), as shown in Fig. S1 (Supporting Information). The observed peaks have one mass unit greater than the neutral solution species, because of the addition of a proton from the medium. Thus, the final envelope corresponds to species [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub> + H<sup>+</sup>]. The conversion of the intermediate into the final product is likely an intramolecular process, because an MS/MS investigation (collision induced decay of the intermediate with maximum at *m/z* = 705) shows that the same transformation also occurs cleanly in the gas phase. An MS/MS study of the isolated product peaks (Fig. 1) reveals various decay patterns, the major ones corresponding to a single and a double loss of 72 mass units. This is easily interpreted as the loss of CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub> units from the mercaptopropionato(2-) ligand, leaving a sulfido bridge on the dinuclear complex. MS/MS/MS on the peak resulting from the first CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub> loss (at *m/z* 615), also shown in Fig. 1, mostly yields the second CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub> expulsion product. The presence of two envelopes 16 *m/z* units lighter than the above fragments (at *m/z* 599 and 529, respectively) is unlikely due to subsequent oxygen atom expulsion. Rather, these peaks could correspond to minor fragmentation pathways involving the elimination of SCH<sub>2</sub>CH<sub>2</sub>CO (*m/z* 88), thereby leaving an oxo bridge on the dinuclear complex.

Table 2  
Selected bond distances (Å) and angles (°) for compound [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>] · (HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>COOH)<sup>a</sup>

Mo(1)–O(1)	1.926(3)	Mo(2)–O(1)	1.933(3)
Mo(1)–CG1	2.0205(4)	Mo(2)–CG2	2.0222(4)
Mo(1)–O(61)	2.056(3)	Mo(2)–O(31)	2.078(3)
Mo(1)–S(1)	2.4506(11)	Mo(2)–S(1)	2.4545(11)
Mo(1)–S(2)	2.4633(11)	Mo(2)–S(2)	2.4439(11)
Mo(1)–Mo(2)	2.6833(6)		
O(1)–Mo(1)–CG1	109.68(9)	O(1)–Mo(2)–CG2	109.22(9)
O(1)–Mo(1)–S(1)	72.39(9)	O(1)–Mo(2)–S(2)	72.42(9)
CG1–Mo(1)–S(1)	124.79(3)	CG2–Mo(2)–S(2)	124.60(3)
O(61)–Mo(1)–S(1)	87.34(9)	O(31)–Mo(2)–S(2)	86.62(8)
O(1)–Mo(1)–S(2)	72.06(9)	O(1)–Mo(2)–S(1)	72.20(9)
CG1–Mo(1)–S(2)	121.07(3)	CG2–Mo(2)–S(1)	120.57(3)
O(61)–Mo(1)–S(2)	86.60(8)	O(31)–Mo(2)–S(1)	86.77(8)
S(1)–Mo(1)–S(2)	112.04(4)	S(2)–Mo(2)–S(1)	112.58(4)
CG1–Mo(1)–Mo(2)	155.67(2)	CG2–Mo(2)–Mo(1)	154.99(2)
O(61)–Mo(1)–Mo(2)	95.41(8)	O(31)–Mo(2)–Mo(1)	94.98(8)
O(1)–Mo(1)–O(61)	141.46(12)	O(1)–Mo(2)–O(31)	140.83(12)
CG1–Mo(1)–O(61)	108.81(8)	CG2–Mo(2)–O(31)	109.92(8)
Mo(1)–S(1)–Mo(2)	66.33(3)	Mo(2)–S(2)–Mo(1)	66.29(3)
Mo(1)–O(1)–Mo(2)	88.09(12)		

<sup>a</sup> CG1 and CG2 are the centers of gravity of the Cp<sup>\*</sup> rings (calculated on the basis of atoms C11–C15 and C21–C35, respectively).

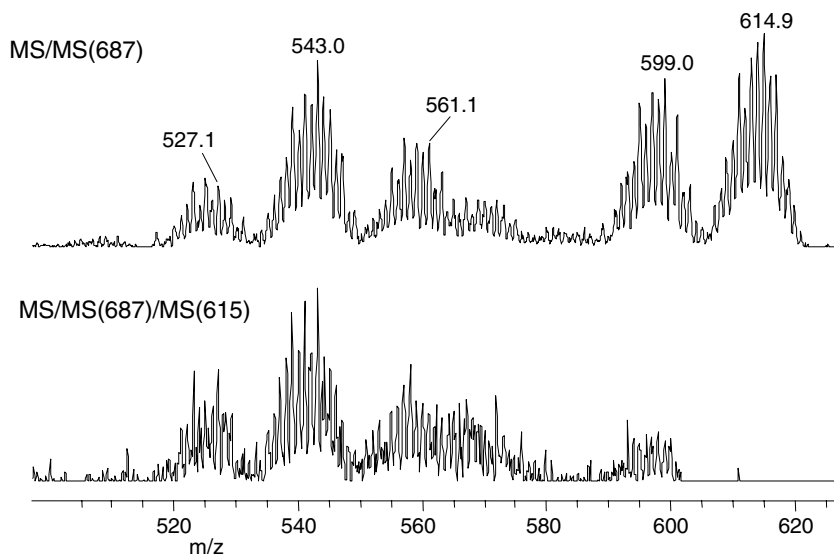
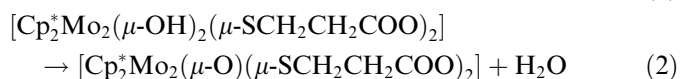
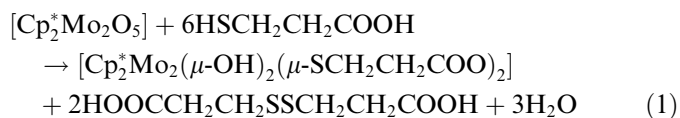


Fig. 1. MS<sup>n</sup> studies of the fragmentation pattern of compound [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>] + H<sup>+</sup> (peak at *m/z* = 687). Relative collision energy at every step is 15%.

The fragment of mass 18 lost during the transformation of intermediate to product must of course correspond to a water molecule. Thus, the likely stoichiometry of the intermediate is [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(OH)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>]. This structural type is preceded, examples being Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>Cl<sub>2</sub>(μ-Cl)(μ-O)(μ-O<sub>2</sub>COH) [28] and Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>X<sub>4</sub>(μ-X)<sub>2</sub> (X = Cl, Br) [29,30]. It probably involves alkylsulfido bridges rather than hydroxo bridges, since the former groups are generally better bridging ligands. The necessary rearrangement leading from two hydroxo ligand to an oxo bridge with loss of H<sub>2</sub>O would account for the relatively slow process. If this is true, the stoichiometry of the first reaction leading to the intermediate follows Eq. (1). In this reaction, 4 equiv. of the mercaptoacid perform the reduction process, providing four protons and four electrons. The latter reduce the two Mo centers from VI to IV. Two additional mercaptoacid molecules coordinate the metal centers, stabilizing the dinuclear product and contribute 4 additional protons. Six of the eight protons are used to liberate three oxo ligands as water molecules, the two residual ones converting the remaining two oxo ligands to OH. The reaction then continues as shown in Eq. (2)



As was the case for the related mercaptoacetic acid reaction, the product obtained with the mercaptopropionic acid co-crystallized together with a molecule of the disulfide by-product, thereby providing direct evidence for its formation (Eq. (1)). A view of the dinuclear Mo compound

is shown in Fig. 2. The coordination geometry around each Mo center can best be described as a four-legged piano stool, the four legs being defined by the three bridging atoms (two S and one O) and by a terminally bonded second O atom from the carboxylate function. It is a member of the relatively large family of triply-bridged dinuclear (CpMo<sup>IV</sup>) compounds, other members of which are Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>Br<sub>2</sub>(μ-Br)(μ-O)(μ-SMe) [31], Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>Cl<sub>2</sub>(μ-O)(μ-Cl)<sub>2</sub> [28], and [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>3</sub>]<sup>+</sup> [32]. The overall geometry is identical to that recently described for the mercaptoacetic acid product [11], the bridging sulfur atom in the latter being replaced by a bridging oxygen atom. The Mo–Mo distance (see Table 2) is over 0.1 Å shorter than in the Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-S)(μ-SCH<sub>2</sub>COO)<sub>2</sub> analogue [2.7929(4) Å] [11]. This is certainly related to the smaller size of the

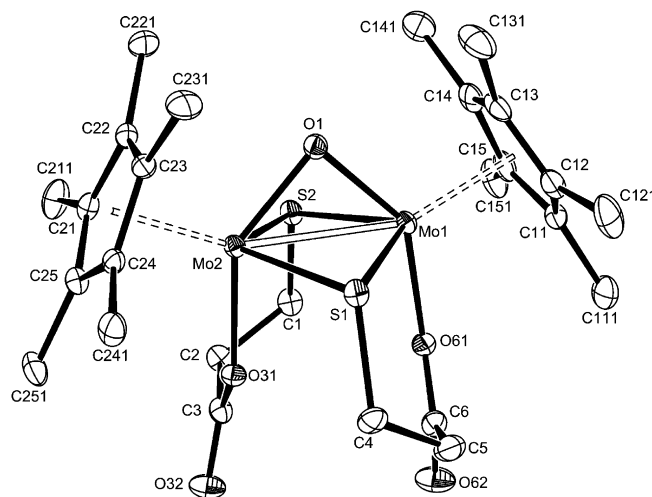


Fig. 2. ORTEP view of compound [Cp<sub>2</sub><sup>\*</sup>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>]. Hydrogen atoms have been omitted for clarity.

bridging O atom relative to S, because the distances from the metal to the bridging thiolato S atoms are identical in the two compounds (averages of 2.453(8) Å and 2.452(15) Å for the O- and S-bridged compounds). The average distances to the Cp\* center of gravity [2.021(1) vs. 2.013(5) Å], and to the terminal carboxylate O donor [2.067(11) vs. 2.090(4) Å] are also very close to those in the thioglycolate analogue. In terms of bond angles, there is an obvious difference at the level of the different bridging atom [Mo–O–Mo, 88.09(12)°; vs. Mo–S–Mo, 74.37(2)]. On the other hand, the average Mo–S–Mo angles involving the thiolato ligand are slightly smaller in the oxo-bridged product reported here [66.30(3)°, vs. 69.4(4)° is the S-bridged product]. This is certainly a secondary effect, related to the shorter Mo–Mo distance. The other geometric parameters are sensibly identical in the two compounds. As already found for the [Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S)(μ-SCH<sub>2</sub>COO)<sub>2</sub>] structure [11], the dinuclear [Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>] product establishes H-bonds with the disulfide by-product. They yield a pseudo dimer by associating two dinuclear complexes and two disulfide molecules, with a graph-set motif of R<sub>4</sub><sup>4</sup>(42) [33,34], as highlighted in Fig. 3. Relevant metric parameters are collected in Table 3.

The presence of the disulfide molecule in the crystal is also revealed by the <sup>1</sup>H NMR study. However, an ordinary spectrum does not allow the clear-cut identification of all protons in the organometallic dinuclear species. Each pair of CH<sub>2</sub> protons is diastereotopic and yields an ABCD system for the CH<sub>2</sub>CH<sub>2</sub> tether, which partially overlaps with the stronger triplets of the free disulfide molecule at δ 2.99 and 2.81. An unambiguous identification of the four

mutually coupled protons of the ABCD system was possible by a 2D-COSY experiment (see Supporting Information). The two stronger triplet resonances only show, as expected, coupling cross-peaks with each other, leading to the straightforward identification of the four resonances of the ABCD system from the additional cross-peaks.

The title compound was also investigated by cyclic voltammetry. As shown in Fig. 4a, the compound undergoes a reversible oxidation wave in CH<sub>2</sub>Cl<sub>2</sub> solution at  $E_{1/2} = 0.06$  V vs. ferrocene. This indicates that the mixed-valence Mo<sub>2</sub><sup>IV,V</sup> product enjoys a certain stability. Conversely, the reduction behaviour is less well defined. A major irreversible wave is observed at  $E_{p,c} = -1.96$  V, with an associated oxidation peak of reduced intensity. This suggests that a chemical process is coupled to the electrochemical reduction. Two less intense reduction waves at less negative potential probably originate from the co-crystallized disulfide by-product. An electrochemical investigation of the related thioglycolate product, [Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S)(μ-SCH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>], was not previously carried out [11], therefore we proceeded to examine this behaviour for comparison purposes with the title compound, see Fig. 4b. This compound shows a reversible oxidation at  $E_{1/2} = 0.32$  V and a reduction at  $E_{p,c} = -1.54$  V. Negligible electrochemical activity is observed in this case at intermediate potentials, since this sample was recovered as a powder after washing away the disulfide by-product with pentane. The shape of the reduction wave of this compound is similar to that of the related mercaptopropionate compound. Therefore, the thioglycolate derivative also gives a non-persistent reduction product. Both waves are shifted to less positive potentials on going from the thioglycolato to the

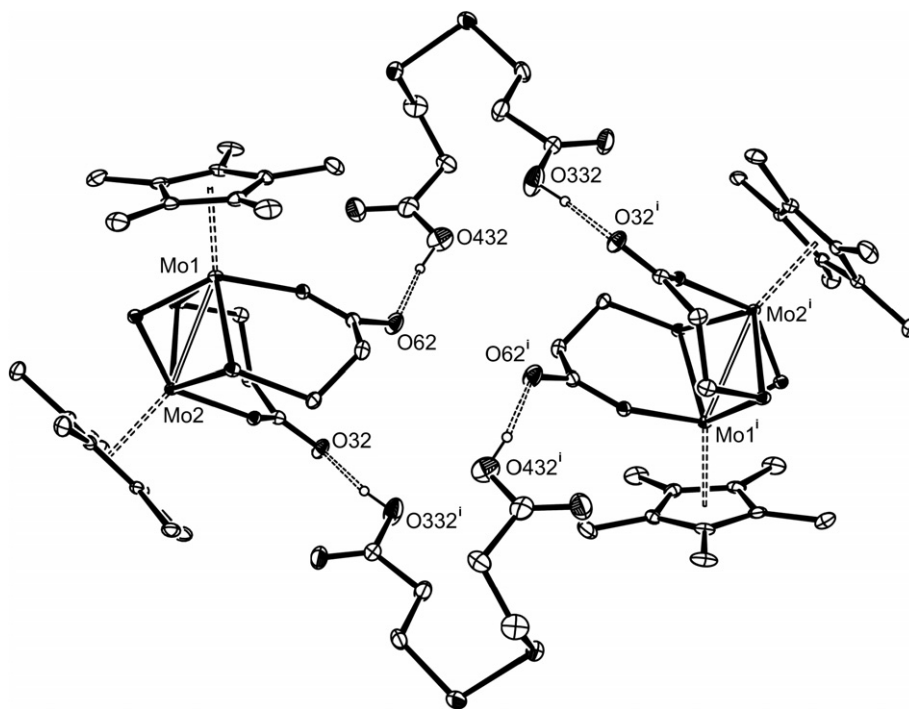
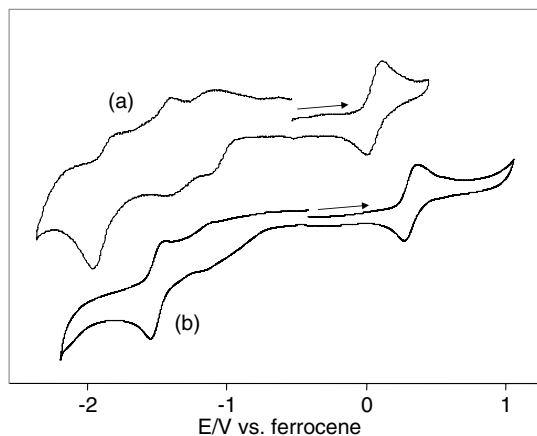


Fig. 3. ORTEP view highlighting the R<sub>4</sub><sup>4</sup>(42) graph-set motif formed by O–H...O hydrogen bonding in the structure of [Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-O)(μ-SCH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>]·HOOCCH<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>COOH.

Table 3

Relevant hydrogen bonding parameters for the structure of compound  $[\text{Cp}_2^*\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)_2] \cdot (\text{HO}_2\text{CCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{COOH})^a$ 

	O–H (Å)	H...O (Å)	O...O (Å)	O–H...H (°)
O432–H432...O62	0.84	1.82	2.605(6)	154
O332–H332...O32 <sup>i</sup>	0.84	1.78	2.587(5)	160

<sup>a</sup> Symmetry code: (i)  $-x, -y, -z + 1$ .Fig. 4. Cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$  solution of: (a) compound  $[\text{Cp}_2^*\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)_2] \cdot (\text{HO}_2\text{CCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{COOH})$ ; (b) compound  $[\text{Cp}_2^*\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CO}_2)_2]$ .

mercaptotopionato derivative ( $\Delta = -0.26$  V for the oxidation process and  $-0.42$  V for the reduction process). Since the coordination mode of the two mercaptoacids is identical, the effect of the additional  $\text{CH}_2$  group in the ligand backbone is probably not having a large effect on the redox potentials. The potential shifts are mostly related to the change of the single atom bridge from sulfur to oxygen. The negative shift is consistent with the harder and stronger  $\pi$ -donating character of the lighter group 16 element, which is then better able to stabilize higher oxidation states (easier oxidation process), whereas the heavier and softer sulfur atom is better able to stabilize lower oxidation states (easier reduction process).

The two compounds were also investigated in a mixed  $\text{MeOH-H}_2\text{O}$  solution (50:50 ratio) at various pH values in the 2–8 range. For both compounds, the oxidation process is pH-independent, whereas the reduction process shifts toward more negative potentials as the pH increases. A figure showing representative data for the mercaptoacetic complex is given in [Supporting Information](#). This is consistent with the molecular structure of the two compounds, since the one-electron oxidation product does not have active protons and therefore cannot be deprotonated. Conversely, the one-electron reduction product can accept a proton from the medium, most likely on the single-atom bridge. The half-wave potential of the pH-independent oxidation process is 0.49 V vs. ferrocene in  $\text{MeOH-H}_2\text{O}$  (vs. 0.32 V in  $\text{CH}_2\text{Cl}_2$ ) for the sulfido-bridged thioglycolate compound and 0.30 V (vs. 0.06 V in  $\text{CH}_2\text{Cl}_2$ ) for the oxo-bridged mercaptopropionate compound. Thus, the negative shift observed for the potentials in  $\text{CH}_2\text{Cl}_2$  on

going from the S-bridged to the O-bridged complex is also reproduced in the mixed  $\text{MeOH-H}_2\text{O}$  solvent, although the difference is less ( $\Delta = -0.19$  V in  $\text{MeOH-H}_2\text{O}$ , vs.  $-0.26$  V in  $\text{CH}_2\text{Cl}_2$ ). Solvation differences in the different solvents, especially for the reduced charged species, are the probable cause of this effect.

The major point of interest in this study is the different outcome of the reactions of  $\text{Cp}_2^*\text{Mo}_2\text{O}_5$  with two closely related substrates,  $\text{HS}(\text{CH}_2)_x\text{COOH}$  ( $x = 1$  or 2), to yield two closely related products,  $\text{Cp}_2^*\text{Mo}_2(\mu\text{-X})[\mu\text{-S}(\text{CH}_2)_x\text{CO}_2]$ , which however surprisingly differ in the nature of the bridging X ligand: S for  $x = 1$  (previously described) [11] and O for  $x = 2$  (described here for the first time). While we do not currently have sufficient information to outline the intimate details of the reaction mechanism, we note that thioglycolates are more facile substrates than alkyl mercaptans for the hydrodesulfurization process. For instance,  $\text{HSCH}_2\text{COX}$  ( $X = \text{OMe}, \text{OEt}, \text{Me}, \text{NMe}_2$ ) are hydrodesulfurized efficiently and with high selectivities to the corresponding  $\text{CH}_3\text{COX}$  under  $\text{H}_2$  (20 bar) with the  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  catalyst, whereas  $\text{HSCH}_2\text{CH}_2\text{COOMe}$ , *n*-octylmercaptan and thiophenol are much less reactive. Compound  $\text{Cp}_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SCH}_2\text{COOEt})_2$  was isolated from the catalytic mixture and structurally characterized [35]. It is therefore likely that mercaptoacetic molybdenum complexes having suitable coordination geometries and/or oxidation states are more susceptible to C–S bond cleavage than longer-chain analogues. The authors of the above catalytic study formulated the hypothesis that the S–C bond is activated in a bimetallic  $\text{Mo-SCH}_2\text{CO(X)-Mo}$  intermediate [35]. The same is probably true for our system. Thus, although the products obtained with  $\text{HS}(\text{CH}_2)_x\text{COOH}$  ( $x = 1$  or 2) are structurally related, they could be formed by quite different mechanisms.

It is highly unlikely that C–S bond cleavage for the mercaptoacetic acid reaction occurs after the formation of an oxo-bridged product, because we see no evidence (by ESI MS) for the formation of an oxo-bridged intermediate in the synthesis of the  $\text{Cp}_2^*\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CO}_2)_2$  product. In addition, compound  $\text{Cp}_2^*\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2)_2$  does not react with an excess of mercaptoacetic acid under the same conditions that lead to its synthesis (50:50  $\text{MeOH-H}_2\text{O}$  mixture, acidified by  $\text{CF}_3\text{COOH}$ , at room temperature). No reaction was detected even after warming the mixture for 1 h at 100 °C. Conversely, no reaction took place under the same conditions when mixing compound  $\text{Cp}_2^*\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CO}_2)_2$  with an excess of mercaptoacetic acid.

#### 4. Conclusion

The interaction of  $\text{Cp}_2^*\text{Mo}_2\text{O}_5$  with  $\text{HSCH}_2\text{CH}_2\text{COOH}$  in an aqueous environment at room temperature quite readily leads to reduction to  $\text{Mo}^{\text{IV}}$  with incorporation of the doubly deprotonated substrate as a ligand, but contrary to the previously reported process with the closely related  $\text{HSCH}_2\text{COOH}$  substrate, a C–S bond cleavage does not occur. This difference relates to a previously established more facile hydrodesulfurization of mercaptoacetic acid with respect to mercaptopropionic acid and to simpler alkylthiols.

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#### Appendix A. Supplementary material

CCDC 632621 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.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](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.02.046](https://doi.org/10.1016/j.jorganchem.2007.02.046).

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