Structure and Electrochemical Properties of the New Triply Bridged Molybdenum(V) Complex $[NBu^n{}_4]_2[Mo_2O_2(\mu\text{-}O)(SCH_2CO_2)_2(\mu\text{-}SCH_2CO_2)]$†

Antonio Cervilla,*[a] **Elisa Llopis,**[a] **José A. Ramírez,**[a] **Antonio Doménech,**[a] **Pedro Palanca,**[b] **Maria T. Picher,**[b] **Carlo A. Ghilardi**[c] **and Annabella Orlandini**[c]

[a] *Departament de Química Inorgànica, Universitat de València, Dr. Moliner 50, 46100-Burjassot (València), Spain*

[b] *Departament de Química Orgànica, Universitat de València, Dr. Moliner 50, 46100-Burjassot (València), Spain*

[c] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132, Florence, Italy*

The reaction of molybdate ions with an excess of thioglycolic acid has been studied in aqueous solution at room temperature by UV/VIS and NMR spectroscopy. As previously observed, spectroscopic data suggest initial formation of the complex $[MoO_2(SCH_2CO_2)_2]^{2-}$ **1**, which is subsequently reduced by the excess of acid. Two molybdenum(V) complexes are formed in equilibrium in this redox reaction. The main product has been isolated as an orange-red solid with the formula $[NBu^n{}_4]_2[Mo_2O_3(SCH_2CO_2)_3]\cdot 2H_2O$ **2**. It crystallizes in the monoclinic space group $P2_1/a$ with $a = 20.761(8)$, $b = 17.441(7)$, $c = 14.587(6)$ Å, $\beta = 101.08(6)°$, and $Z = 4$. The structure contains two cofacial $Mo^VO_2(SCH_2CO_2)_2$ distorted octahedra sharing one oxygen atom and one thioglycolate ligand on a pseudo-symmetry plane (O_t–Mo 1.677, Mo–Mo 2.643, Mo–$S_{t,b}$ 2.489, Mo–$O_{t,b}$ 2.337, Mo–O_b 1.929 Å, Mo–$S_{t,b}$–Mo 64.1, Mo–$O_{t,b}$–Mo 68.9, Mo–O_b–Mo 86.5°; t = terminal, b = bridging). Cyclic voltammetry shows that complexes **1** and **2** undergo a two-electron irreversible reduction at −1.27 and −1.38 V *vs.* the saturated calomel electrode, respectively, in methanol. In both reduction processes the monooxomolybdenum(IV) species $[MoO(SCH_2CO_2)_2]^{2-}$ and $[MoO(SCH_2CO_2)(solv)_2]$ are generated. A reaction mechanism for the oxidation of thioglycolic acid by molybdate ions is proposed from the combined analysis of spectrophotometric, NMR, structural, and voltammetric data. Dimeric molybdenum(V) products are generated from reaction of the above monooxomolybdenum(IV) species with the starting dioxomolybdenum(VI) complex **1**. A particularly remarkable supporting feature is the formation of Me_2S when the reaction is carried out in the presence of Me_2SO.

Previous studies[1] showed that reduction of aqueous molybdate by 2-mercaptoacetic acid (thioglycolic acid) yields solutions exhibiting EPR signals which account for about 10% of the available molybdenum with parameters ($\langle g \rangle = 1.978$; $\langle A \rangle = 36$ G, 3.6×10^{-3} T) similar to those for xanthine oxidase. Thereafter, Martin and Spence demonstrated the capacity of molybdate ions to oxidize thioglycolic acid,[2a] cysteine and glutathione [*N*-(*N*-L-γ-glutamyl-L-cysteinylglycine)[2b] giving disulfide derivatives. The proposed mechanism involves the formation of the $[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-}$ complex which is subsequently reduced by excess of thioglycolic acid to give an EPR-active monomeric molybdenum(V) species which rapidly dimerizes forming an EPR-silent μ-oxo-complex,[2a] equations (1) and (2).

$$[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-} + HSCH_2CO_2H \longrightarrow [Mo^VO_2(SCH_2CO_2)_2]^{3-} + HSCH_2CO_2{}^{\bullet} + H^+ \quad (1)$$

$$2H^+ + 2[Mo^VO_2(SCH_2CO_2)_2]^{3-} \longrightarrow [Mo^V{}_2O_3(SCH_2CO_2)_4]^{4-} + H_2O \quad (2)$$

Such a dimerization equilibrium could also explain why subsequent attempts to isolate this EPR mimic of xanthine oxidase present in aqueous solution have thus far been unsuccessful. To date, the only isolated products are a diamagnetic binuclear molybdenum(V) compound which presumably contains a bridging oxo group, $Na_4[\{MoO(SCH_2CO_2)_2\}_2O]$,[2a] and the X-ray characterized binuclear anion $[Mo_2O_2(SCH_2CO_2)_4]^{2-}$, with two bridging thiolic sulfur atoms from two thioglycolate ligands co-ordinated to different Mo atoms.[3] This last species was not obtained from a mixture of sodium molybdate and thioglycolic acid in water but from the dropwise addition of thioglycolic acid and triethylamine to a solution of $[NBu^n{}_4]_4[Mo_8O_{26}]$ in methanol. Thus, modifications in the nature of the molybdenum precursor, in the counter ions and solvents seem to have profound consequences on the products isolated.

Our recent investigations[4] have demonstrated that the $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ complex containing the ligand 2-mercapto-2,2-diphenylacetate (thiobenzilate), a thioglycolic acid derivative containing *gem*-diphenyl groups, can be quantitatively reduced by the free acid yielding the monomeric molybdenate(V) complex $[MoO\{O_2CC(S)Ph_2\}_2]^-$ the structure of which has been determined by X-ray crystallography. One could therefore conclude that, with sufficiently bulky mercaptoacid ligands, the dimerization reaction (2) is apparently hindered by steric constraints.

In contrast to this behaviour, most neutral dioxomolybdenum(VI) complexes containing S,S′ (dithiocarbamates),[5] O,O′ (acetylacetonate),[5b,6] O,N (quinolin-8-olate),[5b,c] and S,N,O (Schiff bases)[6] chelating ligands are initially reduced to a

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

$Mo^{IV}OL_n$ species which is rapidly intercepted by unreacted $Mo^{VI}O_2L_n$, producing the corresponding oxo-bridged molybdenum(v) dimer [equation (3)]. Such a condensation

$$Mo^{IV}OL_n + Mo^{VI}O_2L_n \longrightarrow L_nOMo^{V}\text{–}O\text{–}Mo^{V}OL_n \quad (3)$$

equilibrium can also be prevented by using sterically hindered molybdenum-(VI) or -(IV) complexes.[7] Thus, $[MoO_2L]$ [H_2L = 2,6-bis(2-mercapto-2,2-diphenylethyl)pyridine],[8a] $[MoO_2L_2]$ [HL = bis(*p-tert*-butylphenyl)-2-pyridylmethanethiol],[8b] and $[MoO_2\{S_2P(OEt)_2\}L]$ [L = tris(3,5-dimethylpyrazolyl)-borate] complexes[9] have been reported to form stable oxomolybdenum(IV) species when chemically reduced by PPh_3 or PhSH.[10]

The mechanistic relationships between relevant molybdenum complexes and molybdenum hydroxylase enzymes have recently been reviewed.[11] The enzyme molybdenum centres cycle between the VI, V and IV oxidation states during catalysis[12] and correlated electron-proton transfers from substrate to the molybdenum site have been proposed.[13] Two-electron reductions have been associated[12,14] with the generation of $Mo^{IV}O(SH)$ or $Mo^{IV}O(OH)$ centres, which upon one-electron reoxidation give EPR signals arising from $Mo^{V}OS$, $Mo^{V}O(SH)$ and $Mo^{V}O(OH)$ centres.[15] This mechanism seems to be more related to that found for neutral complexes than to that proposed by Martin and Spence for the anionic $[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-}$ complex.

All these features have encouraged a more detailed examination of the reaction products of the molybdate–thioglycolic acid system in order to obtain more detailed information on its reaction mechanism. We herein report the results of such an investigation, including the X-ray characterization of the main molybdenum(v) product.

Results and Discussion

Spectrophotometric Measurements.—Martin and Spence[2] reported reaction (4), from which molybdenum-containing

$$2[MoO_4]^{2-} + 6HSCH_2CO_2H \rightleftharpoons [Mo_2O_3(SCH_2CO_2)_4]^{4-} + (HO_2CCH_2S)_2 \quad (4)$$

products were isolated. The molybdenum(v) product formulation was supported by elemental analysis and IR spectroscopy. In addition, the nature of this product was sustained by its preparation in good yield from $[NH_4]_2[MoOCl_5]$ and thioglycolic acid.

These authors observed, spectrophotometrically, that when sodium molybdate was added to a deaerated water solution containing an excess of thioglycolic acid in phosphate buffer (pH 4.5–6.0) at 60 °C the complex $[MoO_2(SCH_2CO_2)_2]^{2-}$ (λ_{max} = 365 nm) was first formed. The oxidation of thioglycolic acid proceeds *via* this complex which is first reduced to a dimeric molybdenum(v) complex (λ_{max} = 355 nm) and then to a stable molybdenum(IV) species [λ_{max} = 355, 510(sh) nm] of unknown structure. Precipitation of the latter species gives only a tarry material, the most significant feature of which is the absence of Mo=O and Mo–O–Mo IR bands. Under these experimental conditions, it was also found that while the molybdenum(v) complex is easily oxidized by air, changing rapidly to the molybdenum(VI) complex, the more reduced molybdenum(IV) complex is quite stable in air.

An analogous reaction has been spectrophotometrically re-examined by us at room temperature, in the presence of air and without phosphate buffer. As shown in Fig. 1, when $Na_2[MoO_4]$ (10^{-3} mol dm^{-3}) was added to a solution of thioglycolic acid (5×10^{-2} mol dm^{-3}) in water an intense band at 365 nm, characteristic of $[MoO_2(SCH_2CO_2)_2]^{2-}$, immediately developed. The time course of the reaction clearly shows decay of this reactant band as new bands at 355 and 440 nm appear. The reaction went to completion, developing two isosbestic points at 335 and 438 nm and displaying a final spectrum which did not change appreciably with time. The presence of these two maxima agree well with those of dithiocarbamate and thiolate complexes[10] containing a $Mo^{V}_2O_3$ unit, which correlates well with spectra displaying principal bands at 330–380 and 500–515 nm.

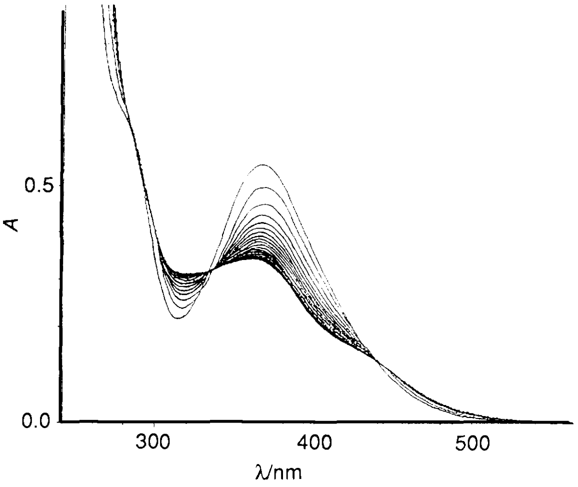


Fig. 1 Spectral changes in the reduction of $[MoO_2(SCH_2CO_2)_2]^{2-}$ **1** (1 mmol dm^{-3}) by thioglycolic acid (5 mmol dm^{-3}) in water at 25 °C. Spectra were recorded every 30 min at a scan rate of 120 nm min^{-1}

The same reaction was carried out on a preparative scale and the final molybdenum products precipitated by adding NBu^n_4Br. Upon redissolution, band maxima for the isolated solid were clearly similar to those reported by Martin and Spence[2] for the dimeric molybdenum(v) complex and the spectrum was indistinguishable from the final spectrum of Fig. 1. Thus, under our experimental conditions, the foregoing results clearly indicate that the molybdenum(v) species is neither reduced further by excess of thioglycolic acid, nor reoxidized by air. Our findings were also corroborated by NMR spectroscopy (see below), which demonstrates that in the presence of air only 1 mol of disulfide (dithiodiglycolic acid) can be progressively generated per 2 mol of sodium molybdate added to the thioglycolic acid solution. Such a stoichiometric ratio is only consistent with a reaction in which irreversible formation of the dimeric molybdenum(v) complex occurs.

The effect of pH on the reaction rate was qualitatively studied by using an excess of a thioglycolic acid–thioglycolate mixture (pH 6.0) instead of only the acid. Although the rate decreased appreciably, no effect of pH was found in the course of the reaction which shows the same isosbestic points and band maxima. In the range pH 4.5–6.0, the conclusion is, therefore, that the product is always the same and that the subsequent further reduction of this species by excess of mercaptoacid is not favoured by increasing pH.

In this regard, as mentioned above, it is interesting that when the sterically hindered $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ complex[4] reacts with an excess of thiobenzilic acid the only complex product is the monomeric molybdate(v) species $[MoO\{O_2CC(S)Ph_2\}_2]^{-}$ with bands at 312, 374 and 505 nm, which is stable under these acidic conditions. However, partial neutralization of thiobenzilic acid results in a further reduction of the latter complex which slowly yields the non-oxo tris(chelate)molybdate(IV) species[16] $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$, also isolated and characterized by X-ray crystallography.[17] Thus, compared to the molybdenum(VI)–thioglycolic acid system, one could conclude that while the monomeric monooxo molybdenum(v) complex can be further reduced by mercaptoacids, dimeric molybdenum(v) complexes do not show any appreciable reactivity at least at room temperature.

NMR Characterization.—The spectrophotometrically observed formation of the initial $[MoO_2(SCH_2CO_2)_2]^{2-}$ complex was also confirmed by NMR spectroscopy. Thus, addition of sodium molybdate to a solution of thioglycolic acid immediately affords ^{13}C and ^1H resonances which are clearly different from those obtained for the free acid. The ^{13}C NMR spectrum only exhibits two peaks at δ 186.3 (carboxylic group) and 36.6 (methylene group) whereas the ^1H NMR spectrum has only one singlet at δ 3.78. Compared to the free acid (δ 177.5 and 28.9), co-ordination of both the carboxylate and the thiolate groups is consistent with the large low-field shifts (≈ 10 ppm) in their respective ^{13}C resonances. Moreover, its sodium salt was precipitated by adding acetone to a freshly prepared stoichiometric aqueous solution of thioglycolic acid and sodium molybdate. Redissolution of this salt in a methanolic solution of $NBu^n{}_4Br$ yields the crystalline salt $[NBu^n{}_4]_2[MoO_2(SCH_2CO_2)_2]$ which gives a ^1H NMR solution spectrum integrating for the presence of 1 mol of thioglycolate for each tetrabutylammonium cation.

From the above number of ligand resonances we conclude that in this complex there is a molecular C_2 axis of symmetry which makes both ligand molecules magnetically equivalent. The structural characterization of the first six-co-ordinated dioxomolybdenum complex containing a $MoO_2{}^{2+}$ core bonded by both thiolate and carboxylate groups of two bidentate thiobenzilate ligands has recently been reported.[18] Such a complex has a two-fold axis bisecting the angle between the two terminal oxygen atoms, making both ligand molecules symmetrically equivalent.

Fig. 2 shows the time course of the reaction between $[MoO_4]^{2-}$ and an excess of thioglycolic acid (molar ratio 1:3) as monitored by ^{13}C NMR spectroscopy. In the carboxylic region, the signal at δ 186.3 from the $[MoO_2(SCH_2CO_2)_2]^{2-}$ complex decreases and five new resonances at δ 188.6, 188.3, 179.2, 179.0 and 178.5 appear with time, whereas in the aliphatic region (methylene groups) the initial signal at δ 36.6 also splits into five signals at δ 44.2, 43.4, 39.3, 35.8 and 34.8. Considering that peaks at δ 178.5 and 44.2 correspond, respectively, to the carboxylic and methylene groups of the dithiodiglycolic acid formed, the remaining four pairs of resonances must be assigned to a reduced molybdenum(v) thioglycolate complex containing four different co-ordination environments for the ligands, or to a mixture of different molybdenum(v) complexes. Although the existence of two isosbestic points in the electronic spectra for this reaction is consistent with the former possibility, it does not rule out that other species may also be present in rapid equilibrium[19] or in a much lower amount.

The ^1H NMR spectrum shows, however, a complicated set of signals corresponding to the bound thioglycolate ligands. The detailed assignment of the ^1H and ^{13}C spectra is not trivial and, therefore, two-dimensional ^1H–^1H and ^1H–^{13}C chemical shift correlations (Fig. 3) have been used for the complete assignment of signals. Thus, the AB spin system with δ_A 3.74 and δ_B 4.35 ($J_{AB} = -17.5$ Hz) and the singlet at δ 4.01 (intensity ratio 2:1 respectively) are assigned to a major complex, whereas the remaining two intensity-equivalent AB multiplets with δ_A 3.77 and δ_B 4.14 ($J_{AB} = -17.4$ Hz) and δ_A 4.18 and δ_B 4.32 ($J_{AB} = -17.8$ Hz) are assigned to the other complex, formed in lower concentration. Integration of the proton spectrum suggests a relative ratio of 5:1 for the major to the minor species.

Thus, unexpectedly based on the previous study,[2a] the present NMR results demonstrate the formation of two different molybdenum(v) products. The predominant one has two types of co-ordinated thioglycolate anions exhibiting magnetically equivalent and non-equivalent methylene protons in a molar ratio of 1:2, respectively. This is not in agreement with the proposed formation of a 2:4 $[Mo^V{}_2O_3(SCH_2CO_2)_4]^{4-}$ complex potentially associated with the two intensity-equivalent AB multiplets assigned to the minor species. Such a condition was fully corroborated by the isolation and X-ray characterization of the major product, the elemental analysis of which was in agreement with the formula $[NBu^n{}_4]_2[Mo_2O_3(SCH_2CO_2)_3]$. It forms an air-stable, water-soluble crystalline powder whose absorption spectrum is identical to the final spectrum in Fig. 1.

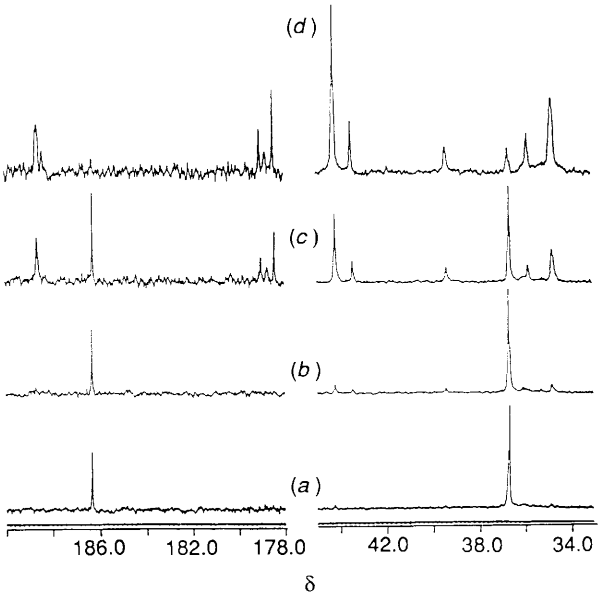


Fig. 2 Time course of the thioglycolic acid oxidation by molybdate anions (mol ratio = 3:1) as monitored by ^{13}C NMR spectroscopy at (*a*) 1, (*b*) 3, (*c*) 9 and (*d*) 15 h

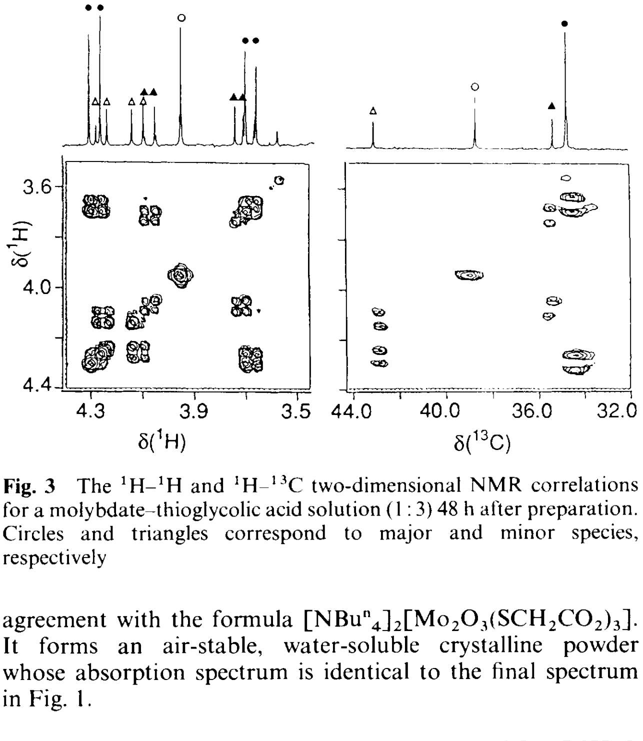


Fig. 3 The ^1H–^1H and ^1H–^{13}C two-dimensional NMR correlations for a molybdate–thioglycolic acid solution (1:3) 48 h after preparation. Circles and triangles correspond to major and minor species, respectively

Crystal Structure of $[NBu^n{}_4]_2[Mo_2O_3(SCH_2CO_2)_3]\cdot 2H_2O$ **2**.—The crystal structure consists of dimeric molybdenum(v) complex anions with tetrabutylammonium as the counter ions and one water molecule per molybdenum atom as solvent of crystallization. The structure and labelling scheme are presented in Fig. 4, while selected distances and angles are listed in Table 1.

The binuclear complex anion exhibits a cofacial bioctahedral geometry (C_s symmetry) which appears to be quite common in molybdenum(v) chemistry.[20] Each molybdenum is bonded to one fully deprotonated terminal thioglycolate dianion, acting as a bidentate ligand through the thiolic sulfur and carboxylic oxygen atoms. As generally observed for triply bridged complexes, one terminal oxo group is bonded to each molybdenum in a *syn* conformation. The distorted-octahedral geometry of each molybdenum is completed by a bridging oxo group and

Table 1 Selected bond distances (Å) and angles (°) for complex **2**

Mo(1)–Mo(2)	2.643(1)		
Mo(1)–S(1)	2.393(3)	Mo(2)–S(2)	2.385(3)
Mo(1)–S(3)	2.476(3)	Mo(2)–S(3)	2.503(3)
Mo(1)–O(1)	1.671(7)	Mo(2)–O(4)	1.682(7)
Mo(1)–O(2)	2.073(7)	Mo(2)–O(5)	2.076(7)
Mo(1)–O(7)	2.357(6)	Mo(2)–O(7)	2.318(6)
Mo(1)–O(9)	1.932(6)	Mo(2)–O(9)	1.926(6)
O(10) ··· O(11)	2.72(1)	O(10) ··· O(3)	2.78(1)
O(10) ··· O(6)	2.76(1)	O(11) ··· O(8)	2.94(1)
S(1)–Mo(1)–S(3)	155.2(1)	S(2)–Mo(2)–S(3)	164.3(1)
S(1)–Mo(1)–O(1)	108.7(3)	S(2)–Mo(2)–O(4)	105.4(3)
S(1)–Mo(1)–O(2)	80.3(2)	S(2)–Mo(2)–O(5)	80.9(2)
S(1)–Mo(1)–O(7)	90.1(2)	S(2)–Mo(2)–O(7)	98.3(2)
S(1)–Mo(1)–O(9)	81.1(2)	S(2)–Mo(2)–O(9)	80.9(2)
S(3)–Mo(1)–O(1)	93.8(3)	S(3)–Mo(2)–O(4)	87.8(3)
S(3)–Mo(1)–O(2)	85.0(2)	S(3)–Mo(2)–O(5)	87.9(2)
S(3)–Mo(1)–O(7)	69.3(2)	S(3)–Mo(2)–O(7)	69.4(2)
S(3)–Mo(1)–O(9)	104.8(2)	S(3)–Mo(2)–O(9)	104.1(2)
O(1)–Mo(1)–O(2)	102.1(3)	O(4)–Mo(2)–O(5)	103.6(3)
O(1)–Mo(1)–O(7)	159.9(3)	O(4)–Mo(2)–O(7)	156.0(3)
O(1)–Mo(1)–O(9)	101.7(3)	O(4)–Mo(2)–O(9)	105.1(3)
O(2)–Mo(1)–O(7)	87.7(2)	O(5)–Mo(2)–O(7)	83.7(2)
O(2)–Mo(1)–O(9)	153.4(2)	O(5)–Mo(2)–O(9)	149.2(3)
O(7)–Mo(1)–O(9)	73.5(2)	O(7)–Mo(2)–O(9)	74.5(2)
Mo(1)–S(3)–Mo(2)	64.1(1)	Mo(1)–O(7)–Mo(2)	68.9(2)
Mo(1)–O(9)–Mo(2)	86.5(3)		

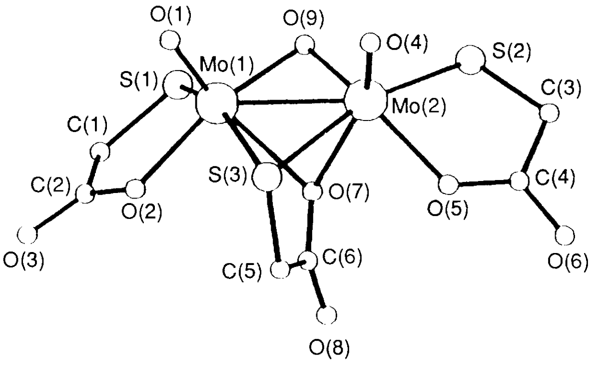


Fig. 4 A PLUTO drawing of the complex anion $[Mo_2O_3(SCH_2CO_2)_3]^{2-}$ of **2**, showing the atom labelling scheme

one dianionic thioglycolate ligand doubly bridging through its thiolic sulfur and carboxylic oxygen atoms.

To our knowledge, complex **2** is the first triply bridged molybdenum(v) complex definitively characterized by X-ray crystallography in which a carboxylate group links two molybdenum centres by the same oxygen atom. Other structures of dimeric molybdenum(v) complexes with μ-carboxylate ligands are known, but in all of them the ligand is bonded to each Mo through a different oxygen atom.[21] The overall symmetry of the donor atoms around the co-ordination sphere of molybdenum is consistent with previous results in oxomolybdenum chemistry.[22] Compared to the μ-oxo group, the stronger *trans* influence of the multiply bonded oxo group[23] can explain the disposition of the other co-ordinated ligand groups, which will arrange themselves so that the weaker π-bonding donor atom is *trans* to this terminal oxo group. The weaker donor is considered to be the oxygen from the bridging carboxylate group, whereas the other carboxylic groups from the terminal thioglycolate ligands are *trans* to the μ-oxo atom of next highest *trans* influence. The remaining sulfur atoms of the bridging and non-bridging ligands complete the last two unoccupied positions in a *trans* disposition. The observed arrangement is consistent with that predicted on the basis of the different π-donor abilities of the donor atoms.[24]

As is usual for oxomolybdenum complexes, the Mo atom is not at the centre of the co-ordination octahedron but is shifted toward the terminal unshared oxygen atom. Distortion from a regular octahedral co-ordination is evident in the values of the axial angles which range from 149.2 to 164.3°. Alternatively, the complex may also be viewed in terms of two square-pyramidal co-ordination polyhedra sharing an edge, with a sixth more distant ligand [carboxylate O(7)] *trans* to both Mo=O bonds.

The measured Mo=O bond lengths of 1.671(7) and 1.682(7) Å fit well with other reported values for Mo^V=O bonds. A pertinent example with alkoxide instead of carboxylate ligation is the complex $[Mo^V{}_2O_2(\mu\text{-}O)(\mu\text{-}SCH_2CH_2O)(OC_9H_6N)_2]$,[25] where the Mo=O bond length (1.693 Å) shows a slight increase as the *trans* ligand varies from ethanolate to carboxylate. The same observation holds when the μ-oxo (1.929 Å) bridging distance of **2** is compared with that found (1.937 Å) in the latter mercaptoethanolate complex.

The Mo–Mo distance of 2.643(1) Å, indicative of a direct single metal–metal bond, as well as the pattern of angles for the triply bridged unit are consistent wih those found for similar triply bridged molybdenum(v) complexes.[26] The doubly bridging thioglycolate ligand is contained on a plane nearly perpendicular to the Mo–Mo vector (87.1°), the largest displacement from the least-squares plane passing through all the atoms being 0.06 Å.

In the solid state, each thioglycolate ligand of complex **2** presents a different hydrogen-bonding interaction between its carbonyl group and protons of two water molecules, located between dimeric complex units, which are also hydrogen bonded to one another (Fig. 5). The hydrogen bond contacts [O(10) ··· O(6) 2.76, O(10) ··· O(3) 2.78, O(11) ··· O(8) 2.94 and O(10) ··· O(11) 2.72 Å] do not involve the tetrabutylammonium cations and create, therefore, an infinite chain of anions. This can explain the magnetic non-equivalence of each of the three thioglycolate ligands in the solid complex, as confirmed by ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectroscopy (Fig. 6). In this spectrum, three carboxylic resonances with similar intensity can be observed at δ 184.7, 183.8 and 174.9, whereas in solution both terminal carboxylic groups became equivalent and gave a single signal at δ 188.6 with intensity double that arising from the bridging carboxylate at δ 179.0.

Electrochemistry.—The cyclic voltammogram of a methanolic solution of complex **2** is shown in Fig. 7. An initial cathodic scan shows only one major reduction peak A at −1.38 V which is coupled with two broad oxidation peaks at −0.48 (B) and −0.18 V (C). Process A is, therefore, highly irreversible, as determined from the shape of the cyclic voltammogram. Anodic scans only show a prominent peak at +0.95 V, attributable to a ligand-centred oxidation by comparison with cyclic voltammograms obtained for uncomplexed thioglycolate solutions.

A study of the peak current as a function of the square root of the scan rate indicates that reduction peak A arises from a diffusion-controlled process. From the value obtained for the current function I_{pc} ($= i_{pc}/cAv^{\frac{1}{2}}$), 800 A cm mol^{-1} V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$ in the sweep rate range 0.05–0.50 V s^{-1}, it is estimated that process A is actually a two-electron reduction [equation (5)], since one-electron reduction of other doubly and triply bridged molybdenum(v) complexes[26,27a] have been reported to give lower I_{pc} values ranging from 300 to 500 A cm mol^{-1} V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$.

$$[Mo^V{}_2O_3(SCH_2CO_2)_3]^{2-} + 2H^+ + 2e^- \longrightarrow [Mo^{IV}O(SCH_2CO_2)_2]^{2-} + [Mo^{IV}O(SCH_2CO_2)(solv)_2] + H_2O \quad (5)$$

Oxidation process B appears after reduction A and is accompanied by a coupled reduction peak B′ if the cyclic voltammetry is reversed immediately after the appearance of the peak B (see Fig. 7). It has been assigned to the one-electron reversible reduction of the mononuclear species $[Mo^VO(SCH_2CO_2)_2]^-$ produced after oxidation process B. Such an

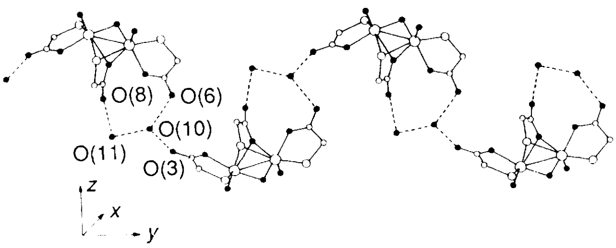


Fig. 5 Hydrogen bonding in the crystal structure of $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_2O_3(SCH_2CO_2)_3}]$ **2**

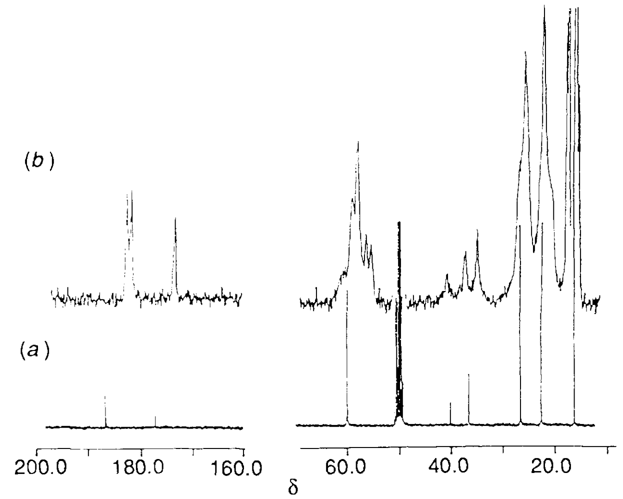


Fig. 6 The ^{13}C NMR spectrum of $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_2O_3(SCH_2CO_2)_3}]$ **2**: (*a*) dissolved in MeOD; (*b*) CPMAS spectrum

assignment is based on previous work on the sterically hindered $[\mathrm{Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2}]^{2-}$ complex which is electrochemically reduced to $[\mathrm{Mo^{IV}O\{O_2CC(S)Ph_2\}_2}]^{2-}$ which is in turn reversibly oxidized to $[\mathrm{Mo^{V}O\{O_2CC(S)Ph_2\}_2}]^{-}$ at or near the same formal potential B–B′ couple.[4] The ratio $i_p(B)/i_p(A)$ increased and approached 0.5:1 when the sweep rate was raised, in agreement with equation (5) where 1 mol of $[\mathrm{Mo^{IV}O(SCH_2CO_2)_2}]^{2-}$ is generated per mol $[\mathrm{Mo^{V}_2O_3(SCH_2CO_2)_3}]^{2-}$ ion.

The peak C at −0.18 V is associated with the one-electron oxidation of $[\mathrm{Mo^{IV}O(SCH_2CO_2)(solv)_2}]$ to give an undetectable $[\mathrm{Mo^{V}O(SCH_2CO_2)(solv)_2}]^+$ species. A similar, unstable, one-electron-reduced product has been detected by EPR spectroscopy in the electrochemical oxidation (−0.180 V) of $[\mathrm{Mo^{IV}O(L')}]$ (H_2L' = *o*-$\mathrm{HSC_6H_4SCH_2CH_2SC_6H_4SH}$-*o*),[27] containing an S_4 tetradentate ligand with aromatic thiolate-thioether groups. No reduction peak for the cationic molybdenum(v) species was observed. Together with the fact that successive scans do not decrease the height of peak A, which remains as in the first scan, this seems to point to a possible regeneration of the starting triply bridged molybdenum(v) complex during the electrochemical cycle, according to equation (6).

$$[\mathrm{Mo^{V}O(SCH_2CO_2)_2}]^- + [\mathrm{Mo^{V}O(SCH_2CO_2)(solv)_2}]^+ + H_2O \longrightarrow [\mathrm{Mo^{V}_2O_3(SCH_2CO_2)_3}]^{2-} + 2H^+ \quad (6)$$

Finally, we should mention that the cyclic voltammogram of the $[\mathrm{MoO_2(SCH_2CO_2)_2}]^{2-}$ complex in MeOH exhibits an initially irreversible cathodic peak at −1.27 V followed by a reversible couple at the formal potential of −0.48 V which clearly resembles the above described B–B′ couple of complex **2**. The relative intensity of these peaks is in agreement with a two-electron proton-assisted process for the initial reduction of the $[\mathrm{MoO_2(SCH_2CO_2)_2}]^{2-}$ complex, as indicated by equation (7).

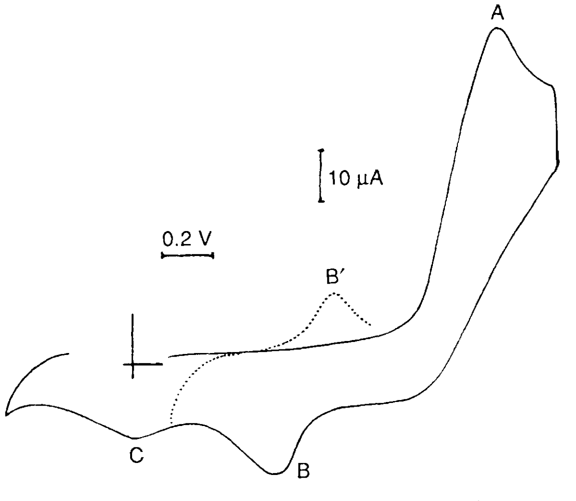


Fig. 7 Cyclic voltammogram of complex **2** (4.3×10^{-3} mol dm^{-3} in MeOH) at a glassy-carbon electrode (v = 0.15 V s^{-1})

$$\begin{aligned}&[\mathrm{Mo^{VI}O_2(SCH_2CO_2)_2}]^{2-} + 2H^+ + 2e^- \longrightarrow\\ &\qquad [\mathrm{Mo^{IV}O(SCH_2CO_2)_2}]^{2-} + H_2O\\ &\qquad\quad \Updownarrow\\ &\qquad [\mathrm{Mo^{IV}O(SCH_2CO_2)(solv)_2}] + SCH_2CO_2^{2-} \qquad (7)\end{aligned}$$

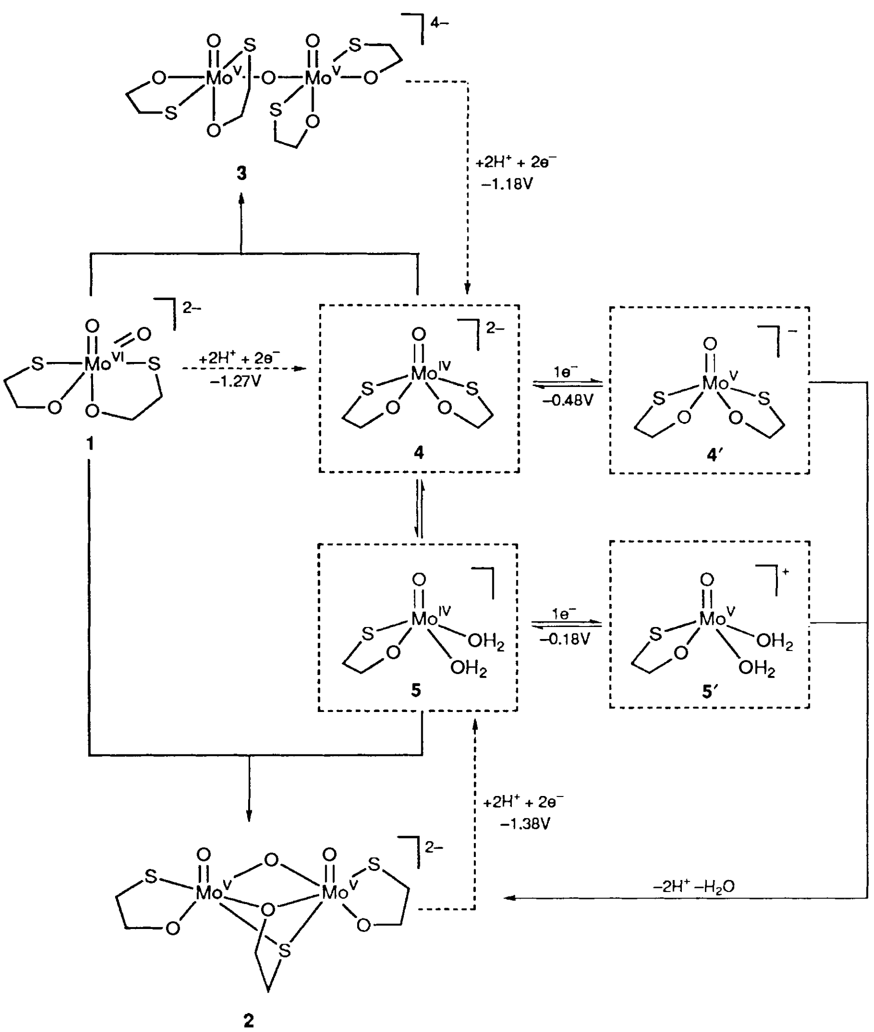
The respective comproportionation of both molybdenum(iv) species with the starting $[\mathrm{Mo^{VI}O_2(SCH_2CO_2)_2}]^{2-}$ complex yields the two dimeric molybdenum(v) complexes above characterized by NMR spectroscopy (see Scheme 1) as indicated by the appearance with time of two new reduction peaks at −1.38 and −1.18 V. Scheme 1 summarizes a redox reaction mechanism for the molybdenum–thioglycolate system which has been derived from the present experimental data.

Reaction Mechanism.—An important conclusion of the above electrochemical study is that the monomeric molybdenum(v) state is clearly unobtainable for these complexes by electrochemical reduction of the corresponding dioxomolybdenum(vi) complexes under the conditions used, since the molybdenum(vi) complex is reduced at potentials considerably more negative than those required for reduction of the molybdenum(v) monomer. This observation is in agreement with the fact that all reported $\mathrm{Mo^{VI}O_2}$ complexes containing sterically bulky ligands are reduced by organic phosphines or aromatic thiols to the molybdenum(iv) oxidation state. In relation to thiolic substrates, Holm and Berg[28] have reported that the above-mentioned $[\mathrm{MoO_2L}]$ [H_2L = 2,6-bis(2-mercapto-2,2-diphenylethyl)pyridine] complex catalyses the oxidation of arenethiols by sulfoxides through reactions such as (8) and (9).

$$[\mathrm{Mo^{VI}O_2L}] + 2RSH \longrightarrow [\mathrm{Mo^{IV}O(L)}] + RSSR + H_2O \quad (8)$$

$$[\mathrm{Mo^{IV}O(L)}] + Me_2SO \longrightarrow [\mathrm{Mo^{VI}O_2L}] + Me_2S \quad (9)$$

All known five-co-ordinate oxomolybdenum(iv) complexes are square pyramidal with the vacant co-ordination site *trans* to the Mo=O bond. As shown in Scheme 1, for the present system, such a structure would imply a significant change in the co-ordination sphere of the starting *cis*-dioxomolybdenum(vi) complex. That is, while in complex **1** the oxo ligands occupy *cis* positions with thiolate groups *trans* to each other and *cis* to both oxo groups,[18] in the reduced complex **4** the thiolate groups are *trans* to the carboxylate groups and *cis* to the oxo atom.[4]



Scheme 1

Such a conformation allows sulfur atoms to compete more efficiently with the oxo group for the available empty d orbital of molybdenum.

A further stabilization of the molybdenum(IV) system can be expected as a result of the loss of one thioglycolate ligand molecule and the subsequent co-ordination of two water molecules at the vacant sites, *cis* to the oxo ligand, to yield complex **5**. This is so because a co-ordinated water molecule has a lower *trans* influence than thiolate or carboxylate groups ($RS^- \gg RCO_2^- > H_2O >$ MeOH) and, thus, such a ligand substitution[23] should increase the π-bonding donor interaction between the remaining thioglycolate ligand and the metal d orbitals. In fact, the formation of a neutral 1 : 1 complex between Mo^{IV} and thioglycolic acid has been studied spectrophotometrically and isolated in the solid state as $[MoO(H_2O)_2(SCH_2CO_2)]$.[29] Herein, the electrochemical study presented provides other experimental evidence on the formation of these two molybdenum(IV) species upon reduction of **2** and **1**.

Since complexes **4** and **5** are probably intermediates in the oxo-transfer reaction to the thiolic substrate, their respective comproportionation with a molecule of **1**, can lead to the observed formation of both dimeric molybdenum(V) products **2** and **3**. Thus, **4** is expected to interact with **1** to form a single μ-oxomolybdenum(V) complex **3** as indicated by equation (3). Indeed, unless sterically prevented,[7] (3) is a very well known reaction in oxomolybdenum chemistry from which more than 20 complexes containing the diamagnetic $[Mo_2O_3]^{4+}$ core in the *syn* and *anti* conformation have been isolated and structurally characterized.[20]

Following similar reasoning, the formation of the triply bridged molybdenum(V) species **2** can be understood as resulting from the interaction between **5** and **1**, through loss of the labile solvent molecules. The positions left by these molecules are then taken by S and O atoms from a thioglycolate of **1** acting as a bridging ligand. Such an interaction is yet another example of the ability of thiolic ligands to stabilize unusual structural features.[30]

Obviously, other possible mechanisms to explain the formation of triply bridged molybdenum(V) complexes have been reported. Specifically, reactions of protic reagents with oxo bridges of complexes containing $[Mo_2O_4]^{2+}$ units have been previously observed.[24] Thus, triply bridged complexes can be formed by the reaction of a bridging oxo ligand with thiols, followed by the elimination of a molecule of water.[31] Nevertheless, in our system, involving a bidentate ligand, no spectral evidence for the formation of a $[Mo_2O_4(SCH_2CO_2)_2(solv)_2]^2$ complex intermediate has been found and consequently this latter mechanism is not considered.

In strong support of our proposed $Mo^{VI} \longrightarrow Mo^{IV} \longrightarrow Mo_2^{V}$ mechanism for the oxidation of $HSCH_2CO_2H$ by molybdate, the results of the following preliminary investigation should be mentioned. When complex **1** was added to a solution containing an eight-fold excess of both Me_2SO and $HSCH_2CO_2H$, ^{13}C NMR spectroscopy indicated that more than 1 equivalent of the acid had been converted into dithiodiglycolic acid. Given that the excess of oxidized acid can be correlated with the corresponding conversion of Me_2SO into Me_2S (δ 17), and since the presently isolated molybdenum(V)

Table 2 Positional parameters (× 10^4) of complex **2**

Atom	*x*	*y*	*z*
Mo(1)	1 909(1)	936(1)	2 847(1)
Mo(2)	2 238(1)	2 439(1)	2 470(1)
S(1)	808(1)	631(2)	2 983(2)
S(2)	1 552(2)	3 444(2)	2 485(2)
S(3)	2 809(1)	1 194(2)	1 995(2)
O(1)	2 417(3)	661(4)	3 823(5)
O(2)	1 782(3)	−72(4)	2 082(4)
O(3)	1 360(4)	−1 226(4)	1 822(5)
O(4)	2 928(3)	2 542(5)	3 250(5)
O(5)	2 395(3)	2 881(4)	1 258(5)
O(6)	2 250(5)	3 844(6)	266(7)
O(7)	1 513(3)	1 597(4)	1 442(4)
O(8)	1 346(3)	1 384(4)	−80(4)
O(9)	1 636(3)	1 936(4)	3 195(4)
O(10)	2 726(5)	2 972(7)	−1 034(6)
O(11)	2 083(6)	1 640(7)	−1 581(6)
N(1)	2 330(4)	2 692(5)	5 954(5)
N(2)	4 591(4)	2 477(5)	869(5)
C(1)	716(5)	−290(7)	2 426(8)
C(2)	1 314(5)	−569(7)	2 097(7)
C(3)	1 921(7)	4 035(8)	1 688(9)
C(4)	2 200(6)	3 566(9)	1 013(10)
C(5)	2 375(5)	10 619(6)	797(7)
C(6)	1 698(5)	1 365(6)	682(8)
C(7)	2 821(5)	2 214(6)	6 614(7)
C(8)	3 190(6)	1 612(7)	6 168(8)
C(9)	3 517(7)	1 042(9)	6 895(11)
C(10)	3 974(9)	490(11)	6 492(14)
C(11)	1 788(50)	2 186(6)	5 431(7)
C(12)	1 396(50)	1 749(7)	6 032(8)
C(13)	882(60)	1 256(7)	5 460(8)
C(14)	441(7)	823(9)	5 980(10)
C(15)	2 052(5)	3 277(6)	6 556(7)
C(16)	1 574(6)	3 840(7)	6 047(8)
C(17)	1 313(7)	4 346(8)	6 742(10)
C(18)	839(8)	4 931(10)	6 252(12)
C(19)	2 648(5)	3 092(6)	5 218(7)
C(20)	3 186(5)	3 656(7)	5 582(8)
C(21)	3 439(6)	4 047(7)	4 778(8)
C(22)	2 959(7)	4 543(8)	4 190(10)
C(23)	5 083(5)	2 471(6)	228(7)
C(24)	4 773(5)	2 395(7)	−809(7)
C(25)	5 280(6)	2 542(8)	−1 399(9)
C(26)	5 018(8)	2 388(10)	−2 438(10)
C(27)	4 158(5)	1 770(6)	719(7)
C(28)	4 515(6)	1 007(7)	970(8)
C(29)	4 069(7)	338(8)	612(10)
C(30)	4 389(8)	−416(10)	900(12)
C(31)	4 973(5)	2 490(6)	1 866(7)
C(32)	4 583(5)	2 485(7)	2 639(8)
C(33)	4 994(6)	2 218(8)	3 562(9)
C(34)	4 646(8)	2 183(10)	4 354(11)
C(35)	4 132(5)	3 163(6)	691(8)
C(36)	4 480(6)	3 929(7)	681(9)
C(37)	3 996(7)	4 575(9)	700(10)
C(38)	3 757(8)	4 663(10)	1 622(11)

dimer does not show any appreciable ability to react with Me_2SO, it is apparent that the oxomolybdenum(IV) species can be generated and partially reoxidized by an oxygen-atom abstraction from Me_2SO. However, the observed number of turnovers, *ca.* 3, was much lower than that reported for the above-mentioned[28] [MoO_2L] complex because in this case the molybdenum(IV) hindered species generated cannot undergo dimerization as the reaction proceeds [equation (8) and (9)].

Conclusion

In this investigation we have observed that the $[MoO_2(SCH_2CO_2)_2]^{2}$ complex is reduced by $HSCH_2CO_2H$ to the stable dimeric molybdenum(V) complexes $[Mo^V{}_2O_3(SCH_2CO_2)_4]^{4-}$ and $[Mo^V{}_2O_3(SCH_2CO_2)_3]^{2}$. The structural characterization of the latter confirms the structural versatility of thiolic ligands, constitutes another example of the proclivity of molybdenum(V) complexes to be dinuclear, and unequivocally demonstrates the stoichiometry of the predominant complex obtained in the previously reported reaction between molybdate ions and thioglycolic acid.

The formation of both complexes as well as the structural and electrochemical properties of $[Mo^V{}_2O_3(SCH_2CO_2)_3]^{2}$ provide a clear indication that two intermediate monooxomolybdenum(IV) species are being formed in the first stage of the reaction. In this sense, non-sterically hindered dioxomolybdenum(VI) thiocarboxylate complexes behave like other neutral [$Mo^{VI}O_2L$] complexes containing sulfur-donor ligands. Such complexes have been assumed to act as oxo-transfer agents generating monooxomolybdenum(IV) species which are rapidly intercepted by unreacted [$Mo^{VI}O_2L$], producing an oxo-bridged molybdenum(V) dimer. Such a reaction has been considered as an inner-sphere electron transfer in which the bridged dimer constitutes the stable product.

According to this conclusion it appears likely that, when sterically encumbered dioxomolybdenum thiocarboxylate complexes are reduced,[4] the formation of monomeric Mo^VO complexes occurs through a reaction of the type (10). In the first step of this transformation it might be assumed that dissociation of a co-ordinated carboxylate group in the $Mo^{VI}O_2$ and/or $Mo^{IV}O$ complex is needed to satisfy the steric requirements for the formation of the μ-oxo bond, which allows the electron-transfer reaction. In the second step, as previously observed,[32] available protons to promote the dissociation of the $[Mo_2O_3L_4]^{4}$ intermediate into monomeric $[Mo^VOL_2]^-$ complexes are required. The lower lability of amine and thiolic groups, as compared to a carboxylate group, explains why no complexes with sterically hindered NS_2[8b] or N_3S[9] donor sets exhibiting this redox behaviour have been reported.

$$[Mo^{VI}O_2L_2]^{2-} + [Mo^{IV}OL_2]^{2-} \longrightarrow [Mo_2O_3L_4]^{4-} \xrightarrow{2H^+} 2[Mo^VOL_2]^- + H_2O \quad (10)$$

Experimental

Starting Materials and Methods.—All chemicals, including thioglycolic acid (Merck) and sodium molybdate (Fluka), were used as purchased. The UV/VIS spectra were recorded on a Perkin-Elmer Lambda-2 spectrophotometer using 10 mm quartz cells, NMR solution spectra with a Varian Unity-300, operating at 299.95 and 75.43 MHz for ^1H and ^{13}C, respectively, and a Varian Unity-400 spectrometer (operating frequency, 399.95 and 100.58 MHz for ^1H and ^{13}C). Chemical shifts in D_2O solutions were measured using dioxane as ^{13}C external reference standard (δ 67.4), and the solvent signal as proton internal reference. High-resolution solid-state ^{13}C NMR spectra were obtained by using the combined techniques of high-power proton decoupling, cross-polarization (CP), and magic angle spinning (MAS), at a spinning frequency of approximately 4.0 kHz. Chemical shifts are given with respect to powdered hexamethylbenzene (aromatic signal at δ 132.0).

Electrochemical experiments were carried out with previously described instrumentation.[32] Cyclic voltammetric measurements were performed at room temperature in MeOH solutions, in the range +1.5 to −1.5 V using tetra-*n*-

butylammonium hexafluorophosphate (0.1 mol dm^{-3}) as the supporting electrolyte. The solvent was purified by distillation and thoroughly degassed with argon before use. An electrochemical cell with a glassy-carbon disc working electrode and a platinum-wire counter-electrode was utilized. Potentials are reported relative to an aqueous saturated calomel reference electrode (SCE), which was separated from the test solution by a salt bridge containing the supporting electrolyte.

Preparation of Compounds.—$[NBu^n_4]_2[MoO_2(SCH_2CO_2)_2]\cdot 2H_2O$ **1**. To a stirred solution of $Na_2[MoO_4]\cdot 2H_2O$ (0.73 g, 3.0 mmol) in water (2.0 cm^3), thioglycolic acid (1.0 cm^{-3}, 14.5 mmol) was added at room temperature. The colour of the solution immediately turned orange-red. Fast addition of acetone (80 cm^3) led to a yellow solid which was filtered off. This solid was dissolved in methanol (10 cm^3) and a solution of NBu^n_4Br (1.9 g, 6 mmol) in methanol (5 cm^3) was added. The yellow microcrystalline solid formed by solvent elimination was separated out, yield 65% (Found: C, 51.9; H, 9.5; N, 3.1; S, 7.6. $C_{36}H_{80}MoN_2O_8S_2$ requires C, 52.2; H, 9.7; N, 3.4; S, 7.7%). IR(KBr): ν(Mo=O) 918 and 878 cm^{-1}. NMR (D_2O); ^1H, δ 3.78 (s, CH_2); ^{13}C, δ 186.28 and 36.64.

$[NBu^n_4]_2[Mo_2O_3(SCH_2CO_2)_3]\cdot 2H_2O$ **2**. Thioglycolic acid (0.71 cm^{-3}, 10.3 mmol) was slowly added over a stirred solution of $Na_2[MoO_4]\cdot 2H_2O$ (0.99 g, 4.1 mmol) in water (50 cm^3) with the pH carefully maintained near 5.0 with dilute HCl and/or NaOH. The mixture was stirred for 1 h and then NBu^n_4Br (2.64 g, 8.2 mmol) in water (10.0 cm^3) was added. By cooling the resulting solution to 5° C overnight, clear red-orange prismatic crystals were obtained, yield 74% (Found: C, 44.85; H, 7.90; N, 2.70; S, 9.35. $C_{38}H_{82}Mo_2N_2O_{11}S_3$ requires C, 44.2; H, 7.95; N, 2.70; S, 9.30%). IR (KBr): ν(Mo=O) 949, 935, 919 and 905, ν(Mo–O$_b$) 727 cm^{-1}. NMR ($CDCl_3$); ^1H, δ 3.88 [2 H, s, $(CH_2)_{bridge}$], 4.21, 3.51 [4H, q, AB, J = 17.0 Hz, $(CH_2)_{terminal}$].

Crystal Structure Determination.—$C_{38}H_{82}Mo_2N_2O_{11}S_3$, M_r = 1031.16, monoclinic, space group $P2_1/a$, a = 20.761(8), b = 17.441(7), c = 14.587(6) Å, β = 101.08(6)°, U = 5183.4 Å^3, Z = 4, D_c = 1.321 g cm^{-3}, $F(000)$ = 2176, μ(Cu-Kα) = 55.6 cm^{-1}, λ(Cu-Kα) = 1.5418 Å.

A red-orange parallelepiped (0.15 × 0.15 × 0.60 mm) was selected and mounted on a glass fibre on a Philips PW 1100 automatic diffractometer. Unit-cell dimensions were determined from least-squares refinement of the setting angles of 25 carefully centred reflections using graphite-monochromated Cu-Kα radiation. Intensity data were collected at room temperature within $2\theta < 100°$ by using the ω–2θ scan method with a scan speed of 0.07° s^{-1} and a scan width calculated according to the formula $A + B \tan\theta$ where A = 0.8 ° and B = 0.15.

Stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections collected every 2 h showed no systematic trend. After background correction the intensities were assigned standard deviations $\sigma(I)$ calculated using a value of 0.03 for the instability factor k.[33] The intensities were corrected for Lorentz-polarization effects and for absorption,[34] the range of the absorption corrections being 0.88–1.50. Of 5832 measured reflections, 3667 having $I > 3\sigma(I)$ were considered observed.

All the calculations were carried out on a Hewlett-Packard 486 personal computer by using the SHELX 76[35] and PLUTO[36] programs. Atomic scattering factors for non-hydrogen atoms were taken from ref. 37 while those for hydrogen atoms were from ref. 38. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms.[39] The structure was solved by the heavy-atom method. Full-matrix least-squares refinements were carried out using anisotropic thermal parameters for molybdenum, sulfur and oxygen atoms and isotropic for the remaining ones, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where w was set equal to $1/\sigma^2(F_o)$. The hydrogen atoms were introduced in their calculated positions but not refined. The convergence was reached at R and R' factors of 0.050 and 0.049 respectively. Final positional parameters are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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