Molybdenum(V) Complexes with Monothio-β-diketones: Thiodipivaloylmethane, Thiodibenzoylmethane and Benzoylthioacetone†

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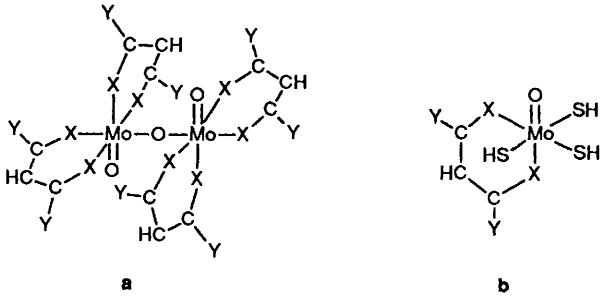
The preparations of oxomolybdenum(V) complexes with thiodipivaloylmethane (Htdpm), $[Mo_2O_3(tdpm)_4]$ **1** and $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$ **2**, thiodibenzoylmethane (Htdbm), $[Mo_2O_3(tdpm)_4]$ **3**, and both benzoylacetone (Hba) and benzoylthioacetone (Hbta), $[Mo_2O_3(ba)_3(bta)]$ **4**, are described. Crystal structures of **1** and **2** have been determined by X-ray diffraction techniques. Complex **1** is dinuclear, the anion of **2** mononuclear, both containing the molybdenum atoms in distorted-octahedral geometry. The charge transfer between the cation and anion of **2** is associated with close contacts between both the dithiolylium sulfurs and the SH-sulfur atom S(3) [S···S 3.335(2) and 3.515(2) Å].

The fact that molybdenum–sulfur bonds are present in molybdoenzymes has extensively stimulated research in molybdenum complexes with sulfur ligand environments. This is particularly true for oxo complexes with molybdenum in its higher oxidation states.[1,2] This class of compounds is interesting also in the study of problems associated with the *trans* influence of the oxygen and sulfur donor atoms.[3,4] Nevertheless, very little is known about such complexes with monothio-β-diketones. So far the only published results are those concerning molybdenum-(IV) and -(VI) complexes with thiodibenzoylmethane (Htdbm). On the basis of chemical analysis and infrared spectra they are described as $[MoCl(tdbm)_3]$, $[Mo(tdbm)_4]$ and $[MoO_2(tdbm)_2]$.[5]

As part of our studies[6,7] on molybdenum complexes with oxygen, sulfur and/or nitrogen donor ligands we describe here the synthesis and structures of molybdenum(V) complexes with thiodipivaloylmethane (Htdpm), $[Mo_2O_3(tdpm)_4]$ **1** and $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$ **2**, and the synthesis of the analogous complexes with thiodibenzoylmethane, $[Mo_2O_3(tdbm)_4]$ **3**, and with both benzoylacetone (Hba) and benzoylthioacetone (Hbta), $[Mo_2O_3(ba)_3(bta)]$ **4**. The neutral complexes **1**, **3** and **4** are dinuclear **a**, while the anion of **2** is mononuclear **b**. The latter is of interest owing to the paucity of structural data on molybdenum complexes with terminal SH groups, and particularly as a possible model for the xanthine oxidase active site which seems to be consistent with an Mo–SH structure.[8]



X = O or S; Y = Me, Bu^t or Ph

Experimental

The starting compounds $[Mo_2O_3(O_2CMe)_4]$[9] and $[Mo_2O_3(dbm)_4]$[10] (Hdbm = dibenzoylmethane), as well as thiodipivaloylmethane and thiodibenzoylmethane[11] and benzoylthioacetone,[12] were prepared as described earlier. All other chemicals were of reagent grade and used as received. Infrared spectra were recorded in Nujol with an FTIR 1600 Fourier-transform spectrophotometer in the 4500–450 cm^{-1} region, optical absorption spectra on a Perkin-Elmer model 200 UV/VIS spectrophotometer.

Preparations of the Complexes.—*μ-Oxo-dioxotetrakis(thiodipivaloylmethanido)dimolybdenum*(V), $[Mo_2O_3(tdpm)_4]$ **1**. A methanolic solution (5 cm^3) of $[Mo_2O_3(O_2CMe)_4]$ (0.5 g, 1.05 mmol) and thiodipivaloylmethane (1.5 g, 7.49 mmol) was heated under reflux for 1 h. The solution was then evaporated under reduced pressure until a crystalline product (0.52 g, 48%) was obtained (Found: C, 52.7; H, 7.6; Mo, 18.6; S, 12.2. Calc. for $C_{44}H_{76}Mo_2O_7S_4$: C, 51.0; H, 7.4; Mo, 18.5; S, 12.4%). IR: 1552s, 1478s, 1223s, 988s, 948s and 786m cm^{-1}.

3,5-*Di*-tert-*butyl*-1,2-*dithiolylium* [*tris*(*hydrogensulfido*)*oxo*(*thiodipivaloylmethanido*)]*molybdate*(V), $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$ **2**. If the reaction mixture for the preparation of complex **1** was left at room temperature, after 25 d a small amount of crystalline product, insufficient for chemical analysis, was obtained. The crystals were characterized by IR and UV/VIS spectroscopy and X-ray analysis. IR: 2600m, 1577s, 1488s, 1415s, 1299s and 950m cm^{-1}.

μ-Oxo-dioxotetrakis(*thiodibenzoylmethanido*)*dimolybdenum*(V), $[Mo_2O_3(tdbm)_4]$ **3**. A mixture of $[Mo_2O_3(O_2CMe)_4]$ (0.40 g, 0.80 mmmol) and thiodibenzoylmethane (0.75 g, 3.2 mmol) was refluxed in methanol (10 cm^3) for 30 min. After 5 d a dark, almost black, microcrystalline product (0.56 g, 56%) was isolated (Found: C, 60.2; H, 3.7; Mo, 15.1; S, 9.1. Calc. for $C_{60}H_{44}Mo_2O_7S_4$: C, 60.2; H, 3.7; Mo, 16.0; S, 10.7%). IR: 1588s, 1525s, 1471vs, 1352s, 1320s, 955s, 758s and 560m cm^{-1}. Alternatively, the same complex was prepared by warming a mixture of $[Mo_2O_3(dbm)_4]$ (0.1 g, 0.90 mmol) and thiodibenzoylmethane (0.1 g, 0.42 mmol) in benzene (5 cm^3). After cooling, a black crystalline product (0.07 g, 66%) was filtered off (Found: C, 61.2; H, 3.3; Mo, 15.5; S, 9.9%). IR: 1588s, 1523vs, 1470vs, 1352s, 1317s, 955s, 758s and 562m cm^{-1}.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Fractional atomic coordinates (× 10^4) for $[Mo_2O_3(tdpm)_4]$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*X*/*c*
Mo	1161(1)	1089(1)	1058(1)
O(1)	758(3)	2559(4)	1473(5)
O(2)	0	0	0
O(3)	2639(3)	1881(4)	2144(4)
O(4)	1905(3)	−733(4)	892(4)
S(1)	1561(1)	1733(2)	−957(2)
S(2)	1120(2)	−58(2)	3133(2)
C(1)	2802(4)	2090(6)	−615(7)
C(2)	3520(5)	2166(7)	636(7)
C(3)	3435(5)	2120(6)	1909(7)
C(4)	3113(5)	2331(7)	−1855(7)
C(5)	4352(6)	2321(9)	3159(8)
C(6)	3003(16)	988(13)	−2572(16)
C(7)	4157(9)	2885(23)	−1535(12)
C(8)	2604(11)	3315(20)	−2704(14)
C(9)	5083(8)	3589(13)	3060(12)
C(10)	4112(9)	2486(19)	4389(11)
C(11)	4846(10)	990(13)	3257(14)
C(12)	1219(5)	−1830(7)	3060(7)
C(13)	1481(6)	−2560(7)	2114(8)
C(14)	1855(4)	−2010(6)	1152(7)
C(15)	1044(6)	−2668(8)	4200(8)
C(16)	2260(6)	−3011(7)	366(8)
C(17)	494(8)	−1937(11)	4955(10)
C(18)	391(10)	−4109(11)	3571(12)
C(19)	2023(8)	−2951(14)	5175(11)
C(20)	1484(9)	−4093(16)	−441(17)
C(21)	2965(12)	−3905(17)	1289(15)
C(22)	2711(15)	−2255(12)	−456(18)

Table 2 Fractional atomic coordinates (× 10^4) for $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$ **2** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*X*/*c*
Mo	2965(1)	1487(1)	2057(1)
O(1)	3369(2)	908(4)	3529(5)
O(2)	2282(2)	2203(5)	314(5)
S(1)	1670(1)	1039(2)	2674(3)
S(2)	2674(1)	−814(2)	328(2)
S(3)	4113(1)	2083(2)	1130(2)
S(4)	3101(1)	3927(2)	3427(2)
S(5)	4896(1)	7036(2)	5300(2)
S(6)	4004(1)	7194(2)	6366(2)
C(1)	1011(4)	1954(6)	1963(7)
C(2)	1061(4)	2716(7)	898(8)
C(3)	1661(3)	2793(6)	105(7)
C(4)	259(4)	1953(8)	2628(8)
C(5)	1611(4)	3629(7)	−1086(8)
C(6)	−500(5)	1666(13)	1398(11)
C(7)	330(6)	3453(11)	3711(11)
C(8)	167(9)	821(16)	3512(18)
C(9)	2033(9)	2973(18)	−2257(14)
C(10)	760(7)	3631(15)	−1871(14)
C(11)	1945(13)	5127(12)	−297(15)
C(12)	4406(3)	7350(5)	3709(6)
C(13)	3624(3)	7603(6)	3710(6)
C(14)	3339(3)	7516(5)	4966(6)
C(15)	4859(4)	7405(6)	2475(7)
C(16)	2513(4)	7734(7)	5266(7)
C(17)	5620(5)	6699(10)	2681(10)
C(18)	4303(5)	6598(9)	963(8)
C(19)	5069(5)	8970(8)	2520(10)
C(20)	1898(4)	7336(10)	3767(10)
C(21)	2281(5)	6764(8)	6261(10)
C(22)	2535(5)	9291(8)	6051(10)

μ-*Oxo-*[*tris*(*benzoylacetonato*)(*benzoylthioacetonato*)]*dioxodimolybdenum*(V), $[Mo_2O_3(ba)_3(bta)]$ **4**. A methanolic solution (10 cm^3) of $[Mo_2O_3(O_2CMe)_4]$ (0.5 g, 1.05 mmol) and benzoylthioacetone (1.0 g, 5.61 mmol) was warmed to 40 °C. After cooling, a violet product (0.1 g, 11%) was obtained and filtered off (Found: C, 53.3; H, 4.4; Mo, 21.7; S, 2.4. Calc. for $C_{40}H_{36}Mo_2O_{10}S$: C, 53.3; H, 4.0; Mo, 21.3; S, 3.6%). IR: 1554s, 1514vs, 1478vs, 1296s, 1069m, 938s, 835s and 766m cm^{-1}.

Crystal Structure Determinations.—Dark red crystals of complex **1** were obtained by slow evaporation of a methanolic solution, while brown crystals of **2** were used as obtained from the reaction.

Crystal data. **1**, $C_{44}H_{76}Mo_2O_7S_4$, $M = 1037.2$, triclinic, space group $P\bar{1}$, $a = 14.487(4)$, $b = 9.401(1)$, $c = 10.579(3)$ Å, $\alpha = 91.26(1)$, $\beta = 109.42(2)$, $\gamma = 96.40(2)°$, $U = 1347.7$ Å^3, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $Z = 1$ (dimer), $D_c = 1.28$ g cm^{-3}, $F(000) = 544$, crystal dimensions 0.05 × 0.27 × 0.15 mm, μ(Mo-Kα) = 6.42 cm^{-1}.

2, $C_{22}H_{41}MoO_2S_6$, $M = 625.9$, triclinic, space group $P\bar{1}$, $a = 17.134(5)$, $b = 9.696(3)$, $c = 9.412(2)$ Å, $\alpha = 103.44(1)$, $\beta = 100.93(1)$, $\gamma = 95.68(2)°$, $U = 1476.4$ Å^3, Mo-Kα radiation as for **1**, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 654$, crystal dimensions 0.39 × 0.23 × 0.05 mm, μ(Mo-Kα) = 8.59 cm^{-1}.

The lattice constants were obtained by least-squares refinement of diffractometer angles of 16 and 20 automatically centred reflections, respectively.

Data collection and refinement. Philips PW 1100 diffractometer at room temperature, ω–2θ (for **1**) and ω (for **2**) scan mode with graphite-monochromated Mo-Kα radiation, scan range 1.6°, scan speed 2.40° min^{-1}; 3281 and 4309 independent reflections ($4 < 2\theta < 60°$, *hkl*). After correction for Lorentz and polarization effects, and absorption for **2**, 3106 and 4097 reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement of **1** and **2**, respectively.

The structures were solved by Patterson and Fourier methods. Full-matrix least-squares refinement with anisotropic thermal motion for all non-hydrogen atoms. Hydrogen atoms were revealed in Fourier difference maps but their contributions (except for those belonging to the SH groups of **2**) were included in the calculations on geometrical grounds (C–H 1.08 Å). Common isotropic thermal parameters were refined separately for the methyl and α-carbon hydrogens (0.18 and 0.10 Å^2 for **1**; 0.16 and 0.13 Å^2 in the anion, and 0.09 and 0.04 Å^2 in the cation of **2**). A final Fourier difference map for complex **2** around S(2), S(3) and S(4) showed a few residual peaks (0.41–0.64 e Å^{-3}) at distances ranging from 0.55 to 0.78 Å which could be attributed to the SH hydrogen atoms. At convergence R and R' were 0.049 and 0.053 (complex **1**) and 0.052 and 0.073 (**2**) for 261 and 284 parameters refined, respectively. The weighting function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1.1192/[\sigma^2(F) + 0.0008F^2]$ and $w = 0.9031/[\sigma^2(F) + 0.0022F^2]$ for **1** and **2**, respectively. Computations were with SHELX 76[13] and SHELXS 86[14] programs with scattering factors as given therein. The ORTEP[15] and PLUTO[16] programs were used for the diagrams. Atomic coordinates for non-hydrogen atoms are given in Tables 1 and 2.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

All four complexes were prepared from the reactions of $[Mo_2O_3(O_2CMe)_4]$ with the corresponding ligands. Both complexes **1** and **2** with thiodipivaloylmethane as a ligand were obtained from the same reaction, initially $[Mo_2O_3(tdpm)_4]$ and then if the reaction mixture was left for 25 d $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$ **2** was formed in small amounts. The formation of **1** is relatively fast while that of **2** takes place slowly and is the result of a few consecutive reactions. First, thiodipivaloylmethane is hydrolysed in acetic acid to dipivaloylmethane with the simultaneous release of H_2S.[17] Hydrogen sulfide causes the formation of dithiodipivaloylmethane which undergoes cyclization, and the synthesis

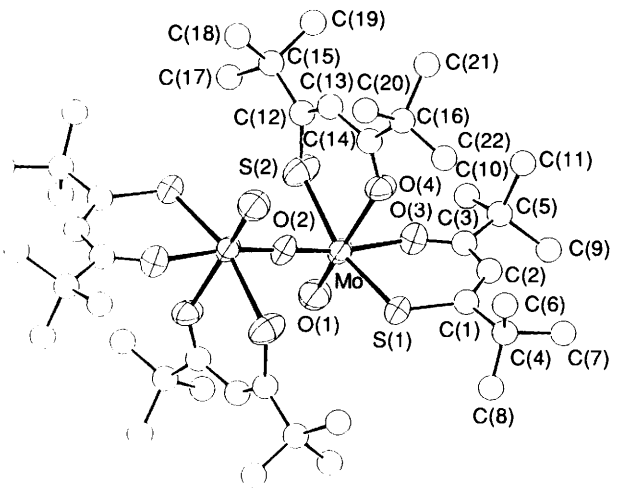

Fig. 1 The structure of $[Mo_2O_3(tdpm)_4]$ **1**, showing the atom numbering scheme. The ellipsoids are drawn at the 50% probability level. Carbon atoms are represented as circles for clarity

Table 3 Selected bond lengths (Å) and angles (°) for $[Mo_2O_3(tdpm)_4]$ **1** with e.s.d.s in parentheses

Mo–O(1)	1.663(5)	C(1)–C(4)	1.536(11)
Mo–O(2)	1.856(1)	C(2)–C(3)	1.394(11)
Mo–O(3)	2.105(4)	C(3)–C(5)	1.521(9)
Mo–O(4)	2.157(4)	S(2)–C(12)	1.690(7)
Mo–S(1)	2.459(3)	O(4)–C(14)	1.237(7)
Mo–S(2)	2.482(3)	C(12)–C(13)	1.377(12)
S(1)–C(1)	1.704(6)	C(12)–C(15)	1.530(12)
O(3)–C(3)	1.256(9)	C(13)–C(14)	1.387(12)
C(1)–C(2)	1.379(8)	C(14)–C(16)	1.528(11)
O(1)–Mo–O(2)	102.3(2)	Mo–O(4)–C(14)	137.4(4)
O(1)–Mo–O(3)	92.1(2)	Mo–S(2)–C(12)	112.4(3)
O(1)–Mo–O(4)	168.9(2)	S(1)–C(1)–C(4)	114.5(5)
O(1)–Mo–S(1)	103.1(2)	S(1)–C(1)–C(2)	126.4(5)
O(1)–Mo–S(2)	92.4(2)	C(2)–C(1)–C(4)	119.1(6)
O(2)–Mo–O(3)	165.5(1)	C(1)–C(2)–C(3)	130.4(7)
O(2)–Mo–O(4)	87.2(1)	O(3)–C(3)–C(2)	125.3(7)
O(2)–Mo–S(1)	90.5(1)	C(2)–C(3)–C(5)	120.4(7)
O(2)–Mo–S(2)	92.9(1)	O(3)–C(3)–C(5)	114.3(6)
O(3)–Mo–O(4)	78.4(2)	S(2)–C(12)–C(15)	115.9(5)
O(3)–Mo–S(1)	86.0(1)	S(2)–C(12)–C(13)	126.2(6)
O(3)–Mo–S(2)	86.7(1)	C(13)–C(12)–C(15)	117.9(6)
O(4)–Mo–S(1)	82.2(1)	C(12)–C(13)–C(14)	128.7(6)
O(4)–Mo–S(2)	81.4(1)	O(4)–C(14)–C(13)	124.3(6)
S(1)–Mo–S(2)	163.0(1)	C(13)–C(14)–C(16)	119.3(6)
Mo–O(3)–C(3)	137.1(4)	O(4)–C(14)–C(16)	116.4(6)
Mo–S(1)–C(1)	111.7(3)		

of 3,5-*tert*-butyl-1,2-dithiolyl species is accomplished by using metal ions as oxidants.[18] Simultaneously, acetic acid formed in the reaction of $[Mo_2O_3(O_2CMe)_4]$ and thiodipivaloylmethane cleaves $[Mo_2O_3(tdpm)_4]$ into mononuclear moieties which with the released H_2S give $[MoO(SH)_3(tdpm)]^-$. The formation of $[Mo_2O_3(ba)_3(bta)]$ by partial hydrolysis of benzoylthioacetone to benzoylacetone occurs as described previously for the preparations of $[Mo_2O_3(acac)_2(tacac)_2]$ and $[Mo_2O_3(acac)_3(tacac)]$ complexes with both acetylacetone (Hacac) and thioacetylacetone (Htacac) as ligands.[7]

The IR spectra of all four complexes confirm the presence of the C–S groups at 1223 (complex **1**), 1299 (**2**), 1317 (**3**) and 1296 cm^{-1} (**4**) as well as of the C–O groups at 1552 (complex **1**), 1577 (**2**), 1523 (**3**) and 1514 cm^{-1} (**4**), respectively. Strong absorption maxima at 948 and 786 (complex **1**), 950 (**2**), 955 and 758 (**3**) and at 938 and 766 cm^{-1} (**4**) belong to the Mo–O(terminal) and to the Mo–O(bridging) stretching frequencies, respectively.

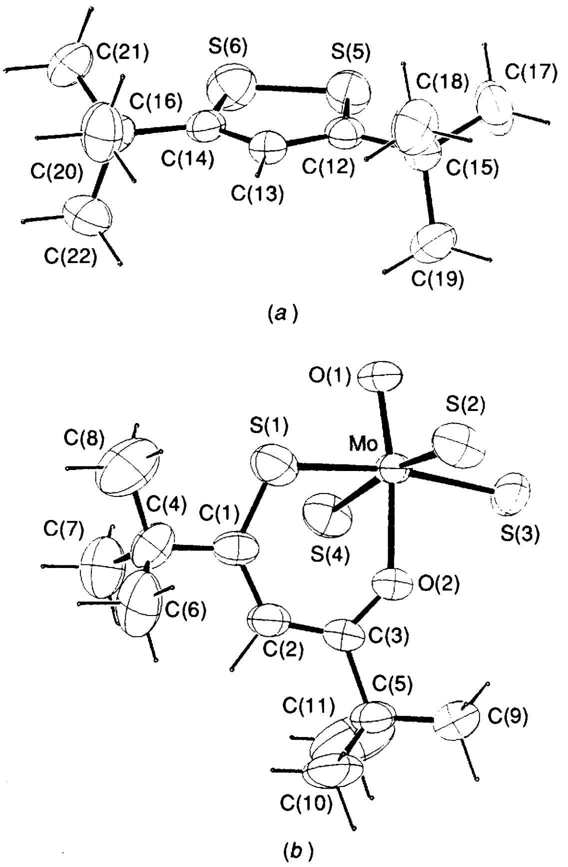

Fig. 2 The structures of the $[Bu^t_2C_3HS_2]^+$ cation (*a*) and $[MoO(SH)_3(tdpm)]^-$ anion (*b*) showing the numbering scheme used. The ellipsoids are drawn at the 50% probability level

Crystal Structure of $[Mo_2O_3(tdpm)_4]$.—The structure is built up from dinuclear molecules with the bridging oxygen atom at a centre of symmetry and therefore with the entire central unit O=Mo–O–Mo=O rigorously *trans* planar. A view of the complex is shown in Fig. 1, the bond lengths and angles are given in Table 3.

Each molybdenum atom is in a distorted-octahedral co-ordination environment being bonded to two oxygen and two sulfur atoms from two bidentate dipivaloylmethanide ligands and to one bridging and one terminal oxo-oxygen atom. The Mo–S[1,7] as well as Mo–O[19] bond lengths are similar to those previously observed. Owing to the *trans* influence of the terminal oxo, the Mo–O bond from the tdpm ligand is longer [2.157(4) Å] than that one *trans* to the bridging oxo [2.105(4) Å]. The bond lengths and angles within the tdpm ligands are as expected.[7,20] Both ligand rings are planar, the largest departures from the least-squares best plane through the ring atoms amounting to 0.033(7) and 0.051(9) Å for C(2) and C(13), respectively. The angle between the two planes is 89.9(2)°.

Crystal Structure of $[Bu^t_2C_3HS_2][MoO(SH)_3(tdpm)]$.—The crystals consist of discrete 3,5-di-*tert*-butyl-1,2-dithiolylium cations and molybdate(v) anions. The structures of both the cation and anion are shown in Fig. 2(*a*) and (*b*) and the interatomic distances and angles are given in Table 4. The present structure is the first example of a dithiolylium salt with a complex anion, all known salts being with simple anions such as chloride,[21] bromide,[22] iodide[23–25] and isothiocyanate[26] or MCl_4 ions (M = Fe^{II},[27,28] Hg^{II},[28] Co^{II}[29] or Fe^{III}[30]).

3,5-Di-*tert*-butyl-1,2-dithiolylium shows an approximate non-crystallographic mirror plane symmetry with a planar five-membered ring. The largest deviations from the least-squares best plane through the ring atoms are −0.018(4) Å [C(13)] and 0.018(3) Å [C(14)]. The bond lengths in the dithiolylium cation

Table 4 Selected bond lengths (Å) and angles (°) for $[\mathrm{Bu^t_2C_3HS_2}][\mathrm{MoO(SH)_3(tdpm)}]$ **2** with e.s.d.s in parentheses

Mo–O(1)	1.670(5)	C(2)–C(3)	1.386(10)
Mo–O(2)	2.122(5)	C(3)–C(5)	1.523(11)
Mo–S(1)	2.422(3)	S(5)–S(6)	1.981(3)
Mo–S(2)	2.379(2)	S(5)–C(12)	1.681(6)
Mo–S(3)	2.372(3)	S(6)–C(14)	1.681(6)
Mo–S(4)	2.382(2)	C(12)–C(13)	1.386(8)
O(2)–C(3)	1.262(7)	C(12)–C(15)	1.522(9)
S(1)–C(1)	1.642(7)	C(13)–C(14)	1.378(9)
C(1)–C(2)	1.386(11)	C(14)–C(16)	1.520(9)
C(1)–C(4)	1.535(11)		
O(1)–Mo–O(2)	170.9(2)	S(1)–C(1)–C(2)	128.7(5)
O(1)–Mo–S(1)	88.0(2)	S(1)–C(1)–C(4)	113.1(5)
O(1)–Mo–S(2)	95.4(2)	C(2)–C(1)–C(4)	118.2(6)
O(1)–Mo–S(3)	101.7(2)	C(1)–C(2)–C(3)	127.5(6)
O(1)–Mo–S(4)	95.1(2)	O(2)–C(3)–C(2)	123.5(6)
O(2)–Mo–S(1)	83.0(1)	O(2)–C(3)–C(5)	115.3(5)
O(2)–Mo–S(2)	85.7(1)	C(2)–C(3)–C(5)	121.2(6)
O(2)–Mo–S(3)	87.3(1)	S(6)–S(5)–C(12)	97.0(2)
O(2)–Mo–S(4)	83.6(1)	S(5)–S(6)–C(14)	95.9(2)
S(1)–Mo–S(2)	88.7(1)	S(5)–C(12)–C(13)	114.4(4)
S(1)–Mo–S(3)	170.3(1)	S(5)–C(12)–C(15)	118.5(4)
S(1)–Mo–S(4)	89.4(1)	C(13)–C(12)–C(15)	127.0(5)
S(2)–Mo–S(3)	91.0(1)	C(12)–C(13)–C(14)	117.0(5)
S(2)–Mo–S(4)	169.3(1)	S(6)–C(14)–C(13)	115.6(4)
S(3)–Mo–S(4)	89.1(1)	S(6)–C(14)–C(16)	116.2(4)
Mo–O(2)–C(3)	137.7(4)	C(13)–C(14)–C(16)	128.2(5)
Mo–S(1)–C(1)	112.7(3)		

are significantly shorter than corresponding single bonds and indicative of π-orbital delocalization over the heterocyclic ring.[31] They do not differ essentially from those found in all the related structures, although some of them, in particular the S–S bond length, might be significant. The S–S bond distance of 1.981(3) Å is the shortest established so far in differently substituted dithiolylium ions, expressing thus even more its double-bond character.[32] The longest S–S bond [2.08(2) Å] was found in the structure of 3,5-diamino-1,2-dithiolylium iodide.[24] Both S–C bonds [mean 1.681(6) Å] and both C–C bonds [1.378(9) and 1.386(8) Å] in the five-membered ring are indicative of the considerable degree of double-bond character.[25,33] All other bond lengths and angles within the 1,2-dithiolylium cation are as expected.

Mononuclear species, and in particular those with SH groups as ligands, such as $[\mathrm{MoO(SH)_3(tdpm)}]^-$, are relatively rare among molybdenum(v) complexes. Although the hydrogens on the terminal sulfur atoms were not unambiguously revealed in the final Fourier difference map, their presence and identity are supported by the following evidence: (*i*) the mean of the three Mo–SH bond lengths [2.378(2) Å] definitely suggests a single bond between molybdenum and sulfur since the typical values established for Mo=S are between 2.085 and 2.129 Å;[34] (*ii*) following a general rule for this type of complex the Mo atom is displaced 0.231(1) Å out of the equatorial plane of the four sulfur atoms in the direction of the double-bonded oxygen atom;[35] (*iii*) the IR band at 2600 cm^{-1} can only be explained by S–H stretching vibrations;[36] and (*iv*) it is reasonable to suppose that the oxidation state of molybdenum has not been changed during the chemical reaction.

In the $[\mathrm{MoO(SH)_3(tdpm)}]^-$ anion the molybdenum atom has a distorted-octahedral co-ordination, being surrounded by one oxygen and one sulfur atom from the bidentate dipivaloylmethanide ligand, three sulfur atoms from the hydrogensulfide ligands and one terminal oxygen atom. The values of the Mo–S and Mo–O bond lengths are close to those found in the structure of **1** and in other similar complexes.[1,7,19] The bond Mo–O(2) [2.122(5) Å] is lengthened due to the *trans* influence of the terminal oxygen atom. The dipivaloylmethane ring is planar within experimental error and its least-squares best plane and the plane through the dithiolylium cation make an angle of 24.40(8).° The bond lengths and angles in the dipivaloylmethanide ligand are in good agreement with the corresponding values in **1** and other related structures.[7,20]

The outstanding feature of the structure is the existence of two significantly short S ··· S contacts between the disulfide group S(5)–S(6) of the cation and the S(3)H group of the anion. Both contacts, S(3) ··· S(5^{I}) and S(3) ··· S(6^{I}) [I 1 − *x*, 1 − *y*, 1 − *z*] of 3.335(2) and 3.515(2) Å, are considerably shorter than the sum of the conventional van der Waals radii of two sulfur atoms.[37] These short contacts are associated with the charge transfer between the dithiolylium cation and the molybdate(v) anion which results in the prominent absorption band at 493 nm (20 280 cm^{-1}) in the visible spectrum. Such short interactions with dithiolylium ions have previously been observed in a large number of dithiolium salts.[27–30,38]

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