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# The Crystal and Molecular Structures of Trichlorobis($\eta^5$-cyclopentadienyl)-$\mu$-hydroxo-di-$\mu$-methanethiolato-dimolybdenum Hemitoluene Solvate and Observations on the Structure of a Possible Trichlorobis($\eta^5$-cyclopentadienyl)-tri-$\mu$-methanethiolato-dimolybdenum

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## Abstract

The crystal structures of trichlorobis($\eta^5$-cyclopentadienyl)-$\mu$-hydroxo-di-$\mu$-methanethiolato-dimolybdenum hemitoluene solvate [$Mo_2(C_5H_5)_2(CH_3S)_2Cl_3(OH).\frac{1}{2}C_7H_8$, $C_{12}H_{17}Cl_3Mo_2OS_2.\frac{1}{2}C_7H_8$], compound (I) [orthorhombic, $a = 22\cdot115$ (2), $b = 16\cdot020$ (2), $c = 11\cdot226$ (6) Å, $Z = 8$, space group $C222_1$, 2231 reflexions, $R_w = 0\cdot049$] and trichlorobis($\eta^5$-cyclopentadienyl)-tri-$\mu$-methanethiolato-dimolybdenum [$Mo_2(C_5H_5)_2(CH_3S)_3Cl_3$, $C_{13}H_{19}Cl_3Mo_2S_3$], compound (II) [monoclinic, $a = 15\cdot441$ (5), $b = 15\cdot678$ (4), $c = 7\cdot257$ (1) Å, $\beta = 97\cdot80$ (2)°, $Z = 4$, space group $P2_1/n$, 1935 reflexions, $R_w = 0\cdot084$] have been determined. Each molecule consists of a $Mo(\eta^5$-$C_5H_5)Cl_2$ moiety and a $Mo(\eta^5$-$C_5H_5)Cl$ moiety linked by three ligands: one hydroxo and two methanethiolato bridges in (I), and three methanethiolato bridges in (II), where problems of disorder and partial hydrolysis were encountered. The Mo$\cdots$Mo distances of 2·726 (1) and 2·852 (2) Å in (I) and (II), respectively, suggest a direct Mo—Mo bond.

## Introduction

The reaction of ($\eta^5$-cyclopentadienyl)molybdenum tetrachloride with methanethiol in diethyl ether yielded at first (II) in the form of orange cube-shaped crystals which were examined by X-ray diffraction. The X-ray analysis ran into difficulties and attempts were made to repeat the preparation. However, all subsequent attempts gave (I) as orange needles (Green & Bunker, 1978). Analytical and spectroscopic data indicate that (I) and (II) are similar and contain $\eta^5$-cyclopentadienyl, methanethiolato, and chloride residues, but give little guidance as to their true nature. Here we report the X-ray structure analyses.

## Results and discussion

(I) was readily identified as the hemitoluene solvate of trichlorobis($\eta^5$-cyclopentadienyl)-$\mu$-hydroxo-di-$\mu$-methanethiolato-dimolybdenum (A). The final atomic positional parameters are given in Table 1,* bond lengths and angles with e.s.d.'s calculated from the variance-covariance matrix in Table 2 and details of important molecular planes in Table 3. A projection of the molecule is shown in Fig. 1. The asymmetric unit contains one molecule in a general position in the unit
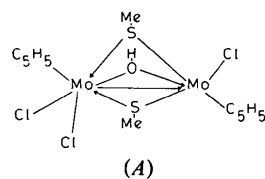


(A)

cell and half a molecule of toluene solvate perpendicular to, and mirrored in, the plane (0·5,0,0). The toluene molecule is planar [plane (5) in Table 3] and interatomic distances and angles are normal, albeit with somewhat high e.s.d.'s, probably a consequence of its high thermal motion. There are no unusual intermolecular contacts.

The coordination about Mo(1) is distorted octahedral, remarkably similar to that in ($\eta^5$-C$_5$H$_5$)NbCl$_3$-[(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$] and {[($\eta^5$-C$_5$H$_4$-CH$_3$)NbCl$_3$OH]$_2$-$\mu$-O} (Daran, Prout, de Cian, Green & Siganporia, 1977). The contact to Mo(2) caps the face defined by S(1), S(2) and O(1). In the distorted octahedron, Cl(1), Cl(2), S(1) and S(2) form a plane with Mo(1) 0·508 below and O(1) 1·386 Å above. S(1), S(2) and O(1) form a triple bridge between Mo(1) and Mo(2). The acute bridging angles Mo(1)–S–

Mo(2), 66·6 (1) and 66·7 (1)°, are consistent with the Dahl criteria for metal–metal bonding (Dahl, de Gil & Feltham, 1969).

The coordination about Mo(2) is distorted trigonal prismatic with S(1), Cl(3) and the $\eta^5$-cyclopentadienyl ligand forming the base, and O(1), S(2) and contact to Mo(1) the top. The bridging ligands are not symmetri-

Table 1. *Fractional atomic coordinates and isotropic temperature factors for compound (I), with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{iso}$ (Å²) |
|---|---|---|---|---|
| Mo(1) | 0·18003 (3) | 0·22406 (4) | 0·13359 (6) | |
| Mo(2) | 0·13364 (3) | 0·37457 (4) | 0·20037 (6) | |
| S(1) | 0·20728 (9) | 0·3658 (1) | 0·0440 (2) | |
| S(2) | 0·07846 (9) | 0·2475 (1) | 0·2352 (2) | |
| Cl(1) | 0·1886 (1) | 0·1106 (1) | 0·2831 (2) | |
| Cl(2) | 0·2920 (1) | 0·2042 (1) | 0·1353 (2) | |
| Cl(3) | 0·0629 (1) | 0·3858 (1) | 0·0357 (2) | |
| O(1) | 0·1950 (2) | 0·2981 (3) | 0·2644 (5) | |
| C(1) | 0·1429 (5) | 0·2269 (7) | −0·0680 (8) | |
| C(2) | 0·1016 (4) | 0·1800 (7) | −0·0016 (9) | |
| C(3) | 0·1302 (6) | 0·1090 (7) | 0·0422 (9) | |
| C(4) | 0·1902 (5) | 0·1104 (6) | 0·000 (1) | |
| C(5) | 0·1983 (5) | 0·1829 (7) | −0·0653 (8) | |
| C(6) | 0·1805 (5) | 0·4745 (5) | 0·3140 (9) | |
| C(7) | 0·1384 (5) | 0·4315 (5) | 0·3890 (8) | |
| C(8) | 0·0800 (5) | 0·4526 (6) | 0·345 (1) | |
| C(9) | 0·0875 (5) | 0·5053 (6) | 0·246 (1) | |
| C(10) | 0·1503 (6) | 0·5178 (5) | 0·2301 (9) | |
| C(11) | 0·2785 (4) | 0·3988 (6) | 0·1048 (9) | |
| C(12) | 0·0864 (5) | 0·2228 (7) | 0·3923 (8) | |
| C(13) | 0·5000 | 0·319 (2) | 0·2500 | |
| C(14) | 0·4500 (8) | 0·363 (2) | 0·204 (2) | |
| C(15) | 0·451 (1) | 0·453 (2) | 0·209 (2) | |
| C(16) | 0·5000 | 0·496 (3) | 0·2500 | |
| C(17) | 0·5000 | 0·224 (2) | 0·2500 | |
| H(11) | 0·1349 | 0·2809 | −0·1092 | 0·0500 |
| H(21) | 0·0582 | 0·1952 | 0·0121 | 0·0500 |
| H(31) | 0·1119 | 0·0646 | 0·0938 | 0·0500 |
| H(41) | 0·2215 | 0·0665 | 0·0152 | 0·0500 |
| H(51) | 0·2366 | 0·2017 | −0·1044 | 0·0500 |
| H(61) | 0·2254 | 0·4718 | 0·3252 | 0·0500 |
| H(71) | 0·1476 | 0·3947 | 0·4576 | 0·0500 |
| H(81) | 0·0410 | 0·4328 | 0·3786 | 0·0500 |
| H(91) | 0·0542 | 0·5292 | 0·1969 | 0·0500 |
| H(101) | 0·1683 | 0·5534 | 0·1654 | 0·0500 |
| H(111) | 0·2898 | 0·4541 | 0·0705 | 0·0500 |
| H(112) | 0·2751 | 0·4035 | 0·1933 | 0·0500 |
| H(113) | 0·3104 | 0·3567 | 0·0844 | 0·0500 |
| H(121) | 0·0640 | 0·1701 | 0·4106 | 0·0500 |
| H(122) | 0·0694 | 0·2695 | 0·4412 | 0·0500 |
| H(123) | 0·1302 | 0·2153 | 0·4120 | 0·0500 |

Table 2. *Interatomic distances (Å) and bond angles (°) for compound (I)*

| Mo(1)–Mo(2) | 2·726 (1) | | |
|---|---|---|---|
| Mo(1)–S(1) | 2·555 (2) | Mo(2)–S(1) | 2·399 (2) |
| Mo(1)–S(2) | 2·547 (2) | Mo(2)–S(2) | 2·406 (2) |
| Mo(1)–O(1) | 1·917 (5) | Mo(2)–O(1) | 1·965 (5) |
| Mo(1)–Cl(1) | 2·481 (2) | Mo(2)–Cl(3) | 2·428 (2) |
| Mo(1)–Cl(2) | 2·497 (2) | Mo(2)–C(6) | 2·295 (9) |
| Mo(1)–C(1) | 2·407 (9) | Mo(2)–C(7) | 2·308 (8) |
| Mo(1)–C(2) | 2·410 (9) | Mo(2)–C(8) | 2·365 (9) |
| Mo(1)–C(3) | 2·380 (9) | Mo(2)–C(9) | 2·385 (10) |
| Mo(1)–C(4) | 2·369 (9) | Mo(2)–C(10) | 2·348 (8) |
| Mo(1)–C(5) | 2·363 (9) | C(6)–C(7) | 1·43 (2) |
| S(1)–C(11) | 1·796 (10) | C(7)–C(8) | 1·42 (2) |
| S(2)–C(12) | 1·816 (9) | C(8)–C(9) | 1·40 (2) |
| C(1)–C(2) | 1·40 (2) | C(9)–C(10) | 1·41 (2) |
| C(2)–C(3) | 1·39 (2) | C(10)–C(6) | 1·35 (2) |
| C(3)–C(4) | 1·40 (2) | | |
| C(4)–C(5) | 1·39 (2) | | |
| C(5)–C(1) | 1·41 (2) | | |

| S(1)–Mo(1)–S(2) | 104·7 (1) | S(1)–Mo(2)–S(2) | 114·4 (1) |
|---|---|---|---|
| S(1)–Mo(1)–O(1) | 73·2 (2) | S(1)–Mo(2)–O(1) | 76·2 (2) |
| S(1)–Mo(1)–Cl(1) | 154·0 (1) | S(1)–Mo(2)–Cl(3) | 83·3 (1) |
| S(1)–Mo(1)–Cl(2) | 83·2 (1) | S(2)–Mo(2)–O(1) | 76·3 (2) |
| S(2)–Mo(1)–O(1) | 73·6 (2) | S(2)–Mo(2)–Cl(3) | 81·9 (1) |
| S(2)–Mo(1)–Cl(1) | 82·6 (2) | O(1)–Mo(2)–Cl(3) | 140·3 (2) |
| S(2)–Mo(1)–Cl(2) | 152·8 (1) | | |
| O(1)–Mo(1)–Cl(1) | 85·5 (2) | | |
| O(1)–Mo(1)–Cl(2) | 84·3 (2) | | |
| Cl(1)–Mo(1)–Cl(2) | 80·0 (1) | | |
| Mo(1)–O(1)–Mo(2) | 89·2 (2) | | |
| Mo(1)–S(1)–Mo(2) | 66·6 (1) | Mo(1)–S(2)–Mo(2) | 66·7 (1) |
| Mo(1)–S(1)–C(11) | 108·6 (3) | Mo(1)–S(2)–C(12) | 108·5 (4) |
| Mo(2)–S(1)–C(11) | 107·4 (3) | Mo(2)–S(2) -C(12) | 107·0 (4) |
| C(5)–C(1)–C(2) | 107 (1) | C(10)–C(6)–C(7) | 110 (1) |
| C(1)–C(2)–C(3) | 109 (1) | C(6)–C(7)–C(8) | 106 (1) |
| C(2)–C(3)–C(4) | 107 (1) | C(7)–C(8)–C(9) | 108 (1) |
| C(3)–C(4)–C(5) | 108 (1) | C(8)–C(9)–C(10) | 108 (1) |
| C(4)–C(5)–C(1) | 108 (1) | C(9)–C(10)–C(6) | 109 (1) |
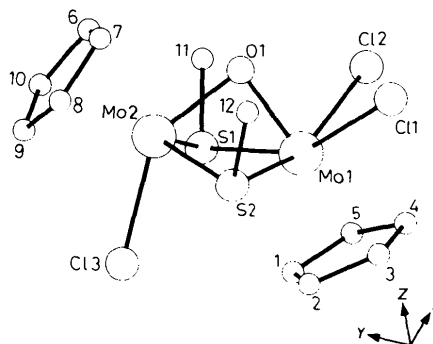


Fig. 1. The molecular structure of (I). For clarity, the C atoms are labelled by their serial number only.

cal. The Mo(2)—S lengths are 2·399 (2) and 2·406 (2) Å, and compare well with those found in Mo complexes where the thiolato ligand is acting as a one-electron donor, e.g. 2·367 (2) in $Mo(S_2C_6H_4)_3$ (Bennett, Cowie, Martin & Takats, 1973), 2·385 (15) in $Mo_2O_4$-$(SO_2NC_5H_{10})_2$ (Drew & Kay, 1971a) and 2·38 (1) Å in $Mo_2S_2O_2(SO_2NC_4H_8)_2$ (Drew & Kay, 1971b). Conversely, the Mo(1)—S lengths of 2·547 (2) and 2·555 (2) Å are significantly longer than the Mo(2)—S distances, and are attributed to be the Mo—S distances for a two-electron donor. In the same way, the Mo(1)—O(1) length [1·917 (5) Å] is assumed to be the one-electron

Table 3. *Least-squares planes in compound* (I)

x, y, and z represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane.

Plane (1): Ring C(1) to C(5)
Equation of plane: $5·998x + 7·928y + 9·267z = 2·027$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| C(1) | −0·001 | | |
| C(2) | −0·005 | Mo(1) | 2·067 |
| C(3) | 0·009 | | |
| C(4) | −0·010 | | |
| C(5) | 0·007 | | |

Normal to Mo(1) meets plane 0·05 Å from centroid.

Plane (2): Ring C(6) to C(10)
Equation of plane: $−0·733x + 12·711y + 6·821z = 8·041$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| C(6) | 0·002 | | |
| C(7) | −0·004 | Mo(2) | −2·010 |
| C(8) | 0·004 | | |
| C(9) | −0·003 | | |
| C(10) | 0·001 | | |

Normal to Mo(2) meets plane 0·09 Å from centroid.

Plane (3): S(1)S(2)Cl(1)Cl(2)
Equation of plane: $5·957x + 8·167y + 9·171z = 4·636$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| S(1) | −0·010 | | |
| S(2) | 0·010 | Mo(1) | −0·508 |
| Cl(1) | −0·013 | O(1) | 1·386 |
| Cl(2) | 0·013 | | |

Plane (4): S(1)S(2)O(1)
Equation of plane: $7·109x − 14·094y − 3·931z = −3·854$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| S(1) | 0·000 | Mo(1) | 1·451 |
| S(2) | 0·000 | Mo(2) | −1·262 |
| O(1) | 0·000 | C(11) | −0·198 |
| | | C(12) | −0·213 |

Plane (5): Toluene solvate
Equation of plane: $8·953x − 0·000y − 10·264z = 1·911$

| Constituent atoms | |
|---|---|
| C(13) | 0·000 |
| C(14) | 0·020 |
| C(15) | −0·021 |
| C(16) | 0·000 |
| C(17) | 0·000 |
| C(14′) | −0·020 |
| C(15′) | 0·021 |

donor and the longer Mo(2)—O(1) length [1·965 (5) Å] the two-electron donor.

The unsymmetrical nature of the bridging ligands is also reflected in the geometries about a plane defined by the three ligand atoms [plane (4), Table 3]; Mo(2) lies 1·262 above, Mo(1) 1·451 Å below the plane, and the methyl groups are bent up out of the plane towards Mo(2). The distinction between one- and two-electron donors in the bridging ligands is feasible because the coordination number is not the same for each Mo. For methanethiolato bridges with an identical distribution of ligands around Mo there is no significant difference in the Mo—S lengths, e.g. 2·451 (1)–2·462 (1) Å in $[(\eta^6\text{-}C_7H_8)Mo(SCH_3)_2]_2^{2+}$ (Silverthorn, Couldwell & Prout, 1978), 2·44 Å in $[(\eta^5\text{-}C_5H_5)Mo(SCH_3)_2]_2^{+}$, and 2·46 Å in $[(\eta^5\text{-}C_5H_5)Mo(SCH_3)_2]_2$ (Connelly & Dahl, 1970).

If the distinction between 2 e- and 1 e-donor bridging ligands is accepted, it follows that the bridging O atom must be a hydroxyl group even though the H is not seen in the electron density and there are no H-bonded contacts. Furthermore, the Mo(1)···Mo(2) contact must be a metal—metal bond in which Mo(1) donates 2 e to Mo(2), so that the 18 e rule is satisfied at both Mo atoms.

The $(\eta^5\text{-}C_5H_5)$ groups are in a *trans* configuration with respect to the Mo(1)···Mo(2) vector and, like the Mo—Cl bonds, their dimensions compare well with those found in $(\eta^5\text{-}C_5H_5)_2MoCl_2$ and related compounds (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The individual rings are planar within experimental error. The Mo—C distances are in the range 2·30 (1)–2·41 (1) Å, the perpendicular distances from the Mo atoms to the rings are 2·067 and 2·010 Å, and the perpendiculars to the rings at the Mo atoms meet the rings close (0·05 and 0·09 Å) to their centroids.

The X-ray analysis of (II) failed to give an unambiguous description of the chemical structure. The general features, the environments of Mo(1) and Mo(2), the Mo(1)—Mo(2) bond, and the triple bridge, are common to both (I) and (II), but the crystals of (II) are clearly disordered. The poor definition of the $\eta^5$-cyclopentadienyl rings and the alternative positions, Cl(3) and Cl(3′), for the Cl ligand at Mo(2) are manifestations of the disorder which also affects the bridging ligands. These appear to be three S atoms, but the associated electron density, four peaks of about 3 e, is not sufficient for three methyl groups. Models in which some fraction of the molecules present had chloro- or sulphido-bridges were considered and rejected on chemical or crystallographic grounds.

The most plausible solution appears to be that the crystals contain an equipollent mixture of (*B*) and its partial hydrolysis product (*A*). The final atomic positional parameters for this model are reported in Table 4, bond lengths and angles with e.s.d.'s calculated from

the variance-covariance matrix in Table 5 and details of molecular planes in Table 6. Fig. 2 gives the molecular structure of (II), showing the apparent disorder.



(B)

This model has its disadvantages. Firstly, it places 6 e at C(12) which is only a 3 e peak in the difference density, so that C(12) after refinement has a very high temperature factor. Secondly, although the model accounts for the exceptionally short Mo(1)—S(3) and Mo(2)—S(3) contacts, because the S(3) site becomes a mean position of S of S—Me and O of OH, there is not the expected elongation of the electron density cloud and thermal ellipsoid. On the other hand, it uses only molecules which have 18 e valence shells at Mo(1) and Mo(2) after taking into account the metal—metal bond, Mo(1)—Mo(2), which at 2·852 (2) Å cannot be very significantly different in bonding character from that in (I). Furthermore, all attempts to repeat the preparation of (II) have given (I).

## Experimental

Samples of both compounds are sensitive to air and moisture and were mounted under dry nitrogen in glass

Table 4. *Fractional atomic coordinates and isotropic temperature factors for compound* (II) *with e.s.d.'s in parentheses*

| | x | y | z | $U_{iso}$ (Å²) |
|---|---|---|---|---|
| Mo(1) | 0·20004 (9) | 0·0729 (1) | −0·0366 (2) | |
| Mo(2) | 0·36309 (9) | 0·1605 (1) | −0·0106 (2) | |
| S(1) | 0·2298 (3) | 0·2224 (4) | −0·1585 (8) | |
| S(2) | 0·3537 (4) | 0·0113 (4) | 0·025 (1) | |
| S(3) | 0·2699 (4) | 0·1507 (5) | 0·201 (1) | |
| Cl(1) | 0·1714 (5) | −0·0239 (4) | 0·2154 (8) | |
| Cl(2) | 0·0734 (4) | 0·1453 (4) | 0·062 (1) | |
| Cl(3) | 0·4011 (5) | 0·0840 (8) | −0·312 (1) | |
| Cl(3') | 0·3845 (7) | 0·1623 (8) | −0·322 (1) | |
| C(1) | 0·122 (1) | 0·071 (1) | −0·334 (2) | 0·097 (5) |
| C(2) | 0·205 (1) | 0·035 (1) | −0·344 (2) | 0·092 (5) |
| C(3) | 0·210 (1) | −0·042 (1) | −0·247 (2) | 0·096 (5) |
| C(4) | 0·131 (1) | −0·054 (1) | −0·176 (2) | 0·100 (5) |
| C(5) | 0·077 (1) | 0·015 (1) | −0·230 (2) | 0·098 (5) |
| C(6) | 0·4134 (8) | 0·262 (1) | 0·223 (2) | 0·092 (5) |
| C(7) | 0·4267 (9) | 0·2954 (9) | 0·052 (3) | 0·089 (5) |
| C(8) | 0·486 (1) | 0·242 (1) | −0·025 (2) | 0·091 (5) |
| C(9) | 0·5087 (8) | 0·1758 (9) | 0·101 (3) | 0·089 (5) |
| C(10) | 0·464 (1) | 0·188 (1) | 0·254 (2) | 0·088 (5) |
| C(11) | 0·234 (2) | 0·220 (3) | −0·435 (5) | 0·05 (1) |
| C(11') | 0·187 (2) | 0·304 (2) | 0·034 (5) | 0·043 (9) |
| C(12) | 0·379 (2) | −0·016 (2) | 0·286 (4) | 0·10 (1) |
| C(13) | 0·214 (3) | 0·262 (3) | 0·240 (6) | 0·05 (1) |

Table 5. *Interatomic distances* (Å) *and bond angles* (°) *for compound* (II)

| | | | |
|---|---|---|---|
| Mo(1)—Mo(2) | 2·852 (2) | | |
| Mo(1)—S(1) | 2·570 (5) | Mo(2)—S(1) | 2·394 (5) |
| Mo(1)—S(2) | 2·544 (6) | Mo(2)—S(2) | 2·361 (6) |
| Mo(1)—S(3) | 2·266 (8) | Mo(2)—S(3) | 2·250 (8) |
| Mo(1)—Cl(1) | 2·463 (5) | Mo(2)—Cl(3) | 2·628 (9) |
| Mo(1)—Cl(2) | 2·451 (5) | Mo(2)—Cl(3') | 2·327 (9) |
| Mo(1)—C(1) | 2·32 (1) | Mo(2)—C(6) | 2·37 (1) |
| Mo(1)—C(2) | 2·32 (1) | Mo(2)—C(7) | 2·35 (1) |
| Mo(1)—C(3) | 2·37 (1) | Mo(2)—C(8) | 2·30 (1) |
| Mo(1)—C(4) | 2·41 (1) | Mo(2)—C(9) | 2·30 (1) |
| Mo(1)—C(5) | 2·38 (1) | Mo(2)—C(10) | 2·34 (1) |
| S(1)—C(11) | 2·02 (4) | S(3)—C(13) | 1·98 (4) |
| S(1)—C(11') | 2·07 (4) | C(11')···C(13) | 1·64 (5) |
| S(2)—C(12) | 1·92 (3) | Cl(3)···Cl(3') | 1·26 (2) |
| C(1)—C(2) | 1·402 (9) | C(6)—C(7) | 1·391 (9) |
| C(2)—C(3) | 1·397 (9) | C(7)—C(8) | 1·401 (9) |
| C(3)—C(4) | 1·399 (9) | C(8)—C(9) | 1·400 (9) |
| C(4)—C(5) | 1·393 (9) | C(9)—C(10) | 1·396 (9) |
| C(5)—C(1) | 1·403 (9) | C(10)—C(6) | 1·394 (9) |
| S(1)—Mo(1)—S(2) | 101·6 (2) | S(1)—Mo(2)—S(2) | 112·9 (2) |
| S(1)—Mo(1)—S(3) | 71·5 (2) | S(1)—Mo(2)—S(3) | 75·2 (2) |
| S(1)—Mo(1)—Cl(1) | 151·2 (2) | S(1)—Mo(2)—Cl(3) | 95·0 (3) |
| S(1)—Mo(1)—Cl(2) | 82·3 (2) | S(1)—Mo(2)—Cl(3') | 77·7 (3) |
| S(2)—Mo(1)—S(3) | 74·5 (2) | S(2)—Mo(2)—S(3) | 78·6 (3) |
| S(2)—Mo(1)—Cl(1) | 83·8 (3) | S(2)—Mo(2)—Cl(3) | 70·3 (3) |
| S(2)—Mo(1)—Cl(2) | 152·3 (3) | S(2)—Mo(2)—Cl(3') | 98·0 (4) |
| S(3)—Mo(1)—Cl(1) | 83·1 (2) | S(3)—Mo(2)—Cl(3) | 140·6 (3) |
| S(3)—Mo(1)—Cl(2) | 81·0 (3) | S(3)—Mo(2)—Cl(3') | 148·6 (3) |
| Cl(1)—Mo(1)—Cl(2) | 80·6 (3) | Cl(3)—Mo(2)—Cl(3') | 28·5 (4) |
| Mo(1)—S(1)—Mo(2) | 70·0 (2) | Mo(1)—S(2)—Mo(2) | 71·0 (2) |
| Mo(1)—S(1)—C(11) | 111 (1) | Mo(1)—S(2)—C(12) | 109 (1) |
| Mo(1)—S(1)—C(11') | 104 (1) | Mo(2)—S(2)—C(12) | 109 (1) |
| Mo(2)—S(1)—C(11) | 107 (1) | Mo(1)—S(3)—Mo(2) | 78·3 (3) |
| Mo(2)—S(1)—C(11') | 106 (1) | Mo(1)—S(3)—C(13) | 114 (1) |
| C(11)—S(1)—C(11') | 138 (2) | Mo(2)—S(3)—C(13) | 112 (1) |
| C(5)—C(1)—C(2) | 107·9 (4) | C(10)—C(6)—C(7) | 108·1 (4) |
| C(1)—C(2)—C(3) | 107·9 (4) | C(6)—C(7)—C(8) | 108·1 (4) |
| C(2)—C(3)—C(4) | 108·1 (4) | C(7)—C(8)—C(9) | 107·8 (4) |
| C(3)—C(4)—C(5) | 108·1 (4) | C(8)—C(9)—C(10) | 107·8 (4) |
| C(4)—C(5)—C(1) | 108·1 (4) | C(9)—C(10)—C(6) | 108·2 (4) |
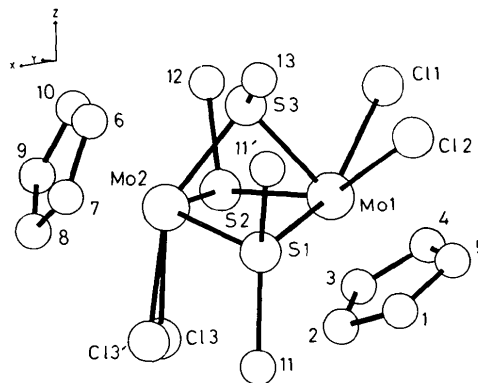


Fig. 2. The molecular structure of (II) showing the apparent disorder. For clarity, the C atoms are labelled by their serial number only.

Table 6. *Least-squares planes in compound* (II)

$x$, $y$ and $z$ represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane.

Plane (1): Ring C(1) to C(5)
Equation of plane: $3\cdot989x + 7\cdot575y + 5\cdot760z = -0\cdot898$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| C(1) | −0·000 | | |
| C(2) | 0·000 | Mo(1) | 2·037 |
| C(3) | −0·000 | | |
| C(4) | 0·000 | | |
| C(5) | −0·000 | | |

Normal to Mo(1) meets plane 0·10 Å from centroid.

Plane (2): Ring C(6) to C(10)
Equation of plane: $10\cdot938x + 8\cdot539y + 2\cdot530z = 7\cdot320$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| C(6) | 0·000 | | |
| C(7) | 0·000 | Mo(2) | −2·004 |
| C(8) | −0·001 | | |
| C(9) | 0·001 | | |
| C(10) | −0·001 | | |

Normal to Mo(2) meets plane 0·08 Å from centroid.

Plane (3): S(1)S(2)Cl(1)Cl(2)
Equation of plane: $-4\cdot374x - 7\cdot574y - 5\cdot678z = -1\cdot783$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| S(1) | −0·006 | | |
| S(2) | 0·006 | Mo(1) | 0·565 |
| Cl(1) | −0·008 | S(3) | −1·683 |
| Cl(2) | 0·008 | | |

Plane (4): S(1)S(2)S(3)
Equation of plane: $13\cdot225x + 7\cdot835y + 0\cdot086z = 4\cdot768$

| Constituent atoms | | Other atoms | |
|---|---|---|---|
| S(1) | 0·000 | Mo(1) | −1·555 |
| S(2) | 0·000 | Mo(2) | 1·290 |
| S(3) | 0·000 | C(11) | 0·016 |
| | | C(11′) | 0·095 |
| | | C(12) | 0·141 |
| | | C(13) | 0·137 |

capillaries. It was not possible to measure their densities.

After survey photography, the selected crystals were set up on a Nonius CAD4-F, PDP8-controlled, kappa geometry diffractometer and cell dimensions and orientation matrix obtained by a least-squares method from the setting angles of 25 reflexions.

*Crystal data*

Compound (I): $Mo_2(\eta^5\text{-}C_5H_5)_2(CH_3S)_2Cl_3$-(OH).$\frac{1}{4}C_7H_8$, $M_r = 599\cdot5$, orthorhombic, $a = 22\cdot115$ (2), $b = 16\cdot020$ (2), $c = 11\cdot226$ (6) Å, $U = 3977\cdot2$ Å$^3$. Systematic extinctions: $hkl$, $h + k = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $h = 2n + 1$. Space group $C222_1$. $D_c = 2\cdot00$ Mg m$^{-3}$ for $Z = 8$. Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot80$ mm$^{-1}$.

Compound (II): $Mo_2(\eta^5\text{-}C_5H_5)_2(CH_3S)_3Cl_3$, monoclinic, $a = 15\cdot441$ (5), $b = 15\cdot678$ (4), $c = 7\cdot257$ (1) Å, $\beta = 97\cdot80$ (2)°, $U = 1740\cdot5$ Å$^3$. Systematic extinctions: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$. Space group $P2_1/n$ ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$). Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = \sim 1\cdot8$ mm$^{-1}$.

For each crystal, the intensities of every independent reflexion with $\sin\theta/\lambda < 0\cdot66$ (I), $0\cdot63$ (II) Å$^{-1}$ were measured with an $\omega/2\theta$ scan, a variable scan rate and an $\omega$ scan angle of $(1\cdot00 + 0\cdot35\tan\theta)°$ (I) and $(1\cdot20 + 0\cdot35\tan\theta)°$ (II). Mo $K\alpha$ radiation was used with a graphite monochromator. Reflexions with $I < 3\sigma(I)$, where $\sigma(I)$ is the e.s.d. based on simple counting statistics, were not included in the subsequent calculations. (I) and (II) gave 2231 and 1935 independent structure amplitudes corrected for Lorentz and polarization effects, but not absorption.

## Structure solution and refinement

(I) was solved by Patterson and Fourier techniques, and refined by blocked-matrix least squares [block 1: scale, dummy overall isotropic temperature factor (Rollett, 1965); block 2: positional parameters; block 3: temperature factors]. All non-hydrogen atoms had anisotropic temperature factors. Difference syntheses showed some evidence for the $\eta^5$-cyclopentadienyl ring and the methyl H atoms at their expected positions. However, they were positioned geometrically (C—H, 1·0 Å, $U_{iso}$ 0·05 Å$^2$), their location being readjusted after each cycle. In the final stages each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r^*(X)$ where $n$ is the number of coefficients, $A_r$, for a Chebyshev series, $T_r^*$ is the polynomial function, and $X$ is $|F_o|/|F_o(\text{max.})|$. Three coefficients, $A_r$, were used with values, 18·1, 25·1 and 8·6 (Rollett, 1965). The final $R_w$ was 0·049 for 2231 reflexions.

For (II), Patterson and Fourier techniques revealed the Mo and S atoms, with the two Cl atoms associated with Mo(1) and the $\eta^5$-cyclopentadienyl rings. The $\eta^5$-cyclopentadienyl rings were not well-resolved and were refined with constraints (Waser, 1963; Rollett, 1969). For each ring the bond lengths were constrained to be 1·40 Å with an e.s.d. of 0·01 Å, the bond angles to be 108° with an e.s.d. of 0·5°, the difference in mean-square displacement along the interatomic vector of two bonded atoms was constrained to be zero with an e.s.d. of 0·005 Å$^2$, and each of the atoms was constrained to lie in a plane with an e.s.d. of 0·01 Å. Difference syntheses revealed the C atoms of the methyl groups bonded to S(2) and S(3) which were included in the refinement. Fourier syntheses also showed the presence of four further regions of electron density, two, each corresponding to about 8 e, at bonding distances from Mo(2), and two, each corresponding to 3 e, at bonding distances from S(1). The

possibility that the compound was an oxygen complex such as ($C$) was rejected on chemical and crystallographic grounds along with other proposals with sulphido and chloro bridges. The equipollent mixture of ($A$) and ($B$) was the most acceptable. For this model the occupancies of Cl(3), C(11) and C(13) were set equivalent, as were the occupancies of Cl(3') and C(11'). The bond lengths and angles about S(3) suggest that it is substantially different from S(1) and S(2), and the shorter Mo—S distances indicate that the bridging ligand could in fact be OH. The separation of C(11') and C(13), 1·64 (5) Å, indicates that both these cannot be present in the same molecule. On this basis, the final model proposed is 49% of ($B$) with Cl(3), C(11), S(3) and C(13) and 51% of ($A$) with Cl(3'), C(11') and O—H. There must be further disorder in the crystals, evidenced by the unstable nature of the refinement of the $\eta^5$-cyclopentadienyl rings, but it was not considered feasible to resolve these problems.



($C$)
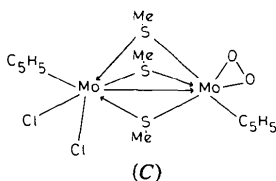
Refinement was by a least-squares procedure with a large-block approximation to the normal matrix: a $3 \times 3$ block was calculated from the derivatives of the scale, dummy overall isotropic temperature factor (Rollett, 1965), and overall isotropic extinction parameter (Larson, 1967), one from those of the positional parameters, and one from the corresponding temperature factors and occupancies of Cl(3), Cl(3'), C(11), C(11') and C(13). Only the Mo, Cl and S atoms had anisotropic temperature factors. H atoms were not located. In the final stages an overall isotropic extinction parameter (94·58) was introduced. Each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r^*(X)$. Three coefficients, $A_r$, were used with values 3·09, 3·96 and 1·94 (Rollett, 1965). The final $R_w$ was 0·084 for 1935 reflexions.

All calculations were performed with the Oxford *CRYSTALS* package (Carruthers, 1975) on the Oxford University ICL 1906A computer and the University of London CDC 7600 computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

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