3·43 Å. An analysis of the shortest intermolecular contacts shows that the chlorine ion and water molecules strongly contribute to hydrogen bonding, $Cl^{i}\cdots OH_2 = 3\cdot19\,(1)$ Å $[(i) = x,\ y-1,\ z]$ and $Cl^{ii}\cdots OH_2 = 3\cdot21\,(1)$ Å $[(ii) = 1-x,\ 1-y,\ 1-z]$.

The support of this work by the Ministero della Pubblica Istruzione (Roma) is gratefully acknowledged. Thanks are also due to the X-ray Diffraction Crystallography Laboratory, University of Padova.

References

Banci, L., Bencini, A., Benelli, C., Gatteschi, D. & Zanchini, C. (1982). *Struct. Bonding (Berlin)*, **52**, 34–86.

Bencini, A., Benelli, C., Gatteschi, D. & Zanchini, C. (1983). *Inorg. Chem.* **22**, 2123–2126.

Horrocks, W. D., Ishley, J. N. & Whittle, R. R. (1982). *Inorg. Chem.* **21**, 3270–3274.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lundberg, B. K. S. (1966). *Acta Cryst.* **21**, 901–909.

McFadden, D. L., McPhail, A. T., Garner, C. D. & Mabbs, F. E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 263–268.

Martinez-Carrera, S. (1966). *Acta Cryst.* **20**, 783–789.

Mighell, A. D. & Santoro, A. (1971). *Acta Cryst.* B**27**, 2089–2097.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Price, E., Mighell, A. D., Reimann, C. W. & Santoro, A. (1972). *Cryst. Struct. Commun.* **1**, 247–252.

Reedijk, J. & Van der Put, P. J. (1974). *Proc. Int. Conf. Coord. Chem.* **16**, 2.27b, 19–24 August, Dublin.

Santoro, A., Mighell, A. D., Zocchi, M. & Reimann, C. W. (1969). *Acta Cryst.* B**25**, 842–847.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sigel, H. & Dekker, M. (1974). *Metal Ions in Biological Systems*, Vol. IV, edited by M. Dekker, p. 16. New York, USA.

Acta Cryst. (1989). C**45**, 585–587

Structure of Dimesityldioxomolybdenum(VI)

By Fatiha Djafri, Richard Lai and Marcel Pierrot

Laboratoire de Cristallochimie – ESIPSOI – UA 126, *Centre de Saint-Jérôme, avenue Escadrille Normandie Niemen,* 13397 *Marseille CEDEX* 13, *France*

(*Received* 5 *May* 1988; *accepted* 26 *October* 1988)

Abstract. Dioxodimesitylmolybdenum(VI), $[MoO_2(C_9H_{11})_2]$, $M_r = 366$, monoclinic, $C2/c$, $a = 13\cdot617\,(4)$, $b = 9\cdot174\,(3)$, $c = 13\cdot681\,(4)$ Å, $\beta = 103\cdot75\,(5)$°, $V = 1660\,(2)$ Å^3, $Z = 4$, $D_x = 1\cdot461$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 7\cdot7$ cm^{-1}, $F(000) = 752$, $T = 263$ K, $R = 0\cdot029$ for 1447 unique diffractometer data with $I > 3\sigma(I)$. The coordination around the metal center, corresponding to a regular tetrahedron, and the geometry of the complex are compared to $ReO_2(mes)_2$ and $OsO_2(mes)_2$.

Introduction. In spite of abundant literature on the chemistry of transition-metal complexes involving the oxo ligand (Griffith, 1970; Holm, 1987) it is only rather recently that oxo complexes bearing other functionalities, such as alkyl (Mayer & Tulip, 1984; Cai, Hoffman, Lappas & Woo, 1987) and (or) carbene groups, have been receiving much attention (Schrock, Rocklage, Wengrovius, Rupprecht & Fellman, 1980).

During the past few years, we have been interested in both the oxo ligand and metal–oxygen bond reactivity in metal–oxo complexes. Most of our preliminary results have been obtained with a dioxo complex of molybdenum(VI), $MoO_2(mes)_2$ (mes = mesityl: C_6H_2-Me_3-2,4,6) (Arzoumanian, Baldy, Lai, Metzger, Nkeng Peh & Pierrot, 1985; Lai, Le Bot, Baldy, Pierrot & Arzoumanian, 1986; Lai, Le Bot & Faure, 1987). This complex belongs to the rare class of metal oxoaryls and was perhaps the only example of a d^0 σ-organometal bearing only oxo and aryl ligands until the rhenium and osmium analogs were recently reported (Stravropoulos, Edwards, Behling, Wilkinson, Motevalli & Hursthouse, 1986). Since some of our results are rather unexpected and could be related to the presence of both the oxo and aryl ligands, and also to the structure of the coordinatively unsaturated dimesityldioxomolybdenum species, we have carried out an X-ray structure determination of this molecule prepared by the literature method (Heyn & Hoffmann, 1976).

Experimental. Crystal (0·4 × 0·2 × 0·3 mm) grown from THF solution, sealed in a capillary under inert atmosphere, mounted on a CAD-4 Enraf–Nonius diffractometer (graphite monochromator for Mo $K\alpha$). Unit-cell parameters refined by least squares on $\sin\theta/\lambda$ values for 25 reflections ($16 < \theta < 18°$). Density obtained by flotation: $D_m = 1\cdot46\,(1)$ g cm^{-3}. Intensities measured using ω–2θ scan of 0·91 to

0108-2701/89/040585-03$03.00

Table 1. *Positional and thermal parameters with their estimated standard deviations in parentheses*

	x	*y*	*z*	*B*(Å^2)*
Mo1	0·000	0·03485 (4)	0·250	1·910 (6)
O1	−0·1042 (2)	−0·0718 (3)	0·2127 (2)	3·07 (5)
C1	−0·0192 (2)	0·1618 (3)	0·3717 (2)	2·06 (5)
C2	−0·1105 (2)	0·2444 (4)	0·3543 (2)	2·35 (6)
C3	−0·1322 (3)	0·3298 (4)	0·4314 (3)	2·77 (6)
C4	−0·0665 (3)	0·3357 (4)	0·5262 (2)	2·64 (6)
C5	0·0245 (3)	0·2569 (4)	0·5425 (2)	2·57 (6)
C6	0·0489 (2)	0·1701 (4)	0·4687 (2)	2·20 (6)
C21	−0·1875 (3)	0·2403 (5)	0·2524 (3)	3·39 (7)
C41	−0·0916 (3)	0·4248 (5)	0·6102 (3)	3·84 (8)
C61	0·1475 (2)	0·0867 (4)	0·4952 (3)	2·77 (6)

* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *found in* (*A*) $MoO_2(mes)_2$, (*B*) $ReO_2(mes)_2$ *and* (*C*) $OsO_2(mes)_2$ *with e.s.d.'s in parentheses*

	(*A*)* *M* = Mo	(*B*)*† *M* = Re	(*C*)† *M* = Os
M—O1	1·699 (3)	1·688 (5)	1·700 (7), 1·690 (7)
M—C1	2·101 (3)	2·062 (6)	2·053 (8), 2·047 (8)
O1—*M*—O1′	109·5 (1)	121·5 (4)	136·1 (3)
C1—*M*—O1	107·8 (1)	106·4 (3)	109·7 (3), 107·7 (3)
C1—*M*—O1′	109·5 (1)	109·4 (3)	100·5 (3), 100·0 (3)
C1—*M*—C1′	112·5 (2)	102·2 (3)	96·0 (3)
M—C1—C2	115·5 (2)	122·9 (4)	121·1 (5), 124·1 (5)
M—C1—C6	126·3 (2)	118·3 (4)	119·9 (5), 116·5 (5)
C1—C2—C21	121·2 (3)	124·1 (4)	123·4 (5), 122·7 (5)
C1—C6—C61	122·5 (3)	122·2 (4)	123·3 (5), 124·7 (5)
C2—C1—C6	118·2 (3)	118·3 (4)	118·9 (5), 119·4 (5)
C21—C2—C3	118·6 (3)	117·6 (4)	118·0 (5), 119·0 (5)
C61—C6—C5	118·0 (3)	117·8 (4)	117·8 (5), 116·7 (5)

* Molecules sited on the twofold axis of symmetry.

† Stravropoulos, Edwards, Behling, Wilkinson, Motevalli & Hursthouse (1986).

$10\cdot06°\ \mathrm{min}^{-1}$, over a range of $(0\cdot8 + 0\cdot35\tan\theta)°$, $\theta_{\max} = 23°$. Intensities of three standard reflections measured every 10 000 s remained constant within 2%, 3272 measured, 779 symmetry-related reflections averaged (agreement factor on $I = 0\cdot034$) and finally 1447 with $I > 3\sigma(I)$ kept for structure determination. $-14 \leq h \leq 14$; $0 \leq k \leq 10$; $0 \leq l \leq 15$.

All computations were performed on a PDP 11/44 using the *SDP* software package (Frenz, 1978). The structure was solved *via* standard heavy-atom procedures and completed by difference Fourier methods. H atoms introduced at idealized positions in the calculation before last refinement cycles but not refined. Full least-squares refinement included anisotropic thermal parameters for non H-atoms, and minimized the function $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2$. Final refinements converged with $R = 0\cdot029$ ($wR = 0\cdot047$); $S = 1\cdot744$; $(\Delta/\sigma)_{\max} = 0\cdot08$; a final difference synthesis did not reveal any peak of density $> 0\cdot35$ e Å^{-3}.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for absorption or secondary extinction.

Discussion. Final positional and thermal parameters are presented in Table 1.* A view of the molecule and the numbering scheme used are given in Fig. 1. Relevant bond angles and bond distances found in compounds (*A*) $MoO_2(mes)_2$, (*B*) $ReO_2(mes)_2$ and (*C*) $OsO_2(mes)_2$ are indicated in Table 2. As mentioned by Stravropoulos and co-workers, it is surprising that crystals (*B*) and (*C*) are not isostructural [(*B*) space group *C*2/*c*; (*C*) space group $P2_1/a$]. On the other hand, $MoO_2(mes)_2$, which is isostructural with (*B*), shows a somewhat different molecular geometry from that found in (*B*) and (*C*). In the case of $MoO_2(mes)_2$ the coordination around the metal center corresponds to a regular tetrahedron, while a more or less distorted tetrahedron has been found in (*B*) and (*C*). The angle between the O—Mo—O and C—Mo—C planes is close to 90°: 88·8 (1)° as compared to 88 and 84° in (*B*) and (*C*) respectively. Most noticeable features are the values of the O—*M*—O angles: 109·5 (1), 121·5 (4) and 136·1 (3)° and of the C—*M*—C angles: 112·5 (2), 102·2 (3) and 96·0 (3)°, in (*A*), (*B*) and (*C*) respectively. The regular variation of these angles is in very good agreement with the hypothesis proposed by Stravropoulos and co-workers and may reflect a variable deforming effect of the filled–unfilled *d* orbitals when going from Os^{VI} to Mo^{VI} complexes.

The orientation of the mesityl ligands, which is different in each complex, is given by: (i) The in-plane rotation of the mesityl moiety. In the case of *M* = Re, the bonding of the mesityl is quite symmetrical with Re—C—C angles differing by *ca* 5°. In contrast, this bonding is unsymmetrical for *M* = Mo, with Mo—C—C

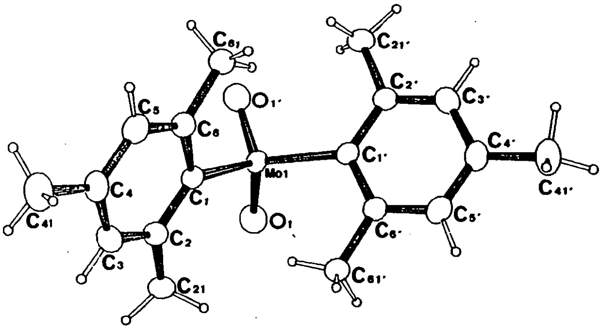

Fig. 1. View of the title compound showing atom-numbering scheme.

---

* Tables of anisotropic thermal parameters, bond angles, bond distances, H-atom coordinates and bond distances, torsional angles and the list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51543 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles differing by *ca* 11° (Table 2). (ii) The rotation of the ligands around the *M*—C bond. The aromatic rings make an angle of 61·4 (1)° with the O—Mo—O plane. In $ReO_2(mes)_2$ the corresponding angle is 66° and in $OsO_2(mes)_2$ the two independent aromatic rings make angles of 40 and 56°. These values reflect the steric repulsion between the O atoms and the C atoms of the methyl groups. Indeed short C···O contacts are found in (*B*) (2·99 and 3·14 Å) as well as in (*C*) (2·93 to 2·95 Å). Values of 3·13 (1) and 3·18 (1) Å are found in $MoO_2(mes)_2$ which appears to be less strained.

References

ARZOUMANIAN, H., BALDY, A., LAI, R., METZGER, J., NKENG PEH, M. L. & PIERROT, M. (1985). *J. Chem. Soc. Chem. Commun.* p. 1151.

CAI, S., HOFFMAN, D. M., LAPPAS, D. & WOO, H. G. (1987). *Organometallics*, **6**, 2273.

FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP–A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

GRIFFITH, W. P. (1970). *Coord. Chem. Rev.* **5**, 459.

HEYN, B. & HOFFMANN, R. (1976). *Z. Chem.* **16**(5), 195.

HOLM, R. H. (1987). *Chem. Rev.* **87**, 1401.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

LAI, R., LE BOT, S., BALDY, A., PIERROT, M. & ARZOUMANIAN, H. (1986). *J. Chem. Soc. Chem. Commun.* p. 1208.

LAI, R., LE BOT, S. & FAURE, R. (1987). *J. Organomet. Chem.* **336**, C5.

MAYER, J. M. & TULIP, T. H. (1984). *J. Am. Chem. Soc.* **106**, 3978.

SCHROCK, R. R., ROCKLAGE, S., WENGROVIUS, J. H., RUPPRECHT, G. & FELLMAN, J. (1980). *J. Mol. Catal.* **8**, 73.

STRAVROPOULOS, P., EDWARDS, P. G., BEHLING, T., WILKINSON, G., MOTEVALLI, M. & HURSTHOUSE, M. B. (1986). *J. Chem. Soc. Dalton Trans.* p. 169.

Acta Cryst. (1989). C**45**, 587–591

Structures of 4-Diphenylphosphinodibenzothiophene and Carbonyl(η^5-cyclopentadienyl)(4-diphenylphosphinodibenzothiophene)iodoiron(II)

BY P. D. ROBINSON*

Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA

AND L. V. DUNKERTON, A. PANDEY AND C. C. HINCKLEY

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA

(*Received* 13 *June* 1988; *accepted* 21 *October* 1988)

Abstract. (I) $C_{24}H_{17}PS$, $M_r = 368{\cdot}43$, triclinic, $P\bar{1}$, $a = 10{\cdot}218\,(1)$, $b = 10{\cdot}257\,(1)$, $c = 9{\cdot}577\,(1)$ Å, $\alpha = 90{\cdot}11\,(1)$, $\beta = 110{\cdot}37\,(1)$, $\gamma = 92{\cdot}68\,(1)°$, $V = 939{\cdot}6\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}61$ cm^{-1}, $F(000) = 384$, $T = 295$ K, $R = 0{\cdot}040$, 2465 unique observed reflections. (II) $[FeI(C_5H_5)(CO)\{P(C_6H_5)_2(C_{12}H_7S)\}]$, $M_r = 644{\cdot}29$, monoclinic, $P2_1/n$, $a = 10{\cdot}381\,(2)$, $b = 17{\cdot}706\,(4)$, $c = 14{\cdot}066\,(3)$ Å, $\beta = 91{\cdot}86\,(2)°$, $V = 2584\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}66$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 19{\cdot}70$ cm^{-1}, $F(000) = 1280$, $T = 295$ K, $R = 0{\cdot}055$, 1720 unique observed reflections. Compound (I) was prepared by treating 4-lithiodibenzothiophene with diphenylphosphinous chloride. Compound (II) was prepared by refluxing a benzene solution of (I), dicarbonyl(η^5-cyclopentadienyl)iodoiron(II) and a catalytic amount of dicarbonyl(η^5-cyclopentadienyl)iron(II) dimer. (I) is a dibenzothiophene molecule to which a diphenylphosphinous group is substituted at the fourth position in the first ring. In (II), the Fe atom is in roughly tetrahedral coordination with the P atom of ligated (I), an η^5-cyclopentadienyl group, the C atom of a carbonyl group and an I atom. The I and carbonyl sites of (II) are disordered.

Introduction. The activation and cleavage of S—H and C—S bonds of S-containing species by transition-metal complexes is of fundamental importance in coal desulfurization (Calhorda, Carrondo, Dias, Dominges, Simoes & Teixeira, 1986). Dibenzothiophenes are among the most abundant organosulfur compounds found in coal (Attar & Messenger, 1983), and the interaction of these aromatic heterocycles with metals is widely assumed to be central to the mechanism of catalytic desulfurization (Lesch, Richardson, Jacobson & Angelici, 1984). To study the type of bonding of a dibenzothiophene-containing ligand to Fe and the effects of substituents at the 4-position of the ligand

---

* To whom all correspondence should be addressed.

0108-2701/89/040587-05$03.00