Crystal and Molecular Structure of Di-μ-phenoxo-bis[dichlorodiphenoxomolybdenum(V)]

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Crystals of the title complex are monoclinic, a = 12.279(4), b = 14.744(5), c = 10.579(3) Å, β = 107.14(2)°, space group $P2_1/n$, Z = 2. The intensities of 1 117 reflections collected on an automatic diffractometer have been used to refine the structure to R 0.047. The dimeric molecule, which has two molybdenum atoms bridged through two phenoxy-oxygen atoms, is located on a centre of symmetry. The molybdenum atoms are octahedrally co-ordinated, being bonded to two chlorine atoms [2.317(3) and 2.360(4) Å] and four phenoxy-oxygen atoms, two of which are terminal [1.806(7) and 1.822(8) Å] and two bridging [2.014(8) and 2.059(8) Å]. The Mo $\cdots$ Mo distance is 2.801(2) Å.

IN many molybdenum compounds the metal atoms are bridged through oxygen or halogen atoms giving bi- or poly-nuclear complexes. For [$\{MoCl_2(OPh)_3\}_2$] a dimeric structure containing two chlorine bridges has been proposed on the basis of spectroscopic, magnetic, and partial crystallographic investigations.[1] In contrast, the present structure analysis shows that the title complex is dimeric with two phenoxo-bridges. A similar bridging system has been found for di-μ-phenoxo-bis[dichlorophenoxotitanium(IV)] [2] and di-μ-phenoxo-bis[phenolatotriphenoxotitanium(IV)].[3]

EXPERIMENTAL

The deep red crystals of [$\{MoCl_2(OPh)_3\}_2$] were prepared by the procedure described by Rosenheim and Nernst.[4]

Crystal Data.—$C_{36}H_{30}Cl_4Mo_2O_6$, M = 892.3, Monoclinic, a = 12.279(4), b = 14.744(5), c = 10.579(3) Å, β = 107.14(2)°, U = 1 824.6 Å^3, D_m = 1.663 g cm^{-3} (pycnometrically in cyclohexane), Z = 2, D_c = 1.623 g cm^{-3}, $F(000)$ = 892. Space group $P2_1/n$ from systematic absences. Mo-K_α radiation: λ = 0.710 7 Å, μ(Mo-K_α) = 6.23 cm^{-1}.

Preliminary cell dimensions and the space-group symmetry were determined from rotation and Weissenberg photographs. Accurate cell parameters were obtained from least-squares analysis of 16 reflections on a Philips PW 1100 computer-controlled diffractometer with graphite-monochromated Mo-K_α radiation. Intensity data were collected by the ω—2θ scan technique (scan width 1.20θ, scan speed 0.03θ s^{-1}) in the range $4 \leqslant 2\theta \leqslant 50°$. Three standard reflections were measured after every 2 h, and their decay was used to bring the reflections to a common scale. Because of crystal decomposition, two crystals of approximate dimensions 0.21 × 0.17 × 0.10 and 0.17 × 0.14 × 0.04 mm were used to minimise the anisotropy of decomposition. The data were rescaled, and corrected for Lorentz and

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polarisation factors (but not for absorption). A total of 1 156 reflections was collected, of which 1 118 had $I \geqslant 3\sigma(I)$ and were considered observed while one reflection was omitted from the refinement as it appeared to be suffering from extinction.

Structure Determination and Refinement.—A three-dimensional Patterson synthesis gave the positions of the molybdenum and the bridging atoms. Two successive Fourier syntheses showed the positions of all the atoms in the structure, except for the atoms of one phenoxo-ring and the hydrogen atoms. Six cycles of least-squares refinement were then carried out with individual isotropic temperature factors, giving R 0.103. A third Fourier synthesis showed clearly the positions of all the non-hydrogen atoms. Further full-matrix least-squares refinement with isotropic temperature factors for all the atoms reduced R to 0.057, and with anisotropic factors for molybdenum, chlorine, and oxygen atoms gave R 0.050. Idealised hydrogen-atom co-ordinates were computed assuming that they are positioned radially at 1.0 Å from the phenoxy-carbon atoms, and it was verified in a difference-Fourier synthesis that these coincide with the regions of positive electron density. Inclusion of fixed hydrogen-atom contributions, all with isotropic temperature factors of the carrier atoms, followed by several further rounds of least-squares adjustment of the non-hydrogen atom parameters reduced R to a final value of 0.047 ($R' = 0.051$). The function minimised was $\Sigma w(|F_o| - |F_c|)^2$. In the final stages of refinement the weight w was taken to be $1/\sigma^2(F_o)$. The values of the atomic scattering factors were taken from ref. 5 with corrections for anomalous scattering for molybdenum and chlorine according to ref. 6. Calculations were made on the UNIVAC 1110 computer of the SRCE (University Computing Centre, Zagreb) with the system of programs developed by Domenicano *et al.*[7] Final atomic parameters are shown in Table 1, and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 21860 (13 pp., 1 microfiche).*

TABLE 1

Atomic positions ($\times 10^4$) and calculated hydrogen positions ($\times 10^3$) together with thermal parameters and the estimated standard deviations (in parentheses)

	x/a	y/b	z/c	B/Å^2
Mo	961(1)	499(1)	−36(1)	*
Cl(1)	2 694(3)	898(2)	1 545(3)	*
Cl(2)	1 466(3)	1 320(2)	−1 678(4)	*
O(1)	345(6)	1 538(5)	376(7)	*
O(2)	1 677(5)	−483(5)	−418(7)	*
O(3)	538(5)	−178(4)	1 443(7)	*
C(11)	131(9)	2 415(8)	658(13)	2.9(3)
C(12)	377(10)	2 635(9)	2 004(14)	5.1(3)
C(13)	51(13)	3 513(11)	2 291(16)	7.8(4)
C(14)	−475(12)	4 116(9)	1 260(17)	6.5(4)
C(15)	−619(11)	3 875(9)	−25(16)	6.1(4)
C(16)	−345(11)	3 020(9)	−350(14)	4.8(3)
C(21)	2 609(10)	−946(8)	−637(12)	3.2(3)
C(22)	2 682(10)	−1 867(8)	−503(13)	4.8(3)
C(23)	3 639(10)	−2 312(8)	−709(13)	4.5(3)
C(24)	4 479(10)	−1 807(8)	−1 007(13)	4.7(3)
C(25)	4 380(10)	−897(8)	−1 150(13)	4.5(3)
C(26)	3 452(10)	−425(8)	−937(12)	4.1(3)
C(31)	1 085(9)	−413(8)	2 726(12)	3.3(3)
C(32)	954(12)	113(9)	3 802(16)	6.2(4)
C(33)	1 523(13)	−179(10)	5 111(16)	6.8(4)
C(34)	2 088(12)	−982(10)	5 317(16)	6.2(4)
C(35)	2 225(12)	−1 499(10)	4 323(16)	6.1(4)
C(36)	1 696(10)	−1 213(8)	2 987(13)	4.5(3)
H(12)	72	218	274	
H(13)	25	373	327	
H(14)	−71	474	144	
H(15)	−103	431	−81	
H(16)	−44	283	−131	
H(22)	206	−221	−24	
H(23)	370	−300	−63	
H(24)	515	−214	−110	
H(25)	500	−55	−142	
H(26)	339	27	−95	
H(32)	41	66	358	
H(33)	148	22	589	
H(34)	241	−123	625	
H(35)	270	−209	452	
H(36)	181	−158	223	

* Anisotropic thermal parameters in the form $\exp-[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ with the coefficients:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2.43(5)	3.65(9)	2.41(8)	−0.10(7)	1.00(5)	−0.03(6)
Cl(1)	3.1(2)	7.0(2)	4.0(2)	−1.4(1)	0.7(1)	−0.3(2)
Cl(2)	4.8(2)	5.9(2)	4.7(2)	−0.5(1)	2.2(2)	1.3(2)
O(1)	2.4(4)	4.6(4)	3.0(5)	−0.6(3)	1.0(3)	−0.2(4)
O(2)	2.3(3)	4.3(4)	3.1(4)	−0.1(3)	0.8(3)	0.3(4)
O(3)	1.5(3)	4.4(4)	2.6(4)	−0.2(3)	0.2(3)	−0.5(4)

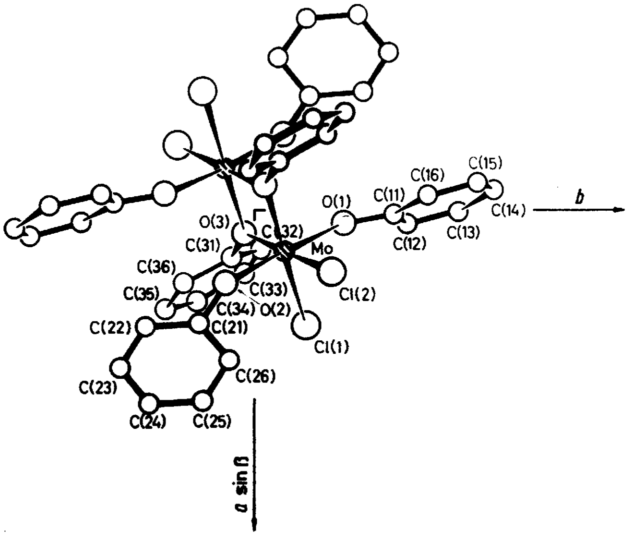

FIGURE 1 View of the structure of $[\{MoCl_2(OPh)_3\}_2]$ down the c axis, showing the atom numbering scheme

DISCUSSION

The dimeric molecule $[\{MoCl_2(OPh)_3\}_2]$ is shown in Figure 1, and the interatomic distances and angles are listed in Table 2. The molecule has crystallographically imposed $\bar{1}$ symmetry. Both molybdenum atoms are bonded to two chlorine atoms and four phenoxy-oxygen atoms, two of which are terminal and two bridging. The co-ordination polyhedra about molybdenum are slightly distorted octahedra sharing a common edge of oxygen atoms. The angles at Mo range from 88.0 to 93.1°.

The Mo • • • Mo distance of 2.801(2) Å is significantly

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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TABLE 2

Molecular geometry of $[\{MoCl_2(OPh)_3\}_2]$

(*a*) Distances (Å)

Mo · · · Mo′	2.801(2)	O(2)–C(21)	1.41(2)
Mo–Cl(1)	2.317(3)	C(21)–C(22)	1.37(2)
Mo–Cl(2)	2.360(4)	C(22)–C(23)	1.42(2)
Mo–O(1)	1.822(8)	C(23)–C(24)	1.39(2)
Mo–O(2)	1.806(7)	C(24)–C(25)	1.35(2)
Mo–O(3)	2.059(8)	C(25)–C(26)	1.41(2)
Mo–O(3′)	2.014(8)	C(26)–C(27)	1.40(2)
O(1)–C(11)	1.37(1)	O(3)–C(31)	1.35(1)
C(11)–C(12)	1.40(2)	C(31)–C(32)	1.43(2)
C(12)–C(13)	1.42(2)	C(32)–C(33)	1.40(2)
C(13)–C(14)	1.39(2)	C(33)–C(34)	1.35(2)
C(14)–C(15)	1.36(3)	C(34)–C(35)	1.35(2)
C(15)–C(16)	1.38(2)	C(35)–C(36)	1.42(2)
C(16)–C(11)	1.37(2)	C(36)–C(31)	1.38(2)

(*b*) Bond angles (°)

Cl(1)–Mo–Cl(2)	90.2(1)	C(15)–C(14)–C(13)	120(2)
Cl(1)–Mo–O(1)	88.2(2)	C(16)–C(15)–C(14)	122(1)
Cl(1)–Mo–O(2)	88.0(2)	C(11)–C(16)–C(15)	119(1)
Cl(1)–Mo–O(3)	88.4(2)	O(2)–C(21)–C(22)	120(1)
Cl(2)–Mo–O(1)	88.5(3)	O(2)–C(21)–C(26)	118(1)
Cl(2)–Mo–O(2)	89.0(3)	C(22)–C(21)–C(26)	123(1)
Cl(2)–Mo–O(3)	177.9(2)	C(21)–C(22)–C(23)	118(1)
O(1)–Mo–O(2)	175.5(3)	C(22)–C(23)–C(24)	120(1)
O(1)–Mo–O(3)	90.0(3)	C(23)–C(24)–C(25)	121(1)
O(2)–Mo–O(3)	92.4(3)	C(24)–C(25)–C(26)	121(1)
O(3)–Mo–O(3′)	93.1(3)	C(25)–C(26)–C(21)	117(1)
Mo–O(1)–C(11)	165.5(7)	O(3)–C(31)–C(32)	121(1)
Mo–O(2)–C(21)	154.4(7)	O(3)–C(31)–C(36)	119(1)
Mo–O(3)–C(31)	136.3(7)	C(32)–C(31)–C(36)	120(1)
Mo–O(3)–Mo′	86.9(2)	C(31)–C(32)–C(33)	118(1)
O(1)–C(11)–C(12)	117(1)	C(32)–C(33)–C(34)	120(2)
O(1)–C(11)–C(16)	121(1)	C(33)–C(34)–C(35)	124(2)
C(12)–C(11)–C(16)	123(1)	C(34)–C(35)–C(36)	118(1)
C(13)–C(12)–C(11)	117(1)	C(35)–C(36)–C(31)	120(1)
C(14)–C(13)–C(12)	120(2)		

Primed atoms are related to unprimed atoms by a centre of symmetry at (0,0,0).

longer than the value which has been considered to correspond to a single Mo–Mo bond (2.6 Å),[8] and the longest established so far for binuclear molybdenum complexes with two oxygen bridges.[9] Consequently, the observed low magnetic moment of this complex [1] is probably only due to the interaction through the two phenoxy-oxygen bridges. It is most likely that the lengthening of Mo–Mo distance is caused by the steric hindrance of the phenoxo-ligands. The O(1) · · · O(3), O(2) · · · O(3), O(1) · · · O(3′), and O(2) · · · O(3′) contacts are 2.75, 2.80, 2.75, and 2.76 Å, while Cl(1) · · · O(3) and Cl(2) · · · O(3′) are both 3.06 Å.

There are two distinctly different Mo–O bonds in the structure [terminal 1.822(8) and 1.806(7), bridging 2.059(8) and 2.014(8) Å]. As far as we know, no previous structure analysis of molybdenum(V) complexes containing molybdenum-terminal alkoxy-oxygen bonds has been reported, thus no direct comparisons can be made. The only example which can be taken for comparison is $[Mo_4Cl_4O_6(OPr)_6]$ in which the molybdenum-terminal propoxy-oxygen distance is considerably longer (2.134 Å), but in this structure the arrangements about the molybdenum atoms are different and the oxidation state of Mo was not defined.[10] However, similar values for Mo–O bond lengths are established in some molybdenum compounds, such as in $Na[NH_4][MoO_3(O_4C_2)]\cdot 2H_2O$ (1.815 and 1.850 Å) [11] and in $[NH_4]_2[MoF_2O_3]$ (1.836 and 1.841 Å).[12] In the two bridges, the Mo–O distances are within the range found in ref. 10 (1.981—2.182 Å). The Mo_2O_4 bridge system is almost square planar; the internal angles Mo–O(3)–Mo′ and O(3)–Mo–O(3′) are 86.9(2) and 93.1(3)°, respectively. The Mo–Cl bond lengths [2.317(3) and 2.360(4) Å] are considerably longer than molybdenum-terminal chlorine bond lengths in $MoCl_3O$ and Mo_2Cl_{10} (2.26 and 2.24 Å).[13,14] This bond lengthening may indicate the *trans* influence of the phenoxo-ligands.

The Mo–O–C bond angles are of interest; the angles at the non-bridging oxygen atoms Mo–O(1)–C(11) and Mo–O(2)–C(21) are 165.5 and 154.4°, respectively, while the Mo–O(3)–C(31) angle at the bridging oxygen is only 136.3°. Similar discrepancies were established also in the case of titanium complexes.[2,3] The angles between the best least-squares planes of the phenyl rings are: (1)—(2) 73.6°; (2)—(3) 74.8°; (1)—(3) 10.2°. Bond lengths and angles within the phenyl rings are normal. The molecules in the crystal are bonded through van der Waals interactions. The packing of molecules in the unit cell is shown in Figure 2.

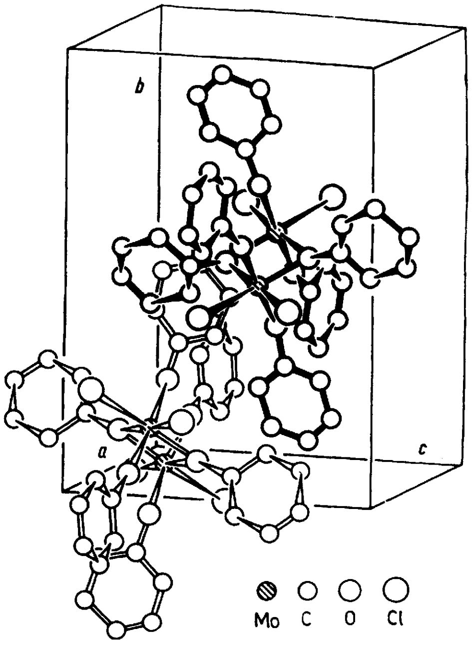

FIGURE 2 Packing of the dimeric molecules of the complex in the unit cell

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