The Crystal Structure of Nonachlorodimolybdenum(V) Heptachlorodioxodimolybdate(V)†

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The compound Mo_2Cl_8O was formed as a minor product in the reaction of molybdic acid with thionyl chloride. Its structure has been determined by the heavy-atom method from 1 265 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to *R* 0.066. Crystals are monoclinic, space group *P2/c*, with *a* = 10.01(1), *b* = 6.27(1), *c* = 17.89(2) Å, β = 101.8(3)°. The structure consists of singly chlorine-bridged, binuclear cations $[Mo_2Cl_9]^+$ and triply chlorine-bridged binuclear anions $[Mo_2Cl_7O_2]^-$ which are linked into chains by weak interactions through the oxygen atoms.

The interaction of thionyl chloride with molybdenum trioxide was reported[1] to yield pure $MoCl_4O$, and recently a crystal obtained from this reaction has been shown to be a solvated form of the compound.[2] The corresponding reaction of thionyl chloride with molybdic acid,[3] however, was reported to produce $MoCl_4O$, $MoCl_6$, $MoCl_3O$, and $MoCl_5$. In an attempt to repeat this preparation of $MoCl_6$ we have isolated, from a mixture of products, crystals of Mo_2Cl_8O.

Experimental

Freshly distilled thionyl chloride (15 cm^3) was added to molybdic acid (2 g), forming a dark red solution immediately. After refluxing for 96 h, the excess of thionyl chloride was removed by distillation and separation of the products attempted by vacuum sublimation. Although no complete separation of pure compounds was achieved, it was obvious that several different compounds were present. Samples of the products were sealed under vacuum in thin-walled Pyrex capillaries and crystals grown by sublimation in a temperature gradient. Three different crystals were isolated in small sections of capillary tube, and unit-cell dimensions established by *X*-ray crystallography. The first crystal studied, which formed thin plates, brown by reflected and green by transmitted light, had cell dimensions and space group identical with those reported[4] for $MoCl_5$. The second crystal, which formed dark red blocks, had a tetragonal unit cell, *a* = 3.9, *c* = 13.9 Å, very similar to that reported[5] for WCl_2O_2 (*a* = 3.87, *c* = 13.87 Å) and was assumed to be $MoCl_2O_2$. The third crystal, which formed dark red, thick plates, was the compound Mo_2Cl_8O. Unit-cell and space-group data were obtained photographically and intensity data were recorded on a diffractometer. No evidence for $MoCl_6$ was obtained, but not all the product of the reaction was investigated.

Crystal Data.—$[Mo_2Cl_9]^+[Mo_2Cl_7O_2]^-$, *M* = 983, monoclinic, *a* = 10.01(1), *b* = 6.27(1), *c* = 17.89(2) Å, β = 101.8(3)°, *U* = 1 100 Å^3, *Z* = 2, D_c = 2.96 g cm^{-3}, *F*(000) = 912, space group *P2/c* or *Pc* from systematic absence *h0l* when $l \neq 2n$. The centric space group *P2/c* was confirmed by the subsequent successful refinement of the structure. Mo-K_α radiation (λ = 0.7107 Å, μ = 39 cm^{-1}).

Table 1. Final atomic positional parameters with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.106 8(1)	−0.183 1(2)	0.375 1(1)
Mo(2)	0.443 2(1)	0.044 8(2)	0.338 9(1)
Cl(1)	0.216 8(5)	−0.322 4(9)	0.485 6(2)
Cl(2)	0.088 7(5)	0.145 5(7)	0.420 9(3)
Cl(3)	−0.097 4(5)	−0.308 1(9)	0.386 9(3)
Cl(4)	0.158 9(4)	−0.437 1(7)	0.299 2(2)
Cl(5)	0	0.000 2(9)	$\frac{1}{4}$
Cl(6)	0.445 6(4)	0.357 9(7)	0.398 9(2)
Cl(7)	0.598 3(4)	−0.125 4(8)	0.428 8(2)
Cl(8)	0.334 9(4)	0.192 3(7)	0.217 4(2)
Cl(9)	$\frac{1}{2}$	−0.234 2(9)	$\frac{1}{4}$
O(1)	0.299 4(14)	−0.056 0(20)	0.357 9(7)

Structure Determination.—Intensity data were collected about the *b* axis (layers, *k* = 0—6) with a Stoe two-circle computer-controlled diffractometer as described previously.[6] Within the range 0.1 < (sinθ)/λ < 0.65, 1 265 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarization factors, but not for absorption, since the crystal was small (dimensions 0.02 × 0.01 × 0.01 mm) and the section of Pyrex capillary not completely symmetrical.

The structure was solved by standard Patterson–Fourier techniques. Refinement was by full-matrix, least-squares methods, with scattering factors for neutral atoms.[7] Initial refinement was with all atoms vibrating isotropically, with layer scale factors refined separately and with unit weights. This resulted in *R* 0.082. Further refinement with layer scale factors held constant and with the introduction of anisotropic thermal parameters for all atoms reduced *R* to 0.066.

The refinement was considered complete with final values of *R* and *R'* $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ of 0.066 and 0.070 respectively with $w = 1.67/[\sigma^2(F) + 0.002F^2]$. Final parameter shifts were $<0.1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing (sinθ)/λ and with increasing fractions of $|F_o|$ was satisfactory. The calculations were carried out on the ICL 1906 A computer at the University of Birmingham Computer Centre using the program[8] SHELX 76. The final positional parameters are given in Table 1 and the interatomic distances and angles in Table 2.

Discussion

The structure determination has established that one product of the interaction of thionyl chloride with molybdic acid is the previously unreported chloride oxide of empirical formula Mo_2Cl_8O. If the shortest bonds to molybdenum are considered

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Mo(1)–Cl(1)	2.235(4)	Mo(2)–Cl(6)	2.237(4)
Mo(1)–Cl(2)	2.240(5)	Mo(2)–Cl(7)	2.262(4)
Mo(1)–Cl(3)	2.238(4)	Mo(2)–Cl(8)	2.406(4)
Mo(1)–Cl(4)	2.223(4)	Mo(2)–Cl(8^{I})	2.777(4)
Mo(1)–Cl(5)	2.549(3)	Mo(2)–Cl(9)	2.506(4)
Mo(1)–O(1)	2.165(14)	Mo(2)–O(1)	1.670(14)
Cl(3)–Mo(1)–Cl(1)	94.2(2)	O(1)–Mo(2)–Cl(6)	99.2(4)
Cl(3)–Mo(1)–Cl(2)	98.3(2)	O(1)–Mo(2)–Cl(7)	99.8(5)
Cl(3)–Mo(1)–Cl(4)	98.0(2)	O(1)–Mo(2)–Cl(8)	94.7(5)
Cl(3)–Mo(1)–Cl(5)	90.8(1)	O(1)–Mo(2)–Cl(9)	100.5(4)
Cl(1)–Mo(1)–Cl(2)	95.6(2)	Cl(6)–Mo(2)–Cl(7)	97.7(2)
Cl(1)–Mo(1)–Cl(4)	97.2(2)	Cl(6)–Mo(2)–Cl(8)	93.1(2)
Cl(2)–Mo(1)–Cl(5)	81.7(2)	Cl(7)–Mo(2)–Cl(9)	84.8(1)
Cl(4)–Mo(1)–Cl(5)	84.0(1)	Cl(8)–Mo(2)–Cl(9)	79.3(1)
Cl(3)–Mo(1)–O(1)	177.1(4)	O(1)–Mo(2)–Cl(8^{I})	170.6(4)
Mo(1)–Cl(5)–Mo(1^{II})	126.4(2)	Mo(2)–Cl(9)–Mo(2^{I})	91.4(2)
Mo(1)–O(1)–Mo(2)	176.3(8)	Mo(2)–Cl(8)–Mo(2^{I})	87.3(2)

Roman numeral subscripts refer to atoms in the positions: I $1 - x$, $y.$, $\frac{1}{2} - z$; II $-x$, y, $\frac{1}{2} - z$.

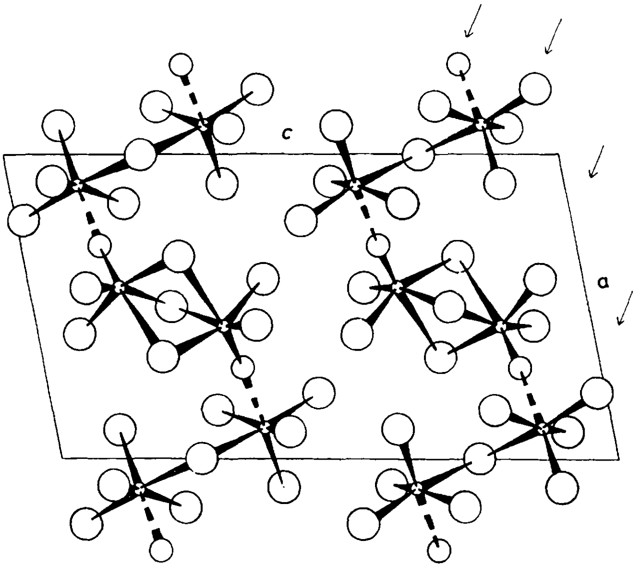

Figure. Projection of the structure down [010] showing the atom numbering and the approach to close packing. The arrows indicate planes of approximately close-packed atoms

(Table 2) the structure can best be described in terms of the ions $[Mo_2Cl_9]^+$ and $[Mo_2Cl_7O_2]^-$.

In the cation the molybdenum atoms have a distorted square-pyramidal co-ordination by five chlorine atoms, with Cl(5), on a two-fold axis, acting as a basal atom and symmetrically bridging the two molybdenum atoms. The average Mo–Cl (terminal) distance is 2.234 Å, which is very similar to the values of 2.24 Å in both[4,9] $MoCl_5$ and $MoCl_3O$, and the Mo–Cl (bridge) distance of 2.549 Å is again similar to the corresponding values of 2.53 Å in $MoCl_5$ and 2.48 Å in $MoCl_3O$. The molybdenum atom is displaced 0.19 Å above the basal plane of the four chlorine atoms in the square-pyramidal arrangement.

Although the anion has the same atomic ratio of metal to non-metal as the cation, the structure is very different, with distorted octahedral co-ordination for the molybdenum atom and a triple chloride bridge. Atom Cl(9), which lies on a two-fold axis, forms a symmetric chlorine bridge. The other bridges are asymmetric with the larger distances *trans* to the terminal oxygen atoms. The Mo–O distance of 1.67 Å is close to the value of 1.64 Å in $MoCl_4O$[3] although rather longer than the 1.60 Å reported[9] for $MoCl_3O$. The average Mo–Cl (terminal) and the Mo–Cl (symmetric bridge) distances of 2.250 and 2.506 Å are very similar to those in the cation discussed above.

The asymmetric Mo–Cl (bridge) distances of 2.406 and 2.777 Å are very similar to the corresponding distances[9] of 2.37 and 2.8 Å in $MoCl_3O$, where the terminal oxygen atom also affects the *trans*-related bridge bond.

If the longer bridge distance is disregarded, then the molybdenum atoms in the anion can be considered to have a square-pyramidal co-ordination, with the oxygen atom in the apical position. The four basal chlorine atoms [Cl(6), Cl(7), Cl(8), and Cl(9)] are coplanar to within 0.05 Å, and the molybdenum atom is displaced from the basal plane 0.34 Å towards the terminal oxygen atom. This displacement is markedly greater than the 0.19 Å in the cation, as expected for an apical oxygen rather than a chlorine atom.

Although the structure has been discussed in terms of the ions $[Mo_2Cl_9]^+$ and $[Mo_2Cl_7O_2]^-$, these ions are linked through the oxygen atoms to give asymmetric oxygen bridges, Mo(1) ••• O(1)–Mo(2). Although the weak bridging interaction Mo(1) ••• O(1) of 2.17 Å is longer than the symmetrical bridge reported[10] for $NbCl_3O$ (Nb–O 1.99 Å), the separation of the molybdenum atoms across the oxygen bridge [Mo(1) ••• Mo(2) 3.84 Å] is less than the corresponding separation of niobium atoms of 3.98 Å. This would imply a stronger overall interaction for the molybdenum compound, and is of particular significance since doubt has been cast on the *X*-ray crystallographic results for $NbCl_3O$ as single-crystal, laser-Raman studies[11] indicate that the Nb–O–Nb bridge is probably asymmetric. The lengthening of the shorter Mo–O distance of 1.67 Å compared with that of 1.60 Å in $MoCl_3O$ can be attributed to the weak bridging interaction.

The oxygen atom, by this weak interaction, completes a distorted octahedral co-ordination arrangement for Mo(1) in the cation and leads to infinite chains of linked cations and anions, parallel to the *a* axis. These chains are packed together as shown in the Figure.

The projection of the structure down the *b* axis, illustrated in the Figure, appears to show well defined planes of atoms, as indicated by the arrows. Closer inspection reveals that these do not conform to either hexagonal or cubic close-packed sequences, in fact the relationship between adjacent layers changes from approximately cubic to approximately hexagonal along the lines of atoms. Thus the angle at the bridging Cl atom in the cation, of 126°, is close to the idealized 132° for filling adjacent octahedral holes in hexagonal close packing and the sequence Cl(7), Cl(6), O(1); Cl(8), Cl(9), Cl(8^{I}); Cl(7^{I}), Cl(6^{I}), O(1^{I}) also corresponds to the hexagonal arrangement. However, the angle at the oxygen atom of 176.3° is much closer to the theoretical 180° for filling adjacent octahedral holes in cubic close packing.

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