The Crystal Structure of $MoO_3,2H_2O$: a Metal Aquoxide with Both Co-ordinated and Hydrate Water[1]

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Summary In the crystal structure of $MoO_3,2H_2O$ one half of the water molecules are co-ordinated to Mo within $[MoO_3(OH_2)]_n$ layers, the other half form hydrogen-bonded hydrate water between the layers.

FROM the determination of approximate Mo parameters in a crystallographic sub-cell, Lindqvist[2] has shown the structural principle of molybdenum trioxide dihydrate ("yellow molybdic acid") to be an arrangement of layers of MoO_6 octahedra with sharing corners. The correct structure, including the true unit cell, space group, oxygen co-ordinates, and functions of the water molecules[3,4] is of considerable interest, but has not been obtained previously.

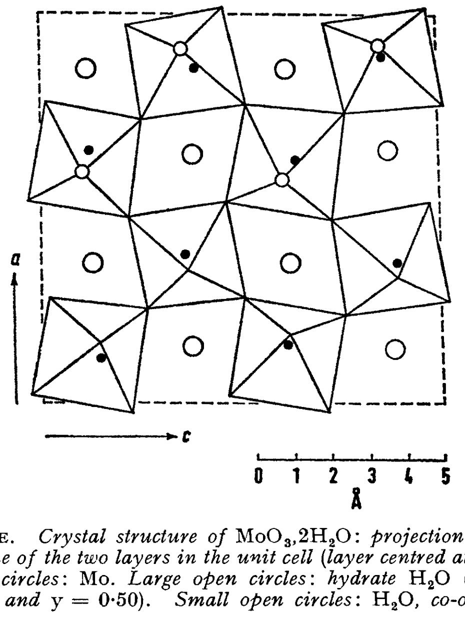

FIGURE. *Crystal structure of* $MoO_3,2H_2O$: *projection parallel to* b *of one of the two layers in the unit cell (layer centred at* $y = 0{\cdot}25$) *Black circles*: Mo. *Large open circles*: *hydrate* H_2O (*at approx.* $y = 0$ *and* $y = 0{\cdot}50$). *Small open circles*: H_2O, *co-ordinated to* Mo.

I report the results of the complete *X*-ray structure determination. Pure single crystals were obtained according to the method of Carpéni.[5]

$MoO_3,2H_2O$ crystallizes in the space group $P2_1/n$ (No. 14) with $a = 10{\cdot}476(5)$, $b = 13{\cdot}822(6)$, $c = 10{\cdot}606(5)$ Å, $\beta = 91{\cdot}62(3)^\circ$, $U = 1535{\cdot}3$ Å^3, $D_m = 3{\cdot}124$, $D_c = 3{\cdot}114$ g/cm^3 (all at 20°) and $Z = 16$.† About 3500 unique nonzero intensities were recorded on a Hilger–Watts four-circle diffractometer with Mo-K_α radiation. The structure was solved from Patterson and Fourier methods, and refined by least squares to an *R* factor of 6·0% with anisotropic temperature factors for Mo, including contributions from calculated H positions. All hydrogen atoms could be located unambiguously from a difference Fourier synthesis.

The structure consists of a system of infinite $[MoO_3(OH_2)]_n$ layers normal to *b*. Five oxygens and one co-ordinated H_2O form a strongly distorted octahedron around every Mo. Every octahedron shares a corner with each of four neighbouring octahedra within the layers. The octahedra form characteristic zig-zag rows within the layers. The distribution of the co-ordinated H_2O groups in "terminal" positions over both sides of the layers is shown in the Figure.

The most striking feature of the structure is the occurence of a second kind of H_2O groups not bonded to Mo which fill the voids between the layers. They are in H-bonding contact with both neighbouring layers. Thus, the compound should be formulated as $[MoO_{4/2}O(OH_2)],H_2O = [MoO_3(OH_2)],H_2O$, molybdenum hydratotrioxide hydrate. The structure can be regarded as a "partially hydrolysed" ReO_3 type.

In the strongly distorted $MoO_5(OH_2)$ octahedra the central Mo is displaced from the centre roughly parallel to

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† This cell is obtained from Lindqvist's incorrect cell[2b] by transformation with the matrix $(\frac{1}{2}, 0, \frac{1}{2}|0, 1, 0|-\frac{1}{2}, 0, \frac{1}{2})$.

one of the threefold axes, resulting in three short and three long bond distances. Mean values are 1·690 (terminal O), 1·762, 1·798, 2·056, 2·159, and 2·293 Å (H_2O). This kind of distortion has recently been found in some other oxides and oxide hydrates of Mo and Re [the Mo_4O_{11} modifications[6], Re_2O_7,[7] $Re_2O_7(OH_2)_2$[8]] and appears to be more common in compounds of these elements with ReO_3 structure fragments than was expected.[9,10] Nonbonded O–O(H_2O) distances in the octahedra range from 2·60 to 2·87 Å, *cis*-bond angles at the Mo from 75·4 to 104·3°. Closest Mo–Mo separations within the layers range from 3·620 to 3·818 Å with Mo–O–Mo bridge angles of 139·7—161·4°. As in the compounds cited above[6–8] the M–O–M bridges are strongly asymmetric with alternating long (>2 Å) and short M–O bond lengths.

The very interesting hydrogen bond system connects every interlayer H_2O as H-donor with one terminal oxygen, and as H-acceptor both with one co-ordinated H_2O in one neighbouring layer and with a second H_2O in the opposite layer. The H-bridges are normal with O · · · HO distances of 2·693—2·841 Å. Every co-ordinated H_2O is, as donor, in H-bridging contact with two inter-layer H_2O groups. The interatomic angles between pairs of three oxygens associated with the H-bridges (83—119°) and the approximate OH · · · O bond angles (160 ± 15°) show the bridges to be slightly bent.

From the crystal structure the relatively easy conversion of $MoO_3,2H_2O$ into stoicheiometric MoO_3,H_2O by moderate heating can be rationalized: if the hydrogen-bond system breaks down by loss of the inter-layer water, easy stabilisation of the intact layer arrangement is possible by shifting every second layer *a*/4 and *c*/4.

In a note which appeared after I described the structure,[1] cell constants of $MoO_3,2H_2O$ are reported.[11] These values are in excellent agreement with ours.

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