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On Molybdenum Oxide Hydroxides Genotypic with MoO_3

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A series of molybdenum oxide hydroxides, which may be assigned the general formula $MoO_{3-x}(OH)_x$ have been prepared by Glemser *et al.*[1-4] by the reduction of crystalline MoO_3 with (*a*) Zn and HCl, (*b*) Mo powder in the presence of water, (*c*) atomic hydrogen, or (*d*) $LiAlH_4$. Four members of this series were prepared, namely those with $x = 0.5$, 1.0, 1.6, and 2.0, and in addition a compound $Mo_5O_8(OH)_8$, which may be formulated $MoO_{1.6}(OH)_{1.2}(H_2O)_{0.2}$. The close connection existing between these reduced phases and MoO_3, demonstrated by the possibility for stepwise reduction and oxidation, has led Glemser and Lutz to describe them as *genotypic with* MoO_3 and to suppose that this chemical relationship would be reflected in their crystal structures [1].

Preliminary X-ray investigations have been made by the present authors in order to study the structural relationships within this genotypic series. Samples of MoO_3 were subjected to different degrees of reduction by methods (*a*), (*b*), and (*c*) above and the X-ray powder patterns of the products were recorded in Guinier focusing cameras with Cu$K\alpha$ radiation using KCl as an internal standard ($a = 6.2921$ Å).

The existence of a number of different crystalline phases was verified. Their powder patterns, which are all very similar to that of MoO_3, could be interpreted in most cases, and the unit cell dimensions thus derived were seen to differ only slightly from those of MoO_3, *viz.* within 5 % for the *a* and *b* axes and within 10 % for the *c* axis. In some cases the cell is slightly monoclinically deformed, the *a* axis being the unique axis. It is thus evident, that the term "genotypic with MoO_3" is also appropriate when considering the structural relationships between these compounds.

Although no data for chemical analysis were available, one phase could be identified as the compound $Mo_4O_{10}(OH)_2$ ($x = 0.5$) described by Glemser and Lutz, since it could be prepared by method (*b*) above, specific for this compound, and its powder pattern (Table 1) was seen to agree with the data given by these authors. The orthorhombic unit cell has the dimensions: $a = 3.888$ Å, $b = 14.082$ Å, $c = 3.734$ Å, which may be compared with the values for MoO_3[5]: $a = 3.963$ Å, $b = 13.855$ Å, $c = 3.696$ Å.

Table 1. X-Ray powder pattern of $MoO_{2.5}(OH)_{0.5}$. Cu$K\alpha$ radiation.

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
m	0.01195	020	0.01199
v st	0.04219	110	0.04231
m	0.04797	040	0.04795
v st	0.05453	021	0.05460
w	0.06626	130	0.06628
st	0.08488	111	0.08492
v w	0.09059	041	0.09057
m	0.10802	060	0.10789
m	0.10895	131	0.10890
w	0.11430	150	0.11423
w	0.15066	061	0.15051
m	0.15719	200	0.15724
st	0.17051	002	0.17046
w	0.20519	240	0.20519
m	0.21173	221	0.21184
m	0.21276	112	0.21277
w	0.21846	042	0.21842
w	0.22885	171	0.22888
v w	0.23460	081	0.23442
v w	0.23677	132	0.23675
v w	0.24794	241	0.24780
v w	0.26509	260	0.26513
w	0.27846	062	0.27836
w	0.28474	152	0.28470

v = very, st = strong, m = medium, w = weak.

The space group of MoO_3 is *Pbnm* (No. 62 of *Int. Tab.* in a different orientation) with the atoms in 4-fold positions 4(*c*):x, y, $\frac{1}{4}$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{4}$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{3}{4}$; $\bar{x},\bar{y},\frac{3}{4}$. The atomic parameter values are [6]:

	x	y
Mo	0.0847	0.0998
O_1	−0.025	0.935
O_2	−0.060	0.600
O_3	0.015	0.230

The intensity distribution in the powder pattern of $MoO_{2.5}(OH)_{0.5}$ is remarkably similar to that of MoO_3, with the important exception that all reflections with $h + k = 2n + 1$ are missing. This indicates a *C*-centering of the lattice, which can be achieved if the four x coordinates above are put equal to zero. The atomic positions are thereby moved to exactly half-way between the glide-planes, and can be described as positions 4(*c*): 0, y, $\frac{1}{4}$; $\frac{1}{2}$, $\frac{1}{2}+y$, $\frac{1}{4}$; $\frac{1}{2},\frac{1}{2}-y$, $\frac{3}{4}$; 0, $\bar{y}$, $\frac{3}{4}$; of the space group *Cmcm* (No. 63), which is a super-group to the preceding one. Structure factors based on this structure model with the same y parameters as above were calculated.

It is probable that the intensities of the powder lines of the hydroxide will be seriously modified by orientation effects, as in the case of MoO_3. It was therefore not possible to obtain very reliable observed $|F|$-values for the hydroxide from intensity measurements. However, the assumption that these effects have the same influence on the intensities in both cases, produced relatively good agreement between calculated and observed values. The y coordinates of the molybdenum atoms are thus evidently fairly close to the values in MoO_3. The corresponding oxygen parameters are of course approximate, as they effect the intensities to a much smaller extent. Single crystal studies appear to be necessary if the precise oxygen positions are to be evaluated.

It is clear that the substitution of two OH groups for one O atom per unit cell of MoO_3 causes a transition to a more ideal structure, at least as regards the metal atom arrangements. The same effect has been observed in the tungsten oxide hydroxides studied by Glemser and Naumann [7]. It is also in accordance with Magnéli's observation on molybdenum and tungsten compounds containing structural elements of ReO_3- or perovskite type, that a lower valency for the metal atom favours a less distorted arrangement [8].

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Mimosaceen-Aminosäuren. Teil VII *

Isolierung von Willardiin (3-(1-Uracyl)-L-Alanin) aus den Samen von *Acacia millefolia, Acacia lemmoni* und *Mimosa asperata*

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In einer früheren Mitteilung wurde die Isolierung von Willardiin, einer neuen pflanzlichen Aminosäure, aus den Samen von *Acacia Willardiana* Rose (*Mimosaceae*)

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