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Studies on Molybdenum and Molybdenum Wolfram Oxides of the Homologous Series Me_nO_{3n-1}

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Members of the homologous molybdenum and molybdenum wolfram oxide series Me_nO_{3n-1} with n equal to 8, 9, 10, 11, 12 and 14 have been prepared. The phase relations of the series have been studied as a function of the wolfram to molybdenum ratio and of the temperature. The former has been found to determine the value of n in the first place, higher homologues forming with increasing relative contents of wolfram.

A comparison is given between previously derived unit cell dimensions for the homologues and those actually observed for preparations of various compositions.

Studies of some chemical properties have been found to indicate that the structural uniformity of the series also corresponds to a very similar chemical behaviour.

The existence of a series of structurally interrelated molybdenum and molybdenum wolfram oxides of the general formula Me_nO_{3n-1} (Me = Mo, W) was recently reported by one of the present authors[1]. Previously known members of this series were the molybdenum oxides Mo_8O_{23} and Mo_9O_{26}[2]. It was found that several molybdenum wolfram oxides of about the same metal to oxygen ratio of 1 : 2.9 are built analogously and detailed structure determinations were carried out for the two double oxides $Me_{10}O_{29}$ and $Me_{11}O_{32}$[3]. The investigation was facilitated by a general discussion of the geometrical properties of structures of this type[4].

A brief description of the structure of *e. g.* $Me_{10}O_{29}$ will serve to illustrate the building principles of this oxide series. (*Cf.* Fig. 1.) The structure may be considered as built up of blocks of ReO_3-type, *i. e.* three-dimensional aggregates of metal-oxygen octahedra joined by sharing corners in a basically cubic arrangement. The blocks are of infinite extension in two dimensions and have a characteristic width of ten octahedra in a third direction. The actual MeO_6 octahedra are distorted, the metal atoms forming puckered networks and the oxygen polyhedra being modified to a square pyramidal arrangement with a remote oxygen atom completing the octahedra. The blocks are mutually

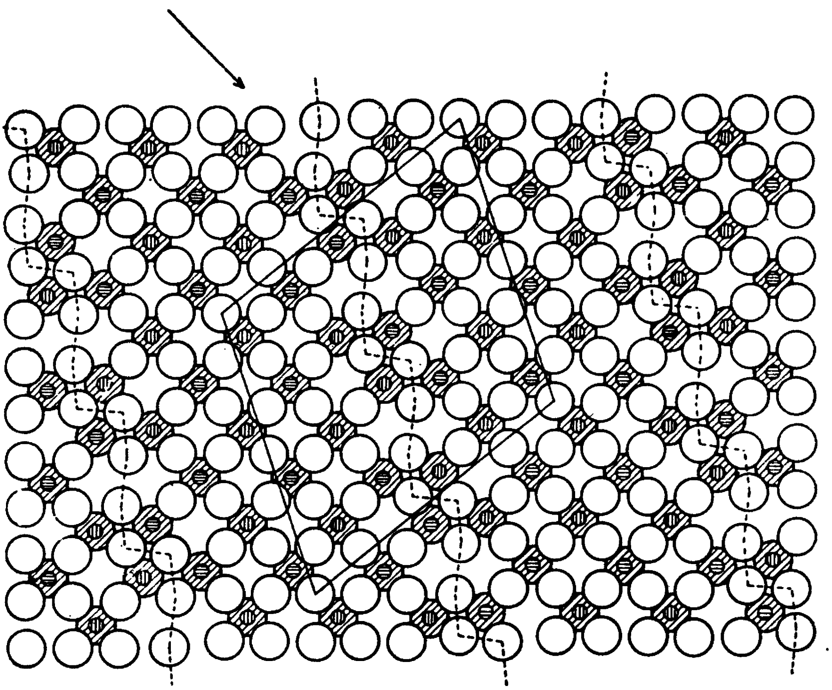

Fig. 1. Structure of the phase $Me_{10}O_{29}$ of the homologous series Me_nO_{3n-1}. The metal atoms (small circles) are slightly displaced normally to the figure, the direction of the displacement being indicated by the different shadowing. The arrow shows the direction of the finite extension of the ReO_3 type blocks, which are indicated by dashed lines.

connected along characteristically folded planes by MeO_6 octahedra sharing edges. The various members of the series, Me_nO_{3n-1}, differ concerning the number of MeO_6 octahedra (n) determining the finite extension of the blocks. It was suggested that this series of compounds, expressible by a general formula and built on common structural principles, be characterized as a *homologous series.*

Further studies on this series have now revealed the existence of the two oxides $Me_{12}O_{35}$ and $Me_{14}O_{41}$ and given some knowledge of the formation conditions and stability of the various phases. Exact unit cell dimensions have been determined and compared with the ideal ones.

EXPERIMENTAL METHODS

The samples were generally prepared by heating weighed mixtures of molybdenum metal, molybdenum trioxide and wolfram trioxide in evacuated, sealed silica tubes for a couple of days. The starting materials were molybdenum powder (Kahlbaum) which had been heated *in vacuo* at about 400° C, molybdenum trioxide (Baker) dried at 400° C and wolframic acid (Kahlbaum) which had been heated for several hours at about 850° C.

Due to the considerable volatility of molybdenum trioxide at the heating temperatures it was necessary to keep the temperature as constant as possible and to minimize the temperature gradient in the silica tubes. The tubes were thus kept in narrow holes, bored in a heavy cylinder of fire-resisting steel, which was covered by a steel lid. The cylinder was heated in a vertical electric furnace. A platinum-platinum rhodium thermocouple was introduced in one of the holes of the cylinder through a narrow opening in the lid. The cold junction of the thermocouple was kept at 0° C in a Dewar flask containing ice and water. A constant voltage, just insufficient to give the temperature wanted was applied to the furnace while a small, additional voltage was controlled by the thermocouple using a Wheelco regulator. In this way the variations of temperature were reduced to about ± 2° at a heating temperature of 600—950° C. The samples were quenched in water from the reaction temperature.

In spite of these precautions it was often found difficult to obtain reproducible results when preparing and heat treating the pure molybdenum oxides. It was found that the phase and stability relations in the molybdenum oxygen system are even more complicated than has been known previously. Further studies on this subject are in progress and a note on some preliminary results has recently appeared elsewhere [5]. It was found that equilibrium was much more quickly attained in samples containing wolfram. For high wolfram contents, however, the reaction rate was rather low and high temperatures had to be used in order to reach equilibrium within a reasonable period of time.

The samples were investigated by taking X-ray powder photographs in a Guinier focusing camera of 80 mm diameter using monochromatized Cu-$K\alpha$ or Cr-$K\alpha$ radiation. The very low background of these photographs greatly facilitated the observation of extraneous phases. The powder patterns were evaluated according to the method given by Hägg [6], which introduces an automatic correction for film shrinkage. In order to increase the accuracy, sodium chloride (a = 5.6398 Å) was always added to the powder specimens as an internal standard. Single crystals from various preparations were also investigated by taking rotation and Weissenberg photographs with Cu-K radiation.

PHASE ANALYSIS

Mixtures of the gross composition $Mo_{1-x}W_xO_{2.9}$ were heated at temperatures between 650° and 950° C for a couple of days. The preparations obtained in this way consisted of dark blue or blue-violet crystals. With low contents of wolfram, the crystals often appeared as aggregates of needles or prisms, grown together parallel to the needle axis. The needle-shape of these species, however, was frequently destroyed due to a very marked cleavage at right angles to the needle axis. The cleavage surface showed a very high reflexion power. With higher contents of wolfram, the crystals were smaller and the needle-shape was more pronounced.

The X-ray powder patterns of the substances investigated were rather complicated throughout. The preliminary analyses of the samples thus had to be carried out by means of photographs of selected single crystals. These diagrams could generally be interpreted by comparison with the ideal structural data previously derived for the various members of the Me_nO_{3n-1} series [4]. The approximate unit cell dimensions thus obtained made possible the interpretation of the powder photographs. Samples containing molybdenum wolfram oxides of this homologous series were found to be fairly homogeneous since, in general, only a few, very weak lines of extraneous phases were observed in the powder patterns.

The results of the phase analysis are illustrated in Fig. 2, which gives a tentative diagram of the phase relations of the homologous series $(Mo_{1-x}, W_x)_n\ O_{3n-1}$ as a function of the value of x and of the formation temperature.

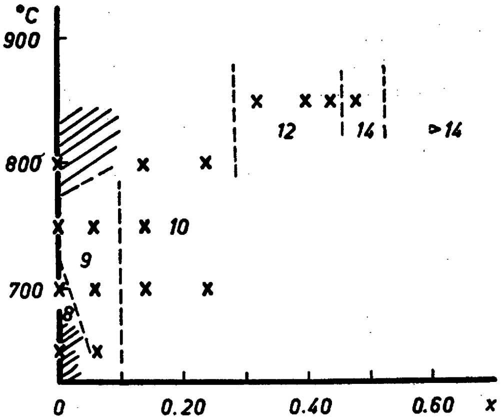

Fig. 2. Tentative diagram showing phases of the homologous series Me_nO_{3n-1}, obtained by heating samples $Mo_{1-x}W_xO_{2.9}$. Crosses denote specimens investigated and figures values of n. Shadowed areas indicate occurrence of phases not belonging to this series.

While the phases Mo_8O_{23} and Mo_9O_{26} — often contaminated by other oxides — could be prepared by heating samples not containing wolfram at rather restricted intervals of temperature around 700° and 750° C respectively, the presence of a small proportion of wolfram ($x = 0.06$) was found to bring about the formation of pure Me_9O_{26} phase within the approximate temperature region 650°—750° C. The phase $Me_{10}O_{29}$ was obtained by heating samples with x equal to 0.14 and 0.24 at temperatures between 700° and 800° C while preparations with x values of 0.32—0.44 and 0.48 heated at 850° C were identified as consisting of the phases $Me_{12}O_{35}$ and $Me_{14}O_{41}$ respectively. With higher contents of wolfram, still higher members of the homologous series were obtained. However, the identity of the phases could no longer be determined with certainty, due to the continually increasing similarity between the powder patterns of the higher homologues.

Attempts to prepare the phases $Me_{11}O_{32}$ and $Me_{13}O_{38}$ in a similar way at 750° C and higher temperatures were not successful. The former compound,

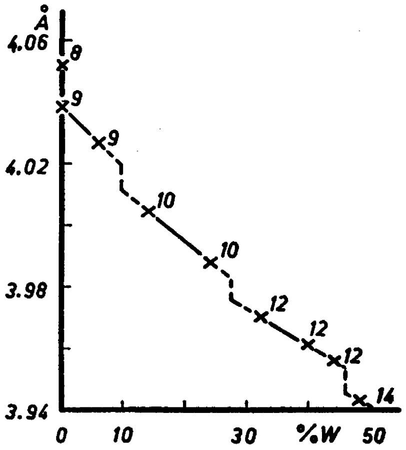

Fig. 3. Length of b *axis of phases of the homologous series $(Mo, W)_nO_{3n-1}$ as a function of the wolfram content.*

however, was obtained as a small amount of tiny, thin crystal needles together with a major constituent consisting of a micro-crystalline substance of the approximate composition $MoWO_6$ when heating an equimolecular mixture of molybdenum trioxide and wolfram trioxide in an evacuated, sealed silica tube at about 700° C for 45 days [3,7]. As this experiment was carried out without special precautions to ensure a constant temperature within the reaction tube, the actual molybdenum to wolfram ratio of the crystal needles is unknown.

The experiments obviously show that the relative wolfram content is a fundamental factor determining the width of the ReO_3-type blocks of the oxide formed. The influence of the formation temperature is obvious for the pure molybdenum oxides but seems to be of minor importance for the mixed oxides within the range of temperature investigated. This might be more fully elucidated by extensive studies of samples prepared at lower temperatures. Due to the low reaction rate even at moderate wolfram contents, such an investigation would be rather tedious. However, the observations reported above might indicate that phases Me_nO_{3n-1} with n are even more stable at high temperatures than those with n odd.

UNIT CELL DIMENSIONS

The fundamental role played by the ReO_3 type building unit in the structures of this oxide series manifests itself as a pronounced substructure effect in the X-ray diffraction patterns. Since the metal atoms of the ReO_3 type blocks form puckered layers (*cf.* Fig. 1), the subcell corresponds to two units of MeO_3 and shows (psuedo)tetragonal symmetry with $a' \approx c' \approx d\sqrt{2}$ and b' (tetragonal axis) slightly longer than d ($d =$ the space diagonal of a regular MeO_6 octahedron) [4]. All strong reflexions of the various members of the homologous series appear in multiplets close to the reciprocal lattice points of the subcell.

The substructure effect causes the X-ray patterns of the homologues to be very similar, the similarity of the diagrams increasing with increasing n. In spite of their considerable complexity, it was possible to interpret the powder photographs of the phases with $n = 8, 9, 10, 12$, and 14 up to fairly high diffraction angles and to derive unit cell dimensions of preparations of various compositions. Representative parts of the powder patterns are listed in Table 1.

Table 2 gives a comparison between the unit cell dimensions thus obtained and the ideal ones, calculated on the basis of the values of $d = 3.750$ Å for the length of the space diagonal of a regular MeO_6 octahedron and of $\delta = 0.21$ for the parameter introduced to allow for the mutual repulsion of the metal atoms of octahedra joined by sharing edges. (The formulae used when calculating the ideal dimensions are given in reference [4].) The accuracy of the observed cell data may be estimated to be better than $\pm$ 0.01 Å for the a and c axes, $\pm$ 0.002 Å for the b axis and $\pm$ 0.02° for the monoclinic angle. The data given in this paper for Mo_8O_{23} and Mo_9O_{26} are thus somewhat more exact than those previously reported [8].

The agreement between observed and ideal values for the length of the a axes is good, the difference amounting to 0.11 Å (0.65 %) for Mo_8O_{23} and

Table 1. Part of the powder diffraction patterns of homologues of the series Me_nO_{3n-1}. Cu-Ka radiation.
(Reflexions marked with an asterisk coincide with other lines of the powder patterns.)

Tetragonal subcell		Me_8O_{23} (0 % W)				Me_9O_{26} (0 % W)				$Me_{10}O_{29}$ (14 % W)				$Me_{12}O_{35}$ (32 % W)				$Me_{14}O_{41}$ (48 % W)			
h'k'l'	$\sin^2\Theta$ calc	*I*	*hkl*	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	*I*	*hkl*	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	*I*	*hkl*	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	*I*	*hkl*	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc	*I*	*hkl*	$\sin^2\Theta$ obs	$\sin^2\Theta$ calc
$10\bar{1}$	.0423	v st	$20\bar{3}$	.0510	.0510	v st	$20\bar{4}$	.0498	.0499	v st*	$20\bar{5}$	.0490	.0490	st	$20\bar{5}$	.0474	.0475	v st*	$20\bar{5}$	.0463	.0466
		st	$20\bar{2}$	.0298	.0298	m+	$20\bar{3}$	.0310	.0311	st—	$20\bar{4}$	.0321	.0321	m*	$20\bar{4}$	.0335	.0335				
		m	$20\bar{1}$	.0158	.0158	m—	$20\bar{2}$	.0178	.0179	w+	$20\bar{3}$	.0194	.0197	w	$20\bar{3}$	.0225	.0226				
101	.0423	m	401	.0333	.0334	w	400	.0339	.0340	m*	$40\bar{1}$	.0343	.0344	w	401	.0350	,0351				
		st	402	.0378	.0379	st	401	.0386	.0387	st	400	.0391	.0391	st	402	.0394	.0395	st	404	.0400	.0399
		st*	403	.0495	.0495	st	402	.0490	.0490	v st	401	.0483	.0484	st	403	.0470	.0470	v st*	405	.0463	.0463
200	.0845					w	$60\bar{3}$	.0937	.0935	v w	$60\bar{5}$	.0921	.0924								
		st	600	.0815	.0815	st	$60\bar{2}$	.0821	.0822	st	$60\bar{4}$	.0825	.0825	v st	$60\bar{2}$	.0825	.0825	st*	600	.0831	.0829
002	.0845	w	204	.0538	.0539	v w	204	.0573	.0574	w	204	.0599	.0600								
		st	205	.0830	.0830	m+	205	.0837	.0837	st	205	.0838	.0839	st	207	.0834	.0835	st*	209	.0831	.0834
		m +*	206	.1194	.1194	v w	206	.1157	.1156	w	206	.1122	.1123								
$20\bar{2}$	.1690	w	$40\bar{6}$	.2038	.2038	w	$40\bar{8}$	.1995	.1998	v w*	$40\overline{10}$	.1960	.1961					v w	$40\overline{10}$	.1863	.1862
		v st*	$40\bar{5}$	.1580	.1579	st+	$40\bar{7}$	.1591	.1593	v st	$40\bar{9}$	.1599	.1600	st	$40\bar{9}$	.1606	.1606	m*	$40\bar{9}$	.1613	.1612
202	.1690	v st	805	.1712	.1711	st+	803	.1725	.1725	v st	801	.1725	.1727	v st*	805	.1718	.1715	st	809	.1715	.1714
010	<.0423	v st*	010	.0361	.0362	v st*	010	.0364	.0364	v st	010	.0371	.0371	v st	010	.0376	.0376	v st	010	.0382	.0382
011	<.0634	st*	112	.0495	.0497	w	112	.0508	.0508	w+	112	.0521	.0521	w	113	.0533	.0535	v w	114	.0546	.0547
		m*	113	.0660	.0661	w	113	.0653	.0653	m—	113	.0651	.0651	w+*	114	.0643	.0639	w	115	.0635	.0639
110	<.0634	w	$31\bar{1}$	.0649	.0649	w	$31\bar{2}$	.0640	.0641	w	$31\bar{3}$	.0638	.0638								
		w	310	.0566	.0566	w	$31\bar{1}$	.0569	.0570	w+*	$31\bar{2}$	.0577	.0577	m	311	.0582	.0583	m	310	.0588	.0589
		m	311	.0554	.0554	m—	310	.0555	.0555	w+	$31\bar{1}$	.0561	.0561					v w	311	.0574	.0573

Table 2. Observed and ideal unit cell dimensions of members of the series Me_nO_{3n-1}.

Phase	% W	a Å		b Å		c Å		β		c sin β Å		
		obs	ideal	obs	ideal	obs	ideal	obs	ideal	obs	ideal	Δ (ideal-obs)
Me_8O_{23}	0	16.88	16.77	4.052	>3.750	13.39	13.82	73°81	73°88	12.86	13.27	0.41
Me_9O_{26}	0	16.80	16.77	4.039	>3.750	14.58	15.00	95°43	94°56	14.51	14.95	0.44
»	6	16.82	16.77	4.027	>3.750	14.59	15.00	95°47	94°56	14.53	14.95	0.42
$Me_{10}O_{29}$	14	16.78	16.77	4.005	>3.750	17.43	17.76	111°74	110°51	16.19	16.63	0.44
»	24	16.83	16.77	3.988	>3.750	17.45	17.76	111°73	110°51	16.21	16.63	0.42
$Me_{12}O_{35}$	32	16.80	16.77	3.970	>3.750	19.61	20.00	89°25	88°61	19.61	19.99	0.38
	40	16.81	16.77	3.961	>3.750	19.62	20.00	89°26	88°61	19.62	19.99	0.37
»	44	16.80	16.77	3.956	>3.750	19.64	20.00	89°23	88°61	19.64	19.99	0.35
$Me_{14}O_{41}$	48	16.78	16.77	3.943	>3.750	24.04	24.43	73°19	72°87	23.01	23.35	0.34

being less (0.01—0.07 Å) for the other preparations. The extension of the lattice in this direction is very little influenced by the value of *n* and the relative content of wolfram.

The *c* axes and monoclinic angles observed are in fair agreement with the ideal values. A spectacular idea of their combined deviation is obtained by comparing the observed and ideal values of the product $c\sin\beta$, representing the finite width of the ReO_3-type blocks. The observed widths are throughout less than the ideal ones. These differences cannot be removed by altering the value of the parameter δ in the formula for the ideal unit cell dimensions (*i. e.* by assuming other interatomic distances between the metal atoms of the MeO_6 octahedra joined by edges) as this would give rise to considerable discrepancies between the observed and ideal metal atom coordinates [4]. The deviations between the observed and ideal widths of the ReO_3-type blocks must evidently be due to a contraction in this direction as compared with the extension in the direction of the *a* axis. It is noteworthy that the absolute value of the contraction is fairly constant irrespective of the value of *n* and thus of the width of the blocks.

The variation of the length of the *b* axis is of special interest as the increase of this dimension in comparison with the space diagonal of the regular MeO_6 octahedron is associated with the puckering of the metal atom layers and the distortion of the oxygen polyhedra. The values of *b* (*cf.* Fig. 3) decrease with increasing wolfram content. The introduction of wolfram atoms in the structures evidently causes a modification of the metal-oxygen polyhedra towards a more regular octahedral arrangement. It is of interest in this connection to notice that the structure of the wolfram oxide $W_{20}O_{58}$ belonging to the series Me_nO_{3n-2} is not puckered and is very probably built up of fairly ideal WO_6 octahedra [9]. The length of the *b* axis of this compound amounts to 3.767 Å [8]. The variation of the *b* axis dimension of the Me_nO_{3n-1} oxides is discontinuous when passing from one homologue to another.

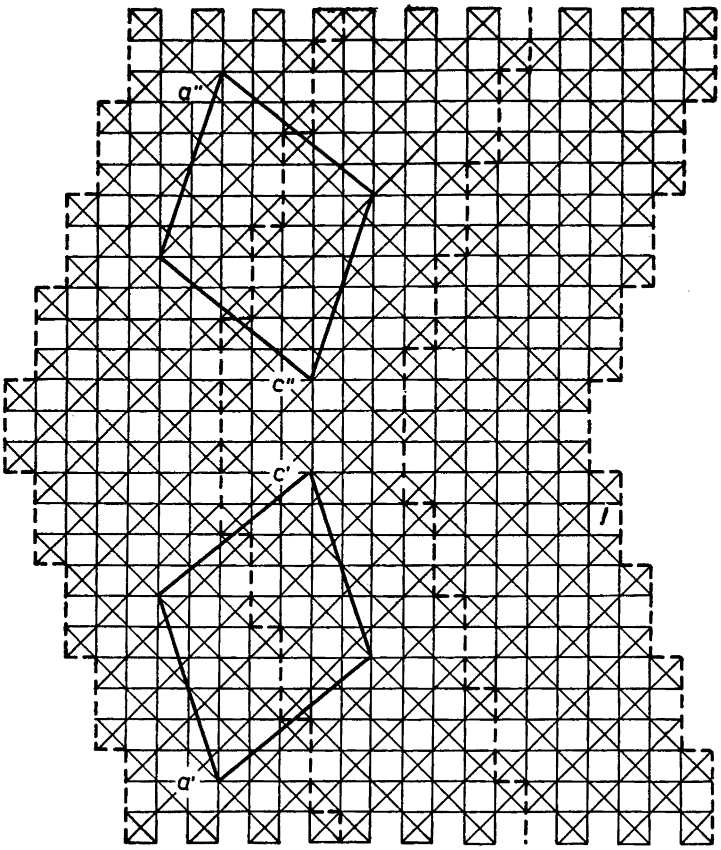

Fig. 4. Twinning of $Me_{10}O_{29}$ (idealized diagram).

TWINNING

As mentioned above the crystals often appear in aggregates, the crystal individuals having grown together parallel to the monoclinic axis. Weissenberg photographs of a crystal of the phase $Me_{10}O_{29}$ revealed the existence of twinning, the angle between the *a* axes of the twins amounting to 144°. This indicates the twinning to be caused by a change of the slope of the ReO_3-type blocks in the way illustrated in Fig. 4, $(30\bar{2})$ being the twin plane. The ideal value according to this scheme for the angle between the *a* directions of the twin individuals is 143.°12 ($= 2\,\beta''$ in the notation used in the discussion of the geometry of these substances 4)). This angle will have the same value also for twins of other members of the homologous series. The general indices for the twin plane of the homologue Me_nO_{3n-1} ($n = 3p+q$, p and q integers) will be (100) for $q = -1$, $(30\bar{1})$ for $q = 0$, and $(30\bar{2})$ for $q = 1$ or generally $(30\,\overline{q+1})$.

Growing together of crystal individuals not governed by a twin law has also been observed.

CHEMICAL PROPERTIES

According to Glemser and Lutz[10], Mo_8O_{23} ("β-molybdenum oxide") and Mo_9O_{26} ("β'-molybdenum oxide") differ considerably in their chemical properties, the former being soluble in dilute ammonia while the latter is not affected by this reagent. Treating a mixture of the two oxides with ammonia was suggested by these authors as a means of preparing Mo_9O_{26} in a pure state.

In view of the close structural relationship a considerable difference between the chemical properties of the two oxides seemed rather improbable. Pure samples (a few crystals) of these compounds and also of the higher homologues were thus tested with various reagents, *viz.* hydrochloric acid, sulphuric acid, nitric acid, sodium hydroxide, and ammonia. The samples were observed under the microscope. In no case could an obvious attack be noticed even after a few hours. A preparation containing ζ-molybdenum oxide[5] was, however, dissolved by ammonia. It thus seems probable that the "β-molybdenum oxide" of Glemser and Lutz, is identical with the ζ-oxide while their β'-oxide is Mo_8O_{23}, Mo_9O_{26} or a mixture of these two phases.

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