

## On Tetramolybdates and Metatungstates

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If the polymolybdates and the polytungstates are divided into groups with different definite mole ratios  $R_2O : MoO_3$  ( $WO_3$ ), there appear in both cases groups with the ratio 1 : 4, tetramolybdates and tetratungstates.

The tetratungstates were already called metatungstates<sup>1</sup> in 1854 in analogy with the metatungstic acid  $H_2O \cdot 4WO_3 \cdot xH_2O$  described by Laurent<sup>2</sup>. This name has later been used in order to draw attention to their close relations to the heteropolyacids, with which they are isomorphous<sup>3</sup>, as is confirmed by X-ray powder photographs<sup>4</sup>. There is no doubt as to the analogy in structure between the metatungstates and such heteropolyacids as phosphotungstic acid  $H_3PW_{12}O_{40}$ , the structures of which have been determined<sup>5-7</sup>. The very complex ion  $PW_{12}O_{40}^{3-}$  is described in modern text-books on inorganic chemistry<sup>8-9</sup> and will not be treated here; nor will we discuss the role of hydrogen in the metatungstate ion, but write it as  $W_{12}O_{40}^{8-}$ . It may be added, however, that a cesium compound  $Cs_3H_3(H_2O_4)(WO_3)_{12} \cdot nH_2O$  has been found to be isomorphous with the heteropolyacids<sup>10</sup>. As this compound can also be written  $Cs_2O \cdot 8WO_3 \cdot nH_2O$ , the octo-

tungstates obviously contain the metatungstate ion  $W_{12}O_{40}^{8-}$  and must be considered as acid metatungstates.

The question then arises whether the tetramolybdates should be considered as heteropolymolybdates, containing a metamolybdate ion  $Mo_{12}O_{40}^{8-}$ , as has been stated by Mylius<sup>11</sup> and Rosenheim<sup>12</sup> (although with an incorrect opinion about the structure of such an ion). Unsuccessful efforts to prepare a metamolybdic acid have, however, been reported<sup>4</sup>. Another theory has been put forward by Jander<sup>13</sup>, who describes the tetramolybdates as acid hexamolybdates, containing an ion  $H_3Mo_6O_{21}^{3-}$ . Finally the existence of an ion  $Mo_4O_{13}^{2-}$  has been stated<sup>14</sup>.

A complete structure determination of some tetramolybdates would of course give an answer to the question of the nature of the tetramolybdate ion. Two such structure determinations have been started by us. The choice of the substances was governed by a desire to get crystals stable in air. All tetramolybdates are described as efflorescent<sup>14</sup>, but as the ammonium-tetramolybdates were reported to be the most stable ones, we prepared them by two different methods, following Wempe<sup>15</sup> and Barbieri<sup>16</sup>. We obtained crystals, stable in air of 30 % relative humidity, with the compositions  $(NH_4)_2O \cdot 4MoO_3 \cdot 2H_2O$  and  $(NH_4)_2O \cdot 4MoO_3 \cdot 2.5H_2O$ . (The analytical methods have been described earlier<sup>17</sup>):

$(NH_4)_2O \cdot 4MoO_3 \cdot 2H_2O$ :		
Calc.	5.12 % $NH_3$ ,	86.8 % $MoO_3$ ,
	8.08 % $H_2O$	
Found	5.15 % $NH_3$ ,	86.5 % $MoO_3$ ,
	8.35 % $H_2O$	

$(NH_4)_2O \cdot 4MoO_3 \cdot 2.5H_2O$		
Calc.	5.05 % $NH_3$ ,	85.7 % $MoO_3$ ,
	9.25 % $H_2O$	
Found	5.08 % $NH_3$ ,	85.6 % $MoO_3$ ,
	9.32 % $H_2O$	

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Powder photographs taken with monochromatized  $\text{CuK}\alpha$  radiation immediately after the crystals had been taken from their mother-liquors, clearly indicated the existence of two different compounds. Rotation and Weissenberg photographs were taken with  $\text{CuK}$  radiation. Both compounds are triclinic, for which reason a structure determination probably would be very intricate and timeconsuming, if it is even possible.

From the photographs  $a$ ,  $b^*$ ,  $c^*$ , and  $\alpha^*$  were determined, however, and thus the volume of the unit cell could be calculated. The density values were obtained by means of the buoyancy method. The knowledge of the  $\text{MoO}_3$  content then permits a calculation of the number of Mo atoms in the unit cell,  $n$ .

$(\text{NH}_4)_2\text{O} \cdot 4\text{MoO}_3 \cdot 2.5\text{H}_2\text{O}$ :  $a = 9.78 \text{ \AA}$ ,  
 $b^* = 0.134 \text{ \AA}^{-1}$ ,  $c^* = 0.105 \text{ \AA}^{-1}$

$\alpha^* = 80^\circ$   $V = 707 \text{ \AA}^3$   $d = 3.1$   $n = 7.9$

$(\text{NH}_4)_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ :  $a = 10.0 \text{ \AA}$   
 $b^* = 0.143 \text{ \AA}^{-1}$   $c^* = 0.108 \text{ \AA}^{-1}$

$\alpha^* = 70^\circ$   $V = 686 \text{ \AA}^3$   $d = 3.1$   $n = 7.8$

Although the accuracy of the determinations is not very great, it is undoubtedly established that there are eight Mo atoms in the unit cell, and we may consider the consequences of this result.

It can be explained in two essentially different ways. There may be discrete ions containing 8, 4 or 2 Mo atoms, or else infinite ions of some kind. In the first case it seems almost certain, that the ions in the mother-liquor must contain 8, 4 or 2 Mo atoms. In the second case we have the further possibility, that there are ions containing multiples of 8 Mo atoms in the solution. If we assume that the diffusion experiments by Jander<sup>13</sup> (giving hexamolybdate ions) are at least approximately correct there remain only the alternatives with 8 or 4 atoms. It is not probable that

the molecular weights obtained by Jander are too large (*cf.* the discussion of the method by Souchay<sup>18</sup> and of the paramolybdate ion  $\text{Mo}_7\text{O}_{24}^{6-}$  by Lindqvist<sup>19</sup>). Therefore it is most probable that the tetramolybdates crystallize from solutions containing octomolybdate ions. In any case the meta- and hexamolybdate theories are undoubtedly ruled out by this investigation. We intend to study these problems further.

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