

Table 1. Continued.

4 2 $\bar{4}$	24047	{24012 24040	vw	1.5744
6 2 $\bar{3}$				
3 3 2	24541	{24556 24562	w	1.5548
4 4 1				
4 6 0	25266	25258	w	1.5324

Both compounds are monoclinic with the cell dimensions

$[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$: $a = 10.202 \pm 0.006$ Å, $b = 12.780 \pm 0.008$ Å, $c = 6.575 \pm 0.008$ Å, $\beta = 120.08 \pm 0.04^\circ$, $V = 741.8$ Å³. $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$: $a = 10.696 \pm 0.010$ Å, $b = 13.075 \pm 0.017$ Å, $c = 6.877 \pm 0.007$ Å, $\beta = 120.24 \pm 0.07^\circ$, $V = 830.0$ Å³. (The errors given are 3σ). The axial ratio $a:b:c$ is thus 1.552:1.944:1.000 for $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ and 1.555:1.901:1.000 for $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$. Systematic absences have been observed for planes of the type hkl with $h+k=2n+1$ for both compounds. The above evidence, together with the observation that the Patterson functions are very similar, strongly supports isomorphism. Possible space groups are $C2$ (No. 5), Cm (No. 8), and $C2/m$ (No. 12). Although the intensity distribution test for $hk0$ reflexions for $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ shows the distribution expected for a centrosymmetric crystal this does not prove that the space group is $C2/m$.

The density of $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$, as determined by weighing a sample in air and in benzene, is 3.06. The density for a unit cell containing two formula units is 3.197 g/cm³.

Observed and calculated $\sin^2\theta$ values are listed in Table 1 and 2. For $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$ the indexing refers to a reduced cell (I-centered, transformation matrix $\{101/010/100\}$) with $a = 6.877$ Å, $b = 13.075$ Å, $c = 9.359$ Å, and $\beta = 99.16^\circ$.

The structure work is in progress and a full report will be published in a forthcoming paper.

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1. Cox, E. G., Pinkard, F. W., Wardlaw, W. and Webster, K. C. *J. Chem. Soc.* **1935** 459.
2. Nyholm, R. S. *Chem. Rev.* **53** (1953) 278.
3. Sone, K. and Kato, M. *Z. anorg. allgem. Chem.* **301** (1959) 277.
4. Brown, B. W. and Lingafelter, E. C. *Acta Cryst.* **16** (1963) 753.

5. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Ithaca, Cornell Univ. Press, Ithaca, p. 168.

6. Harris, C. M. *J. Proc. Roy. Soc. N. S. Wales* **85** (4) (1951) 142.

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Studies on Peroxidomolybdates

III. Unit Cell Dimensions for Two Peroxidoheptamolybdates

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It has been found by Stomberg and Trysberg¹ that two peroxidomolybdates can be obtained from potassium molybdate solutions containing hydrogen peroxide, with an $\text{H}_2\text{O}_2:\text{Mo}$ ratio equal to 0.1–0.8 in the pH range 5.8–6.8. The empirical formulae of these two compounds are:

1. $\text{K}_6\text{Mo}_7\text{O}_{22}(\text{O}_2)_3 \cdot 9\text{H}_2\text{O}$ (o-rh.)
2. $\text{K}_6\text{Mo}_7\text{O}_{24-x}(\text{O}_2)_x \cdot 9\text{H}_2\text{O}$ (mon.)
($0.5 < x < 3$)

The exact limits for x have not yet been settled.

The above formulae are consistent with the replacement of an oxygen ion in the molybdenum complex by a peroxide group. It is, however, impossible to say at the present stage of the investigation whether or not this is so. The peroxide could equally well partly or completely be hydrogen peroxide of crystallization. For compound 2 there is even a slight indication (see 2 below) that the latter possibility is the most probable one.

The unit cell dimensions and the conditions limiting possible reflexions were determined for the two crystalline materials by rotation, Weissenberg, and powder diffraction methods. Accurate unit cell parameters were obtained from measured

$\sin^2\theta$ values, obtained with a Guinier focusing camera, by a least-squares procedure using 35 of the observed lines for compound 1 and 51 for compound 2 and a programme written by Lindqvist and Wengelin² for the SAAB D21 computer. Observed and

Table 1. Observed lines in the powder diagram (Guinier focusing camera) of $K_6Mo_7O_{22}(O_2)_2 \cdot 9H_2O$ (o-rh.) $\lambda(CuK\alpha_1)=1.54051 \text{ \AA}$. Internal standard $Pb(NO_3)_2$ ($a=7.8566 \text{ \AA}$).

hkl	$\sin^2\theta_{obs} \times 10^5$	$\sin^2\theta_{calc} \times 10^5$	I_{obs}	d_{obs}
0 0 2	594	595	w	9.994
0 2 0	656	654	w	9.510
0 2 1	806	803	st	8.579
1 1 0	986	987	st	7.757
1 1 1	1136	1136	vst	7.227
1 1 2	1584	1582	w	6.120
0 2 3	1991	1993	w-	5.459
1 3 0	2290	2296	m+	5.090
0 0 4	2381	2379	vw-	4.992
1 3 1	2450	2444	vvw	4.921
0 4 0	2617	2617	vvw	4.761
0 4 1	2763	2765	w+	4.634
2 0 0	3297	3295	vw	4.242
1 1 4	3364	3367	vw	4.200
2 0 2	3881	3890	w-	3.910
2 2 0	3944	3949	m+	3.879
2 2 1	4096	4098	w	3.806
0 2 5	4374	4372	w	3.683
2 2 2	4550	4544	w	3.611
1 1 5	4705	4705	m	3.551
1 5 0	4908	4912	w+	3.477
0 4 4	5003	4996	vvw-	3.444
1 5 1	5058	5061	st	3.425
2 0 4	5678	5674	vvw	3.232
2 4 0	5910	5911	st	3.168
1 3 5	6004	6013	st-	3.144
2 4 1	6058	6060	st-	3.129
0 4 5	6336	{6334	st	3.060
1 1 6		{6345		
0 6 2	6498	{6482	vvw-	3.022
2 4 2		{6506		
2 4 3		{7245		
1 5 4	-7294	{7292	vvw	-2.852
3 1 0	7570	7577	vw	2.799
1 3 6	7646	7649	m	2.786
0 4 6	7969	7970	m	2.729
3 1 2	8166	8172	vw	2.695
0 6 4	8273	{8267	w	2.678
1 1 7		{8274		
2 4 4		{8291		
2 0 6	8642	8648	st	2.620
1 7 0	8837	8837	w	2.591
3 3 1	9047	9034	vvw	2.561
2 2 6	9311	9303	w	2.524

calculated $\sin^2\theta$ powder values are given in Table 1. The density of the crystals was determined by weighing a sample in air and in benzene. The following results have been obtained.

1. $K_6Mo_7O_{22}(O_2)_2 \cdot 9H_2O$ (o-rh.) is orthorhombic with $a=8.487 \pm 0.005 \text{ \AA}$, $b=19.047 \pm 0.015 \text{ \AA}$, $c=19.974 \pm 0.014 \text{ \AA}$, $V=3228.8 \text{ \AA}^3$. (The errors given are 3σ).

In all photographs only reflexions from planes of the type hkl with $h+k=2n$ were found. Possible space groups are therefore $Cmmm$ (No. 65), $C2mm$ (No. 38), $Cmm2$ (No. 35), and $C222$ (No. 21). $h0l$ reflexions with $h+l=2n+1$ were all either very weak or not observable. This indicates additional approximate symmetry elements for at least the molybdenum atoms.

The density of the crystals is 3.075 g/cm^3 . The density calculated for a unit cell containing four formula units is 3.053 g/cm^3 . The close agreement strongly supports the formulation of the compound as a heptamolybdate. Further indication as to the polynuclear character is obtained from the three-dimensional Patterson function. The largest maximum appears at (0, 0, 0.1648) corresponding to a Mo-Mo vector of 3.26 \AA . Such short distances have been found in the normal heptamolybdate investigated by Lindqvist.³

2. $K_6Mo_7O_{24-x}(O_2)_x \cdot 9H_2O$ (mon.) is monoclinic. The cell dimensions of crystals with $x=1.30$ are $a=16.656 \pm 0.011 \text{ \AA}$, $b=10.560 \pm 0.007 \text{ \AA}$, $c=19.819 \pm 0.007 \text{ \AA}$, $\beta=103.90 \pm 0.04^\circ$, $V=3384.0 \text{ \AA}^3$.

Observed and calculated $\sin^2\theta$ values are given in Table 2. The cell dimensions are not very sensitive to variations in x . This might indicate that the peroxide also appears as hydrogen peroxide of crystallization.

Systematically absent reflexions are $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$. This uniquely determines the space group as $P2_1/c$ (No. 14).

The observed density is 2.900 g/cm^3 . The density calculated for a unit cell containing four formula units is 2.891 g/cm^3 . The agreement between the observed and the calculated density is, even in this case, good. It is therefore highly probable that the monoclinic form is also a heptamolybdate. It seems, moreover, natural that both compounds should show the same degree of polymerization as they crystallize from solutions of identical stoichiometry, and that minor, probably time-dependent, factors influence the preferential formation of one or the other of the crystalline solids.

Table 2. Observed lines in the powder photograph (Guinier focusing camera) of $K_2Mo_7O_{24-x}(O_2)_x \cdot 9H_2O$ (mon.). $\lambda(CuK\alpha_1)=1.54051$ Å. Internal standard $Pb(NO_3)_2$ ($a=7.8566$ Å).

h	k	l	$\sin^2\theta_{obs}$ $\times 10^5$	$\sin^2\theta_{calc}$ $\times 10^5$	I_{obs}	d_{obs}	h	k	l	$\sin^2\theta_{obs}$ $\times 10^5$	$\sin^2\theta_{calc}$ $\times 10^5$	I_{obs}	d_{obs}	
1	0	0	229	227	vw	16.10	1	3	$\bar{2}$	5472	5473	m	3.293	
0	0	2	642	641	vvw	9.613	4	2	$\bar{1}$	5552	5553	m	3.269	
1	0	$\bar{2}$	688	{685	st	9.268	2	3	0	5693	5696	vst	3.228	
0	1	1		{692			4	2	0	5754	5759	m	3.211	
1	1	0	757	759	st	8.853	1	2	$\bar{5}$	5910	5904	w	3.168	
1	1	$\bar{1}$	829	828	st	8.460	5	1	$\bar{1}$		5908			5908
2	0	0	907	908	vst	8.325	2	3	$\bar{2}$	5984	5971	vvw	3.149	
1	1	1	1011	1011	m+	7.660	0	2	5	6139	{6135	st	3.109	
1	0	2	1049	1051	m	7.521	3	0	$\bar{6}$		{6164			6164
2	0	$\bar{2}$	1182	1183	m-	7.085	5	1	0	6205	6206	vw	3.092	
2	1	$\bar{1}$	1412	1417	m	6.482	5	1	$\bar{3}$	6266	6274	st	3.077	
2	1	0	1437	1440	m	6.425	2	1	5	6366	6363	w+	3.053	
2	1	$\bar{2}$	1707	1715	vvw	5.895	1	0	6	6538	6547	m+	3.012	
2	1	1	1780	1783	vvw	5.773	2	3	2	6719	{6703	w	2.972	
0	1	3	1969	1975	w	5.489	3	3	$\bar{1}$	{6716	6716			
0	2	0	2130	{2128	m	5.278	1	2	5	6820	{6820	w	2.949	
3	0	$\bar{2}$		{2134			5	1	1		{6824			6824
1	2	0	2349	2355	w	5.025	3	3	0	6927	6831			
1	0	4	2423	2425	w	4.948	3	3	$\bar{2}$	6927	{6922	vw	2.927	
1	2	1	2599	2607	st-	4.778	5	1	$\bar{4}$	{6938	6938			
1	2	$\bar{2}$	2815	2813	vw	4.591	4	0	6	7194	7203	m	2.872	
2	2	$\bar{1}$	3017	3013	st-	4.434	0	3	4	7356	7353	vvw	2.840	
0	1	4	3097	3097	vw	4.377	5	2	$\bar{1}$	7501	7504	m	2.812	
3	1	$\bar{3}$	3199	3193	vw	4.311	0	2	6	7898	7898	w	2.741	
3	0	2	3235	3233	w	4.284	1	3	4	7962	{7946	w	2.730	
2	1	3	3441	3432	st	4.158	2	2	5		{7959			7959
4	0	$\bar{2}$	3545	3540	w	4.094	1	1	$\bar{7}$	{7972	7972			
4	1	$\bar{1}$	3956	3957		3.873	4	1	4	8190	8194	vvw	2.691	
3	1	$\bar{4}$	4069	{4040	st	3.818	3	3	$\bar{4}$	8301	{8296	w	2.673	
3	2	$\bar{1}$		{4056			4	2	3		{8301			8301
4	1	$\bar{2}$		{4072			6	1	$\bar{1}$		{8313			8313
4	1	0	4166	{4163	m	3.774	4	3	0	8418	{8419	w	2.655	
3	2	0		{4171			5	2	1		{8420			8420
2	0	4	4216	4205	w+	3.751	5	0	6	8695	8696	w	2.612	
3	2	$\bar{2}$	4267	4262	vvw	3.729	2	3	5	8791	8787	vvw	2.598	
1	1	$\bar{5}$	4302	4308	vw	3.714	0	3	$\bar{5}$	8791	8787	vw	2.565	
4	1	$\bar{3}$	4529	{4507	w	3.619	5	1	3		9019			9023
2	1	$\bar{5}$		{4531			5	1	$\bar{6}$	9235	9228	vw	2.535	
0	1	5		{4539			4	1	$\bar{7}$	9468	{9452	m	2.503	
3	2	1	4607	4606	m	3.589	3	0	6	9468	{9462	vw	2.489	
0	3	1	4946	4948	vvw	3.463	1	2	$\bar{7}$		9579			9568
4	0	2	5014	5005	vvw	3.440	2	4	1	9760	9763	vw	2.466	
1	3	$\bar{1}$	5085	5084	vvw	3.416	1	4	$\bar{3}$	9898	{9907	vw	2.488	
3	1	$\bar{5}$	5213	5208	vvw	3.374	6	2	$\bar{1}$		{9909			9909
4	1	$\bar{4}$	5255	{5262	w	3.360	6	0	2	9999	{9911	w	2.436	
1	3	$\bar{1}$		{5267			3	1	6		{9994			9994
0	3	2	5423	5429	m	3.308	4	1	5	{10003	10003			

Further work on the formation and structure of these compounds is in progress and will be published later.

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1. Stomberg, R. and Trysberg, *Acta Chem. Scand.* **23** (1969). *In press*.
2. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
3. Lindqvist, I. *Arkiv Kemi* **2** (1950) 325.

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Studies on Peroxidomolybdates

IV. Preparation and Crystal Data for a Peroxidomolybdate of Empirical Composition KMoO_4

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Peroxidomolybdates are formed when hydrogen peroxide is added to aqueous solutions of molybdates. A large number of peroxidomolybdates have been reported in the literature (see, e.g., the review article by Connor and Ebsworth¹). The best established ones are those formed at high concentrations of hydrogen peroxide, viz. the tetraperoxidomolybdates,¹ $\text{M}_2\text{I}[\text{Mo}(\text{O}_2)_4]_2$, and the tetraperoxidodimolybdates,^{1,2} $\text{M}_2\text{I}[(\text{H}_2\text{O})(\text{O}_2)_2\text{OMoOMoO}(\text{O}_2)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_2$. The structure of the potassium salt of the latter series has recently been determined.³ At low hydrogen

peroxide contents several phases may crystallize successively during evaporation. As has already been pointed out,³ the uncertainties in the composition of the peroxidomolybdates determined by chemical analysis probably depend on the fact that the analyses have often been performed on mixtures of peroxidomolybdates. In order to get as unambiguous results as possible we have felt it necessary to combine chemical and X-ray single crystal or powder methods.

In the present paper we report on a peroxidomolybdate with the empirical composition KMoO_4 . Péchard⁴ has described a peroxidomolybdate with the formula $\text{KMoO}_4 \cdot 2\text{H}_2\text{O}$ and Moeller⁵ one with the composition $\text{K}_2\text{Mo}_2\text{O}_7$. Both have described their crystals in detail. Since they have not specified exactly the conditions of their syntheses we have not been able to repeat their preparations. During our investigations of peroxidomolybdates we have, however, found one with the empirical composition KMoO_4 . Its crystal habit is quite different from those described by these authors. Furthermore, in their study of the ammonium peroxidomolybdates Hansson and Lindqvist⁶ draw the conclusion that the compound $\text{NH}_4\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, described by Péchard, is identical with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{28-x} \cdot 6\text{H}_2\text{O}$ ($0 < x < 0.5$).

KMoO_4 can be prepared in the following way. To an approximately 1 M aqueous solution of K_2MoO_4 is added hydrogen peroxide until the $\text{H}_2\text{O}_2:\text{Mo}$ ratio is about 0.4. The pH is adjusted with nitric acid to 7.5. Well-developed tetragonal bipyramidal crystals separate within a few hours on slow evaporation of the solution. In order to get a pure product it is preferable to have the $\text{H}_2\text{O}_2:\text{Mo}$ ratio slightly below 0.5.

Approximate unit cell dimensions and the conditions limiting possible reflexions were determined from rotation and Weissenberg photographs. Accurate cell dimensions were calculated from measured $\sin^2\theta$ values, obtained from powder photographs taken in a Guinier focusing camera. The calculations were made by a least-squares procedure using 67 unequivocally indexed lines. A programme, written by Lindqvist and Wengelin⁷ for the SAAB D21 computer, was then used for the refinement of the cell parameters.

The density of the crystals has been determined by weighing a sample in air and in benzene.