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

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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 Ebsworth [1]). The best established ones are those formed at high concentrations of hydrogen peroxide, *viz.* the tetraperoxidomolybdates,[1] $M_2^I[Mo(O_2)_4]$, and the tetraperoxidodimolybdates,[1,2] $M_2^I[(H_2O)(O_2)_2OMoOMoO(O_2)_2(H_2O)](H_2O)_2$. 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,[2] 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 $KMoO_4$. Péchard [4] has described a peroxidomolybdate with the formula $KMoO_4{\cdot}2H_2O$ and Moeller [5] one with the composition $K_2Mo_2O_8$. 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 Lindqvist [6] draw the conclusion that the compound $NH_4MoO_4{\cdot}2H_2O$, described by Péchard, is identical with $(NH_4)_6Mo_7O_{26-x}{\cdot}6H_2O$ $(0<x<0.5)$.

$KMoO_4$ can be prepared in the following way. To an approximately 1 M aqueous solution of K_2MoO_4 is added hydrogen peroxide until the H_2O_2: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 H_2O_2: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 Wengelin [7] 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.

Table 1. Powder diagram of $KMoO_4$. Internal standard $Pb(NO_3)_2$ ($a = 7.8566$ Å). $\lambda(CuK\alpha_1) = 1.54051$ 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 1	979	979	w	7.864	3 1 6	12866	12855	vw	2.147
1 0 2	1335	1333	st	6.666	3 2 4	13080	13075	m	2.130
1 1 0	1724	1721	vw	5.866	3 0 7	13540	13530	vvw	2.093
1 1 1	1845	1839	vw	5.671	4 0 0	13776	13766	w	2.075
0 0 4	1893	1890	vst	5.599	2 1 9	13875	13868	vw	2.068
1 0 3	1925	1923	vw	5.552	3 2 5	14145	14137	vw	2.048
1 1 2	2200	2193	vw	5.193	3 3 2	15975	15959	vw	1.9271
1 0 4	2755	2750	vw	4.641	2 1 10	16131	16112	vvw	1.9178
2 0 0	3446	3442	vw	4.149	3 0 9	17323	17310	vw	1.8506
2 0 1	3566	3560	m	4.079	2 0 11	17756	17732	vw	1.8279
2 1 0	4310	4302	vw	3.710	3 1 9	18174	18170	vw	1.8068
2 1 1	4425	4420	vw	3.662	2 2 10	18708	18693	vvw	1.7808
2 0 3	4513	4504	st	3.626	3 2 8	18757	18743	vw	1.7785
2 1 2	4779	4774	vw	3.523	3 3 6	19749	19738	vw	1.7332
1 0 6	5116	5112	vw	3.405	4 2 5	20179	20160	vvw	1.7147
2 0 4	5336	5331	vw	3.334	3 2 9	20765	20751	vvw	1.6903
2 0 5	6403	6394	m	3.044	5 0 2	22002	21982	w	1.6421
1 0 7	6653	6647	vw	2.986	2 0 13	23392	23401	vvw	1.5926
2 2 1	7010	7001	vw	2.909	5 2 1	25070	25069	vw	1.5384
2 2 2	7359	7355	st	2.839	5 0 6	25768	25761	vw	1.5203
0 0 8	7567	7559	vw	2.800	5 2 3	26015	26014	vvw	1.5102
2 0 6	7703	7693	vw	2.775	3 3 10	27305	27297	vw	1.4741
3 0 1	7864	7862	vw	2.747	2 1 14	27455	27450	vvw	1.4700
2 2 3	7952	7946	vw	2.731	5 3 1	29369	29371	vw	1.4213
3 0 3	8815	8806	vw	2.594	5 3 3	30326	30316	vvw	1.3987
2 0 7	9239	9228	vw	2.534	5 2 7	30741	30738	vw	1.3892
2 1 7	10097	10089	vw	2.424	5 3 5	32217	32205	vvw	1.3570
3 0 5	10704	10696	vw	2.354	5 0 10	33328	33320	vvw	1.3342
3 2 0	11189	11185	vw	2.303	5 2 9	34543	34517	vw	1.3106
3 2 1	11312	11303	vw	2.290	5 3 7	35056	35040	vvw	1.3009
3 1 5	11567	11556	vw	2.265	5 3 9	38831	38819	vw	1.2361
3 2 2	11663	11657	vw	2.255	5 0 14	44643	44657	vvw	1.1528
2 2 7	12686	12670	vw	2.163	6 4 1	44879	44858	vvw	1.1498
					7 2 4	47469	47490	vvw	1.1180

$KMoO_4$ is tetragonal with $a = 8.304 \pm 0.002$ Å, $c = 22.413 \pm 0.003$ Å, $V = 1545.5$ Å^3. Space group: $P4_12_12$ or $P4_32_12$. $\varrho_{obs} = 3.41$ g/cm^3, $\varrho_{calc.} = 3.421$ (for 16 formula units in the cell).

Observed and calculated $\sin^2\theta$ values are given in Table 1.

A complete set of three-dimensional intensity data has been collected and the structure is under consideration.

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