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Studies on Peroxidomolybdates

I. The Crystal Structure of Potassium μ-oxido-bis(oxidodiperoxidoaquomolybdenum(VI)) Dihydrate, $K_2[(H_2O)(O_2)_2OMoOMoO(O_2)_2(H_2O)](H_2O)_2$

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The crystals of the compound $K_2Mo_2O_{11}\cdot 4H_2O$ have been shown by three-dimensional X-ray analysis and least-squares refinement to be built up of potassium and μ-oxido-bis(oxidodiperoxidoaquomolybdenum (VI)) ions and water of crystallization. The yellow crystals are triclinic, belonging to space group $P\bar{1}$, with a = 10.086 Å, b = 11.444 Å, c = 6.257 Å, α = 108.14°, β = 109.52°, γ = 88.49° and V = 644.4 Å^3. There are two formula units in the cell.

The two molybdenum atoms of the dinuclear anion are linked together by a single non-linear oxygen bridge. Each molybdenum atom is surrounded by seven oxygen atoms in a pentagonal bipyramidal arrangement, the equatorial plane of which contains four peroxidic oxygen atoms and the bridging oxygen atom. The apical positions are occupied by one double-bonded oxygen atom and one water molecule. The molybdenum atoms are displaced 0.38 Å out of the equatorial planes towards the double-bonded oxygen atoms. The equatorial planes within the anion make an angle of 66.9° with one another.

Average bond distances are: $Mo-O_{peroxido}$ 1.96 Å, $Mo-O_{bridging}$ 1.93 Å, $Mo{=}O$ 1.66 Å, $Mo-O_{water}$ 2.45 Å and $O-O$ 1.48 Å. The $Mo-O-Mo$ angle is 136.1°.

The analysis has shown that the crystals of $K_2Mo_2O_{11}\cdot 4H_2O$ and $K_2W_2O_{11}\cdot 4H_2O$, although not isomorphous, are in both cases composed of potassium ions, water molecules, and isomorphous anions.

The elucidation of the formation and structure of transition metal peroxides is the aim of one of the research programmes at this department. Of the many known transition metal peroxides only a few have been the subject of structure analysis. The best known hitherto are the peroxidochromates, of which seven structures have been determined, namely, $K_3[Cr(O_2)_4]$,[1–3] $K_3[Cr(O_2)_2(CN)_3]$,[4] $[Cr(O_2)_2(NH_3)_3]$,[5,6] $[Cr(O_2)_2(H_2O)en](H_2O)$,[7] $[CrO(O_2)_2py]$,[8,9] $[CrO(O_2)_2phen]$,[10] and $[CrO(O_2)_2dipy]$.[11] The results of all but the last of these investigations have been summarized in a dissertation.[12] Other known structures are those of $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$,[13] $K_2[(H_2O)(O_2)_2OWOWO(O_2)_2(H_2O)](H_2O)_2$,[14] and $K_2[MoO(O_2)F_4](H_2O)$.[15]

Interest has now been focused upon the peroxidomolybdates which are far more complex than the peroxidochromates owing to the ability of molybdenum to form polyanions in aqueous solution (see, *e.g.*, the review article by Connor and Ebsworth[16]). The conditions conducive to the formation of the peroxidomolybdates are now being studied and the results of these investigations will be published later. From these investigations it can be concluded that the degree of condensation and the number of peroxido groups per molybdenum atom depend both on the pH and on the hydrogen peroxide concentration as well as on the temperature. From alkaline solutions containing potassium and molybdate ions and hydrogen peroxide only the mononuclear compound $K_2[Mo(O_2)_4]$ crystallizes, while in neutral or acid solutions ($pH > 4$) the dinuclear species $K_2Mo_2O_{11}\cdot 4H_2O$ is formed over a wide range of hydrogen peroxide concentrations (H_2O_2 in excess). It is only from solutions of very low hydrogen peroxide concentrations that the more complex peroxidopolymolybdates are formed (at $pH < 6.5$). In some of these crystalline products the peroxide content is not stoichiometrically fixed. Single crystal work has shown the existence of an orthorhombic peroxidomolybdate with $a = 8.48$ Å, $b = 19.0$ Å, and $c = 20.0$ Å, which, on account of the empirical formula, the cell volume, and the density, is believed to be a heptamolybdate, of a monoclinic modification, probably also a heptamolybdate, with $a = 16.7$ Å, $b = 10.6$ Å, $c = 19.8$ Å and $\beta = 104°$, and of a tetragonal form, $K_2Mo_2O_8$, with $a = 8.31$ Å and $c = 22.4$ Å. The structures of these peroxidomolybdates are now being investigated, while the structure of the dinuclear peroxidomolybdate is described in this paper. The preparation and analysis of the remaining peroxidomolybdates will be described in a forthcoming publication.

EXPERIMENTAL

Preparation of crystals. 10 ml hydrogen peroxide (30 %) was added in the cold to a solution of 5 g potassium molybdate in 100 ml water. Concentrated hydrochloric acid was then added drop-wise to the dark red alkaline solution until it became light red (about 1.5 ml hydrochloric acid), and 1 M hydrochloric acid was subsequently added until the red colour just disappeared to leave a light yellow solution, from which needle-shaped crystals of $K_2Mo_2O_{11}\cdot 4H_2O$ separated.

Analysis. Molybdenum was determined as lead molybdate according to Vogel[17] and potassium by passing a solution of the compound through a hydrogen ion saturated cation exchanger and titrating the eluate with a standardized sodium hydroxide solution. The peroxide content was established by titration with permanganate. (Found: Mo 36.97; K 15.15; $O_{peroxide}$ 24.3. Calc. for $K_2Mo_2O_{11}\cdot 4H_2O$: Mo 37.03; K 15.09; $O_{peroxide}$ 24.7).

X-Ray methods. Approximate cell dimensions were obtained from rotation and Weissenberg photographs and more accurate dimensions from X-ray powder photographs taken in a Guinier focusing camera with Cu*K*α radiation, using lead nitrate ($a = 7.8566$ Å at 21°C) as an internal standard.

For the single crystal work multiple-film (5 films) equi-inclination Weissenberg photographs were taken of crystals of approximate dimensions $0.05 \times 0.05 \times 0.2$ mm with rotation about [001] (layer lines 0–5), [100] (layer lines 0–1) and $[10\bar{1}]$ (layer lines 0–1), using copper radiation. The exposure times ranged from 5 to 15 h. Due to the low stability of the compound (lower than that of $K_2W_2O_{11}\cdot 4H_2O$) new crystals had to be mounted for each layer line. A total of 2021 independent reflexions was obtained.

The reflexion intensities were estimated visually by comparison with an intensity scale obtained by the rotating sector method, and were corrected using Lorentz and polarization factors. Absorption and extinction effects were not considered (if the crystals were taken to be cylindrical, μR was in most cases less than 0.5). The $|F_0|$-values were brought on to an absolute scale by comparison with the finally calculated structure factors.

Computing methods. The computational work, including the Lorentz and polarization correction, Fourier summations, structure factor least-squares refinement and calculation of interatomic distances and angles and molecular planes, was performed on the electronic computer SAAB D21 with the aid of a set of crystallographic programmes written by Abrahamsson, Aleby, Larsson and Selin.[18-22]

The atomic scattering factors used in the calculation of the structure factors were taken from Volume III of the *International Tables for X-ray Crystallography*, 1962.

STRUCTURE DETERMINATION

Unit cell and space group. The unit cell dimensions were obtained from the measured sin $^2\theta$ values by a least-squares procedure using 56 of the observed lines. All diffraction data were indexed on the basis of the non-reduced working cell described in the subsequent discussion.

$K_2Mo_2O_{11}\cdot 4H_2O$ is triclinic with

$a = 10.086 \pm 0.004$ Å $\alpha = 108.14 \pm 0.03°$
$b = 11.444 \pm 0.005$ Å $\beta = 109.52 \pm 0.03°$
$c = 6.257 \pm 0.004$ Å $\gamma = 88.49 \pm 0.04°$

Calculated and observed $\sin^2\theta$ values are given in Table 1.

The working cell may be transformed to a Delauny reduced cell by means of the matrix

$$\begin{bmatrix} 1 & 0 & \bar{1} \\ 0 & 1 & \bar{1} \\ 0 & 0 & 1 \end{bmatrix}$$

The reduced cell has the dimensions

$a = 9.935 \pm 0.004$ Å $\alpha = 103.92 \pm 0.03°$
$b = 11.205 \pm 0.005$ Å $\beta = 106.89 \pm 0.03°$
$c = 6.257 \pm 0.004$ Å $\gamma = 90.61 \pm 0.04°$
$V = 644.4$ Å

Of the two possible triclinic space groups $P\bar{1}$ was considered to be the correct one judging from the number and relative weights of the Mo—Mo vectors in the three-dimensional Patterson function. It was eventually shown to be possible to fit all the atoms into the unit cell according to $P\bar{1}$.

The density of the crystals, as determined by weighing a sample in air and in benzene, is 2.58 g/cm³. The density calculated for a unit cell containing two formula units is 2.66 g/cm³.

Molybdenum positions. The three-dimensional Patterson function showed two large peaks of about equal magnitude at (0.3571; 0.0393; 0.0325) and (0.7028; 0.4364; 0.0662) interpreted as being double-weight Mo_1—Mo_2 vectors. The two next largest peaks at (0.0611; 0.4816; 0.0936) and (0.3485; 0.3961;

Table 1. Observed lines in the powder diagram (Guinier focusing camera) of $K_2Mo_2O_{11}\cdot 4H_2O$. $\lambda(CuK\alpha_1) = 1.54051$ Å.

$h\,k\,l$	$10^5\cdot\sin^2\theta_{obs}$	$10^5\cdot\sin^2\theta_{calc}$	I_{obs}	d_{obs}
$0\,1\,0$	506	505	m	10.83
$1\,0\,0$	663	662	m	9.460
$1\,\bar{1}\,0$	1065	1067	m	7.464
$1\,1\,0$	1265	1267	vvw	6.848
$1\,1\,\bar{1}$	1765	1770	m	5.798
$1\,0\,\bar{1}$		1794		
$0\,0\,1$	1898	1902	st	5.591
$0\,2\,0$	2018	2022	st	5.422
$1\,\bar{2}\,0$	2481	2483	st	4.890
$0\,\bar{2}\,1$	2661	2665	vst	4.722
$1\,\bar{1}\,\bar{1}$	2822	2828	w	4.585
$2\,\bar{1}\,0$	2949	2951	w	4.485
$2\,0\,\bar{1}$	3006	3009	vw	4.443
$2\,1\,\bar{1}$	3084	3085	vw	4.386
$1\,\bar{1}\,1$	3105	3109	w	4.371
$2\,1\,0$	3353	3352	m	4.206
$1\,\bar{2}\,1$	3891	3895	vvw	3.905
$2\,\bar{1}\,\bar{1}$	3940	3943	w	3.880
$2\,2\,\bar{1}$	4168	4172	w	3.773
$0\,\bar{3}\,1$	4558	4562	st	3.608
$1\,\bar{2}\,\bar{1}$	4867	4874	vvw	3.491
$1\,\bar{3}\,0$	4907	4909	vw	3.477
$2\,2\,0$	5066	5069	w	3.422
$0\,2\,1$	5178	5182	m	3.385
$3\,0\,\bar{1}$	5545	5547	st	3.271
$3\,0\,0$	5964	5954	w	3.154
$1\,1\,\bar{2}$	6067	6076	w	3.127
$3\,\bar{1}\,0$	6160	6159	vvw	3.103
$2\,3\,\bar{1}$	6266	6270	vw	3.077
$2\,\bar{3}\,0$	6617	6593	vvw	2.995
$2\,1\,\bar{2}$		6622		
$0\,\bar{1}\,2$	6849	6854	w	2.943
$3\,2\,\bar{1}$	6901	6911	vw	2.932
$2\,2\,\bar{2}$	7073	7080	vw	2.896
$0\,\bar{2}\,2$	7106	7111	m	2.889
$2\,0\,\bar{2}$	7168	7175	vvw	2.877
$3\,\bar{2}\,0$	7367	7374	vvw	2.838
$2\,1\,1$	7415	7423	vvw	2.829
$0\,\bar{4}\,1$	7461	7470	vvw	2.820
$0\,0\,2$	7613	7608	vvw	2.792
$2\,3\,0$	7790	7796	vvw	2.760
$1\,3\,\bar{2}$		7802		
$1\,\bar{3}\,\bar{1}$	7921	7930	vvw	2.737
$3\,\bar{2}\,\bar{1}$	8232	8226	vvw	2.685
$0\,3\,1$	8344	8339	w	2.667
$1\,\bar{4}\,0$		8347		
$3\,2\,0$	8578	8577	w	2.630
$2\,\bar{1}\,\bar{2}$	8734	8739	vvw	2.606
$3\,0\,\bar{2}$	8938	8943	m	2.576
$1\,\bar{2}\,2$	9114	9112	vvw	2.551
$2\,4\,\bar{1}$	9386	9379	vvw	2.514
$2\,2\,1$	9750	9769	m	2.467
$3\,\bar{1}\,1$		9740		
$2\,\bar{4}\,0$	9928	9930	vw	2.445

Table 1. Continued.

$4\,\bar{1}\,\bar{1}$ $3\,0\,1$	10167	10142 10165	w	2.416
$0\,4\,\bar{2}$	10658	10658	m	2.359
$4\,2\,\bar{1}$ $2\,4\,\bar{2}$ $3\,\bar{3}\,\bar{1}$	10938 -11083	10973 11028 11081	vvw	2.329 -2.314
$2\,\bar{2}\,\bar{2}$	11316	11313	vvw	2.290
$0\,5\,\bar{1}$	11387	11389	vw	2.283
$1\,1\,2$ $4\,1\,\bar{2}$	11683	11673 11682	vw	2.254
$4\,\bar{2}\,\bar{1}$	11901	11886	vvw	2.233
$1\,\bar{4}\,\bar{1}$	12015	11997	vw	2.222
$4\,2\,\bar{2}$	12338	12340	vvw	2.193
$1\,\bar{4}\,2$	12470	12458	m	2.181
$0\,5\,0$	12636	12635	w	2.167
$1\,\bar{5}\,0$ $2\,\bar{4}\,\bar{1}$	12803	12795 12811	vw	2.153
$3\,\bar{2}\,\bar{2}$	12897	12881	w	2.145
$2\,3\,1$	13137	13126	vw	2.125
$2\,5\,\bar{1}$	13488	13499	vvw	2.097
$1\,5\,0$	13815	13798	vvw	2.072
$0\,\bar{5}\,2$	13953	13948	vw	2.062
$1\,1\,\bar{3}$	14184	14187	vvw	2.045
$2\,\bar{5}\,0$ $1\,4\,1$	-14368	14278 14338	vvw	-2.032
$3\,\bar{4}\,\bar{1}$ $5\,1\,\bar{1}$	14952	14948 14969	w	1.9920
$3\,2\,\bar{3}$ $3\,1\,\bar{3}$	-15055	14990 15061	w	-1.9852
$3\,4\,0$ $5\,\bar{1}\,\bar{1}$ $0\,\bar{2}\,3$ $2\,1\,2$	15338	15243 15226 15362 15298	vw	1.9668
$4\,\bar{2}\,\bar{2}$	15779	15772	vvw	1.9391
$3\,3\,\bar{3}$	15929	15929	vvw	1.9299
$0\,\bar{3}\,3$	16000	16001	vvw	1.9256
$3\,0\,\bar{3}$	16131	16144	vvw	1.9178
$5\,1\,\bar{2}$	16187	16197	vvw	1.9145
$2\,5\,0$ $4\,3\,0$ $5\,2\,\bar{1}$	16362	16284 16336 16357	vvw	1.9042
$2\,4\,\bar{3}$	16502	16480	vw	1.8961
$3\,5\,\bar{2}$	16786	16787	vvw	1.8800
$1\,\bar{6}\,1$ $3\,\bar{1}\,2$	17144	17149 17126	w	1.8603
$2\,4\,1$	17498	17494	vw	1.8414
$5\,1\,0$	17555	17545	vvw	1.8384

0.0357) were about half the magnitude of those mentioned above and were consequently interpreted as being single-weight Mo_1—Mo_1 and Mo_2—Mo_2 vectors. The molybdenum atoms thus occupy two general two-fold positions in space group $P\bar{1}$ with the approximate coordinates:

Mo_1	0.030	0.239	0.048
Mo_2	0.674	0.198	0.017

which are very close to the final refined parameters (see Table 3). A structure factor calculation based on these positions led to an *R*-value of 0.35.

Potassium and oxygen positions. No attempt was made to derive approximate coordinates for the four potassium atoms in the cell from the Patterson function. These were instead obtained from a Fourier summation of the observed structure factors, the signs of the Fourier coefficients being determined by the contribution from the molybdenum atoms. In addition to the molybdenum peaks, clearly resolved potassium peaks were now apparent. The resulting potassium parameters (two two-fold positions), namely

K_1	0.231	0.022	0.492
K_2	0.812	0.595	0.298

were, moreover, consistent with the peaks in the Patterson function.

A new structure factor calculation based on these molybdenum and potassium parameters yielded an *R*-value of 0.27. An electron density function was then computed using the signs of the Fourier coefficients thus obtained. This revealed a number of new peaks of which twelve were chemically possible oxygen peaks. At this stage the *R*-value was 0.23. The three remaining oxygen positions were obtained from an electron density difference map and when these were also inserted in the structure factor calculation the discrepancy factor dropped to 0.16. As it seemed likely that a correct structure had been arrived at, refinement of the parameters was begun.

Structure refinement. The structure was refined by the structure factor least-squares method using all 2021 observed reflexions and the programme mentioned above. For each reflexion the weight w was computed according to

$$w = \frac{1}{1 + \left(\frac{|F_o| - a}{b}\right)^2}$$

with $a = 100$ and $b = 63$. The refinement was considered complete when the parameter shifts were less than 10 % of the standard deviations (after about ten cycles) at which stage the *R*-value for all observed reflexions had dropped to 0.104. Observed and calculated structure factors are given in Table 2. The contributions from the hydrogen atoms to the structure factors have not been taken into account.

The atomic parameters with their standard deviations and the isotropic temperature parameters of all the atoms excluding hydrogen are listed in Table 3. The calculated interatomic distances and their standard deviations are given in Table 4. All distances were found to be within the normal range, thus supporting the correctness of the coordinates arrived at in the last cycle. In Table 5 hydrogen bond distances are listed and the cation environment is given in Table 6.

The result obtained from the refinement was further checked by calculating a three-dimensional electron density difference map. This showed only small residual maxima or minima, the largest maximum having a magnitude of about 25 % of the height of a true oxygen peak in the $|F_o|$-synthesis.

Table 2. Observed and calculated structure factors for $K_2Mo_2O_{11} \cdot 4H_2O$.

k	$\lvert F_o \rvert$	F_c
0 k 0		
1	67	51
2	149	-127
3	84	-79
4	10	7
5	167	163
6	7	7
7	24	-20
9	11	12
10	13	11
11	11	-12
12	15	17
13	8	-8
1 k 0		
-13	33	37
-12	14	14
-11	28	-31
-10	9	9
-9	43	49
-8	73	81
-7	44	-50
-6	77	-83
-5	74	68
-4	97	95
-3	98	89
-2	132	-120
-1	68	-68
0	64	64
1	21	17
2	29	27
3	59	-49
4	4	3
5	67	-66
6	72	-69
7	38	37
8	10	12
9	9	-10
10	49	-47
11	21	-22
12	32	37
2 k 0		
-13	23	28
-12	27	31
-11	5	-6
-10	38	-44
-9	12	-13
-8	33	33
-7	9	-8
-6	12	-11
-5	42	-39
-4	77	-75
-3	57	-52
-2	17	-17
-1	75	78
0	13	8
1	171	-144
2	135	-118
3	43	35
4	104	93
5	59	-59
6	113	-106
7	7	-8
8	60	63
9	36	40
10	47	-47
11	36	-37
12	12	14
13	18	22
3 k 0		
-13	7	-8
-12	11	-11
-11	13	-14
-9	33	37
-8	21	-22
-7	83	-90
-6	14	16
-5	44	45

k	$\lvert F_o \rvert$	F_c
-4	34	36
-3	50	-53
-2	89	-84
-1	81	75
0	95	90
1	32	-31
2	116	-106
3	9	5
4	101	95
5	17	17
6	20	-22
7	32	-32
8	23	23
9	24	26
11	16	16
13	3	-5
4 k 0		
-13	24	31
-12	6	-7
-11	52	-52
-10	20	-22
-9	67	67
-8	48	53
-7	42	-36
-6	71	-79
-5	20	19
-4	77	79
-3	7	-4
-2	43	37
-1	19	-16
0	17	17
1	55	54
2	58	-55
3	57	56
4	10	9
5	41	-40
6	19	18
7	41	41
8	43	44
9	31	-34
10	27	-29
11	15	18
12	25	33
5 k 0		
-13	17	25
-12	29	31
-11	19	-19
-10	13	-15
-9	11	12
-8	13	13
-7	20	22
-6	7	-4
-5	33	31
-4	18	-19
-3	38	-40
-2	60	64
-1	66	67
0	40	37
1	96	-89
2	42	-42
3	80	79
4	48	47
5	17	-14
6	66	-73
7	18	19
8	64	59
9	9	-9
10	24	-25
11	18	-21
12	7	10
6 k 0		
-12	7	-9
-10	36	37
-9	22	20
-8	27	-28
-7	56	-61
-6	14	14
-5	90	100

k	$\lvert F_o \rvert$	F_c
-4	13	11
-3	76	-79
-2	52	-54
-1	56	52
0	67	65
1	39	-40
2	69	-69
3	17	-17
4	32	30
6	29	-33
7	7	-6
9	12	-13
7 k 0		
-12	14	-24
-11	27	-32
-9	38	39
-8	8	10
-7	68	-62
-6	42	-40
-5	23	22
-4	23	22
-3	23	-20
-2	24	-24
-1	19	-19
0	20	-22
1	19	-19
2	8	-5
3	16	16
4	15	-16
5	48	-45
7	48	43
8	10	13
9	31	-31
10	23	-25
8 k 0		
-11	12	-13
-10	9	-11
-8	16	-14
-6	11	8
-4	15	-13
-3	32	-31
-2	40	39
-1	56	57
0	39	-37
1	48	-46
2	10	10
3	75	66
4	44	42
5	44	-39
6	26	-25
7	34	33
8	45	43
9 k 0		
-10	21	25
-9	20	23
-8	29	-30
-7	19	-18
-6	32	32
-5	57	54
-4	10	11
-3	56	-51
-2	14	10
-1	56	51
0	35	29
1	18	-13
2	34	27
3	30	26
4	16	13
5	8	3
6	6	5
10 k 0		
-8	4	-4
-7	19	-18
-6	15	-15
-5	31	28
-4	17	15

k	$\lvert F_o \rvert$	F_c
-3	11	-10
-1	20	-17
0	13	-12
1	13	-12
2	21	17
3	16	14
4	34	-33
5	25	-24
11 k 0		
-6	10	10
-4	38	-38
-3	20	-19
-2	25	21
-1	26	23
0	26	-26
1	47	-44
2	8	8
3	28	25
4	6	4
12 k 0		
-3	21	-27
-2	4	-5
-1	26	32
0	4	5
1	13	-19
0 k 1		
-9	33	30
-8	19	-16
-7	68	-61
-6	11	-12
-5	119	103
-4	43	36
-3	159	-133
-2	195	158
-1	22	29
0	128	148
1	10	-10
2	179	-149
3	76	-73
4	75	73
5	44	35
6	52	-53
7	59	-55
8	10	-10
9	11	10
1 k 1		
-14	10	11
-13	22	27
-11	64	-61
-10	31	-31
-9	44	46
-8	63	65
-7	76	-69
-6	118	-99
-5	35	29
-4	15	13
-3	39	-30
-2	93	-82
-1	67	-61
0	69	72
1	15	14
2	56	-51
3	9	6
5	14	-14
6	10	-9
7	44	39
8	34	37
9	30	-26
10	27	-25
11	14	15
12	49	46
1 k -1		
-13	16	21
-11	35	-33

k	$\lvert F_o \rvert$	F_c
-10	42	-36
-9	29	27
-8	40	45
-7	31	-33
-6	99	-99
-5	19	-17
-4	133	119
-3	56	45
-2	73	-77
-1	67	-72
2	18	-13
3	14	-10
4	10	10
5	42	37
6	15	10
7	22	21
8	53	55
10	58	57
12	42	39
13	25	27
14	15	-17
2 k 1		
-14	17	-25
-13	20	24
-12	21	23
-11	25	-23
-10	20	20
-9	15	13
-8	30	29
-7	10	8
-6	14	-15
-5	54	49
-4	9	-10
-3	28	-22
-2	26	23
-1	97	86
0	31	30
1	60	-64
2	75	64
3	110	100
4	120	105
5	38	-37
6	114	-118
7	48	50
8	77	83
9	34	30
10	27	-24
11	35	-35
12	20	19
2 k -1		
-13	7	9
-12	42	42
-10	37	-43
-7	36	39
-5	38	-39
-4	49	50
-3	35	-33
-2	28	26
-1	104	100
0	49	53
1	59	-63
2	106	-106
3	88	87
4	76	85
5	43	41
6	59	-52
7	32	-31
8	105	101
9	31	29
10	40	-36
11	29	-29
13	38	41
3 k 1		
-13	13	14
-12	16	-18
-10	37	34
-9	43	41
-8	31	32

k	$\lvert F_o \rvert$	F_c
-7	62	-60
-6	29	31
-5	101	90
-4	13	9
-3	30	-27
-2	47	-47
-1	157	135
0	79	82
1	63	-60
2	59	-60
3	8	-9
4	88	86
6	52	-50
7	23	-24
10	11	-11
11	9	7
3 k -1		
-12	12	12
-11	11	-11
-10	21	21
-9	31	36
-7	30	-34
-6	30	-32
-5	123	119
-4	81	85
-3	45	-46
-2	66	-65
-1	25	-18
0	192	196
1	19	20
2	101	-113
4	28	31
5	58	59
6	14	14
7	43	-36
11	17	-14
13	12	-12
4 k 1		
-13	27	37
-12	16	-21
-11	32	-34
-9	64	70
-8	35	34
-7	76	-73
-6	48	-51
-4	71	65
-3	36	-32
-2	78	-72
-1	28	-29
0	41	-40
1	10	9
4	42	-40
5	81	-76
6	14	-14
7	42	36
8	24	23
9	47	-40
10	44	-37
11	25	20
4 k -1		
-12	9	8
-11	43	-48
-10	12	-12
-9	41	43
-8	45	54
-7	37	-40
-6	83	-73
-5	22	22
-4	60	61
-3	34	33
-2	84	87
-1	55	-51
0	20	20
1	31	33
2	32	-31
3	26	-28
4	16	-15
5	36	-38

k	$\lvert F_o \rvert$	F_c
6	31	-32
7	27	21
9	38	-35
10	51	-48
12	38	39
5 k 1		
-13	12	18
-11	27	-30
-10	23	-22
-6	31	-30
-5	18	-18
-4	36	-35
-3	71	-69
-2	51	58
-1	68	62
0	33	-30
1	77	-73
2	34	-33
3	77	72
4	44	42
5	45	-39
6	49	-41
7	23	21
8	58	49
9	11	-5
10	18	-20
5 k -1		
-12	14	17
-11	15	-18
-10	31	-32
-9	12	-12
-7	17	-18
-5	13	-12
-4	28	-29
-3	48	-48
-2	30	-32
-1	61	64
0	11	-11
1	107	-110
2	63	-66
3	40	44
4	101	104
5	26	-27
6	66	-75
8	53	47
9	46	36
10	33	-28
11	19	-18
12	19	23
6 k 1		
-10	38	35
-9	21	21
-8	62	-53
-7	38	-35
-6	36	33
-5	91	88
-4	10	6
-3	98	-96
-2	26	-24
-1	76	75
0	100	95
1	18	-20
2	41	-41
3	14	14
5	34	30
8	20	17
9	21	-17
10	11	10
6 k -1		
-12	11	-15
-9	22	24
-8	18	-17
-7	73	-67
-6	32	35
-5	64	66
-4	27	25

Table 2. Continued.

k	$\|F_o\|$	F_c
-3	54	-52
-2	62	-64
-1	96	93
0	83	88
2	78	-77
3	17	20
4	96	104
5	19	20
6	10	10
7	22	-21
9	30	25
11	25	23
7 k 1		
-12	9	-16
-11	22	-29
-10	37	37
-9	42	41
-7	38	-34
-6	26	-27
-5	65	64
-4	24	25
0	29	27
1	11	-10
2	34	33
3	21	20
4	43	-37
5	23	-21
7	58	48
8	9	6
9	34	-35
7 k -1		
-11	22	-27
-10	10	-12
-9	53	59
-8	27	27
-7	19	-19
-6	15	-11
-5	15	16
-4	68	67
-3	17	-16
-1	23	24
0	11	-11
1	25	26
2	29	-29
3	34	37
4	14	15
5	44	-47
6	11	9
7	22	23
8	18	16
9	44	-40
10	43	-36
11	17	18
8 k 1		
-6	15	15
-5	12	8
-4	56	-46
-2	36	33
-1	51	45
0	27	-30
1	89	-75
2	20	17
3	43	43
4	13	12
5	46	-44
6	37	-34
7	25	23
8	15	16
8 k -1		
-10	10	-13
-9	10	9
-5	16	16
-4	16	-17
-3	47	-52
-2	23	22
-1	17	16
0	14	-15
1	51	-56
2	22	-26
3	61	67
4	12	11
5	62	-56
6	64	-54
8	55	47
10	31	-32
9 k 1		
-8	34	-38
-7	26	-28
-6	36	35
-5	18	22
-4	22	-23
-3	54	-48
-2	12	-11
-1	55	50
1	43	-39
2	20	-20
4	11	9
5	10	-8
9 k -1		
-10	13	-19
-9	17	19
-8	24	-25
-7	43	-44
-5	46	46
-3	49	-49
-2	24	-24
-1	22	23
0	26	26
1	36	-38
2	34	-31
3	21	-17
4	25	22
6	21	-21
10 k 1		
-8	6	-9
-7	23	-26
-2	10	7
0	16	-16
2	16	15
3	17	18
4	17	-17
5	15	-17
7	47	46
10 k -1		
-7	29	-32
-6	19	19
-5	31	29
-4	12	12
-2	13	-10
2	29	26
3	12	16
4	12	-10
5	32	-29
7	47	46
11 k 1		
-4	17	-20
-2	40	41
-1	23	24
0	18	-18
1	18	-18
2	11	13
11 k -1		
-6	18	19
-4	23	-21
-2	26	25
-1	48	46
0	23	-21
1	46	-40
2	11	15
3	43	38
4	31	30
5	21	-21
6	29	-28
12 k -1		
-3	38	-41
-1	39	40
0	13	11
1	10	-10
2	17	-19
0 k 2		
-12	18	-20
-11	8	5
-10	20	24
-9	45	50
-7	111	-102
-6	44	36
-5	126	101
-4	170	127
-3	10	-8
-2	150	-145
-1	87	119
0	47	54
1	4	2
2	19	-21
3	17	-16
4	111	106
5	12	14
6	22	-25
7	19	-23
9	20	19
10	15	-14
11	12	14
1 k 2		
-14	19	35
-13	59	42
-12	18	-18
-11	43	-39
-10	13	-16
-9	90	92
-8	44	44
-7	62	-59
-6	49	-40
-5	22	21
-4	205	137
-3	50	-44
-2	63	-69
-1	7	5
0	23	-23
1	58	56
2	32	-32
3	7	10
5	50	-51
6	10	11
7	17	20
8	18	21
9	36	-38
10	42	-44
11	17	19
1 k -2		
-12	21	29
-11	21	-23
-10	34	-38
-9	31	29
-8	55	55
-7	42	43
-6	66	-66
-5	24	-25
-4	117	111
-3	32	31
-2	7	-2
-1	39	-42
0	5	9
2	12	-15
3	56	-42
4	18	-18
5	21	20
6	24	-22
8	35	35
9	43	-46
10	49	-56
11	21	24
12	22	24
13	34	35
14	26	-30
2 k 2		
-13	15	21
-12	15	15
-11	23	-23
-10	21	-20
-9	17	17
-6	24	-21
-5	14	11
-3	72	-64
-2	25	30
-1	28	31
0	35	-43
1	95	-100
2	34	-34
3	95	98
4	39	43
5	54	-57
6	68	-78
8	52	55
10	33	-34
11	12	-14
2 k -2		
-12	29	39
-10	32	-31
-9	22	-22
-8	15	18
-7	27	26
-6	30	-30
-5	10	-9
-4	10	9
-3	36	-36
-2	47	41
-1	55	-48
0	15	-9
1	49	-59
2	92	-84
3	14	14
4	21	21
5	17	-15
6	132	-112
7	46	-49
8	68	72
9	27	29
10	37	-41
11	60	-59
13	34	40
14	5	10
3 k 2		
-12	15	-16
-11	10	-26
-10	25	24
-9	16	14
-8	54	-50
-7	42	-38
-6	29	26
-5	71	67
-4	16	-13
-3	150	-131
-2	65	-66
-1	92	92
0	67	67
1	66	-68
2	59	-62
4	31	34
5	22	24
6	28	-30
8	9	10
9	8	-9
10	9	8
3 k -2		
-12	7	-9
-11	13	-15
-7	69	-64
-6	66	-58
-5	59	57
-4	67	63
-3	36	-34
-2	160	-144
-1	66	-51
0	127	116
1	21	16
2	27	-34
3	56	-54
4	54	51
5	105	93
6	28	-29
7	21	-16
9	33	34
10	14	12
12	22	23
13	8	-4
14	9	1
4 k 2		
-13	16	25
-12	23	-28
-11	39	-47
-9	39	44
-7	59	-60
-6	31	-30
-5	65	56
-4	31	26
-2	36	-36
-1	10	-11
0	33	34
1	9	-11
2	51	49
3	38	41
4	10	-14
5	17	-20
7	56	54
8	9	9
9	23	-25
10	11	-14
4 k -2		
-11	33	-37
-10	20	-21
-9	31	32
-8	61	61
-7	31	-25
-6	60	-60
-5	11	13
-4	122	106
-3	60	53
-2	98	-81
-1	11	8
0	24	22
1	86	78
2	65	66
3	31	-30
4	59	60
5	18	-17
7	47	49
8	21	22
10	48	-51
12	43	46
13	9	11
5 k 2		
-13	17	31
-8	17	17
-7	11	8
-6	48	47
-5	18	18
-4	35	-30
-2	25	24
-1	89	86
0	12	-11
1	54	-57
2	28	31
3	47	51
4	29	30
5	49	-52
6	32	-30
7	34	33
8	18	19
5 k -2		
-10	25	-24
-9	16	17
-8	29	25
-7	9	8
-6	24	21
-5	7	-8
-4	33	29
-3	14	-12
-2	19	-20
-1	82	78
0	9	7
1	81	-71
2	56	-60
3	66	65
4	99	95
5	21	-22
6	93	-86
7	50	-55
8	51	57
9	39	38
10	46	-42
11	25	-23
6 k 2		
-12	12	-19
-11	10	9
-10	34	38
-9	24	26
-8	42	-42
-7	38	-37
-6	49	48
-5	47	46
-4	13	-9
-3	74	-76
-2	28	-25
-1	93	60
0	10	11
1	39	-40
2	40	-44
4	16	14
5	17	-16
6	12	-11
7	13	-14
8	14	-13
6 k -2		
-9	24	23
-8	13	-13
-7	28	-27
-5	49	48
-4	16	15
-3	107	-100
-2	85	-79
-1	63	61
0	115	102
1	21	-20
2	119	-121
3	43	-46
4	54	51
5	40	38
6	12	-15
7	40	-43
8	12	-13
11	12	10
12	6	9
7 k 2		
-11	19	-32
-9	30	33
-8	22	-20
-7	41	-42
-5	16	15
-4	13	-10
-3	31	-28
-2	23	-21
1	14	-10
2	13	12
3	12	11
4	38	36
5	26	23
6	23	21
7	30	30
7 k -2		
-10	11	-12
-9	26	26
-8	21	19
-7	38	-34
-6	48	-45
-5	17	18
-4	38	39
-3	12	-13
-2	58	-55
-1	28	-27
0	14	14
1	11	8
2	8	3
3	20	19
4	16	-14
5	41	-44
6	17	-16
7	35	33
8	32	32
9	29	25
10	34	-34
12	10	40
8 k 2		
-9	13	-7
-8	11	-8
-6	17	16
-4	41	-40
-2	43	50
-1	33	29
0	28	-25
1	40	-38
2	29	-25
3	67	57
5	36	-33
8 k -2		
-10	14	-16
-6	9	8
-4	26	-24
-3	19	-20
-1	60	58
0	19	21
1	48	-71
2	7	-6
3	49	54
4	49	49
5	21	-17
6	60	-56
7	22	22
8	48	49
9	18	15
10	22	-20
11	11	-12
9 k 2		
-8	15	-23
-6	32	40
-5	30	33
-4	30	-31
-3	22	-21
-2	19	17
-1	38	40
0	11	13
1	32	-30
3	13	13
4	8	8
9 k -2		
-9	20	23
-7	51	-45
-6	20	18
-5	68	56
-4	18	15
-3	33	-28
-2	44	-39
-1	50	51
0	51	54
2	25	-26
4	45	47
6	8	-8
9	11	11
10 k 2		
0	16	-16
1	19	-2
10 k -2		
-8	17	18
-7	29	-26
-6	10	-10
-4	29	27
-2	16	-13
-1	9	10
3	12	11
4	11	-11
5	46	-43
7	26	22
11 k -2		
-4	26	-25
-3	33	-32
-2	29	19
-1	33	26
0	22	-19
1	59	-52
2	19	-19

Table 2. Continued.

k	$\lvert F_o\rvert$	F_o
3	53	42
4	20	17
5	38	-36
6	39	-35
12 k -2		
-4	46	-14
-3	40	-37
-1	31	27
0	35	30
1	21	-18
2	26	-21
3	14	15
4	10	11
0 k 3		
-13	7	10
-11	11	-9
-10	45	41
-9	22	20
-8	56	-46
-7	88	-77
-6	9	3
-5	101	89
-4	27	29
-3	103	-116
-2	98	-114
-1	40	49
0	59	57
1	50	-44
2	94	-84
3	42	-37
4	17	18
6	26	-25
7	7	-7
9	17	-7
10	18	-10
1 k 3		
-14	15	19
-13	21	22
-12	38	-34
-11	62	-52
-10	7	-6
-9	68	65
-8	11	-10
-7	126	-114
-6	59	-52
-5	28	25
-4	68	75
-2	77	-89
-1	23	-27
0	11	12
1	8	-0
2	23	20
3	27	27
4	13	-15
5	28	29
6	16	17
7	47	44
8	21	21
9	16	-19
10	18	-23
1 k -3		
-11	13	-22
-10	33	-40
-9	10	-10
-8	46	47
-7	8	10
-6	62	-63
-5	35	-32
-4	34	30
-3	70	59
-2	52	-40
-1	100	-84
0	26	22
1	68	72
2	31	57
3	29	-27
4	11	7
5	18	17
6	19	-13
7	53	43
8	31	26
9	15	16
10	21	-19

k	$\lvert F_o\rvert$	F_c
11	24	-24
12	47	44
13	36	36
14	5	-7
2 k 3		
-13	24	25
-11	24	-21
-10	20	-19
-9	21	20
-8	7	6
-7	6	4
-6	31	28
-5	9	6
-4	9	-1
-3	16	-18
-2	64	68
-1	91	102
0	19	-22
1	53	-57
2	15	-17
3	78	83
4	66	69
5	39	-44
6	20	-22
7	19	20
8	34	33
10	17	26
2 k -3		
-11	9	14
-10	26	-32
-9	20	-20
-8	48	44
-7	23	19
-6	16	14
-5	20	-19
-3	63	53
-2	22	-18
-1	61	45
0	29	30
1	8	-12
2	7	-10
3	11	10
4	136	120
5	19	17
6	86	-77
7	51	-48
8	44	40
9	85	78
10	17	-18
11	49	-46
13	28	29
14	16	18
3 k 3		
-11	13	11
-10	40	34
-9	39	36
-8	53	-58
-7	25	-26
-6	64	68
-5	74	76
-4	9	13
-3	91	-98
-1	77	76
0	38	39
1	38	-40
2	63	-70
3	32	31
4	26	28
6	11	-11
7	17	-18
9	9	-10
3 k -3		
-11	8	11
-9	22	22
-8	22	19
-7	29	-29
-6	16	-17
-5	36	37
-4	97	81
-3	42	-37
-2	119	-91
-1	16	-14
0	62	71

k	$\lvert F_o\rvert$	F_c
1	88	112
2	55	-85
3	81	-90
4	59	55
5	38	36
6	9	-9
7	57	-51
8	27	-22
9	28	26
11	11	-11
12	9	-6
14	9	-12
4 k 3		
-13	14	17
-12	14	-13
-11	49	-48
-10	14	11
-9	59	50
-8	13	-11
-7	30	-29
-6	20	-22
-5	22	23
-3	25	-26
-1	7	-7
1	38	-39
3	20	19
4	25	-27
5	20	-19
7	26	27
8	6	-8
4 k -3		
-11	12	-26
-10	24	-29
-9	31	35
-8	48	49
-7	7	-10
-6	73	-77
-5	33	-30
-4	77	67
-3	30	30
-2	51	-41
-1	59	-60
0	11	-6
1	26	32
2	6	-7
3	14	-17
4	8	-6
5	22	-26
6	40	-44
7	7	-6
8	38	37
9	21	-15
10	42	43
11	11	-11
5 k 3		
-11	18	-16
-10	9	-8
-9	25	-24
-8	8	-8
-6	22	24
-5	16	17
-4	62	-62
-3	21	-19
-2	24	27
-1	19	19
0	26	-28
1	53	-53
2	22	19
3	48	50
5	50	-50
6	19	-18
7	35	35
5 k -3		
-10	23	-29
-9	12	-12
-8	13	11
-7	15	16
-6	22	-21
-5	11	-9
-4	15	-11
-3	45	-44
-2	12	-10
-1	20	21

k	$\lvert F_o\rvert$	F_c
0	27	32
1	44	-50
2	53	-66
3	28	30
4	48	54
5	6	6
6	97	-100
7	31	-31
8	78	78
9	35	38
10	14	-14
11	44	42
13	30	35
6 k 3		
-10	31	31
-8	42	-37
-7	40	-37
-6	45	43
-5	39	39
-4	27	-23
-3	35	-35
-1	53	51
1	35	-32
3	18	14
4	31	27
6 k -3		
-7	32	-32
-6	37	-36
-5	63	62
-4	21	21
-3	36	-36
-2	46	-50
-1	13	12
0	106	122
2	43	50
3	25	25
4	45	52
5	67	76
6	22	-28
9	19	21
10	20	18
12	20	22
13	7	-8
7 k 3		
-10	20	19
-9	33	33
-7	37	-34
-6	18	16
-5	24	21
-4	14	14
-1	11	9
0	19	-17
1	18	15
2	33	32
3	9	9
4	11	-11
5	25	-26
7 k -3		
-9	19	24
-8	43	47
-7	20	-19
-6	38	-38
-5	17	21
-4	52	53
-3	42	41
-2	43	-49
-1	6	8
0	25	29
1	16	18
2	50	55
3	16	-17
5	24	-25
6	28	-33
7	46	51
8	23	28
9	19	-17
10	45	-46
12	26	34
8 k 3		
-9	7	8
-7	10	11

k	$\lvert F_o\rvert$	F_o
-6	30	28
-5	17	-16
-4	29	-25
-2	49	43
-1	21	18
0	53	-46
1	27	-24
2	10	9
3	35	35
8 k -3		
-8	20	21
-3	17	-18
-2	7	9
-1	55	54
1	65	-65
2	46	-52
3	15	13
4	49	49
5	26	-29
6	59	-60
7	19	-18
8	31	28
9	18	13
10	40	-39
11	16	-15
9 k 3		
-6	23	24
-5	15	13
-4	29	-30
-3	41	-42
-2	13	14
-1	16	15
0	9	-9
9 k -3		
-8	15	-20
-7	44	-45
-5	44	37
-4	20	18
-3	72	-62
-2	67	-66
-1	26	27
0	48	53
2	55	-58
3	27	-27
4	22	18
5	11	9
7	10	-8
8	8	9
10	5	-8
10 k -3		
-7	18	-22
-6	34	-31
-4	43	37
3	30	29
5	19	-16
7	30	27
8	32	31
9	23	-20
11 k -3		
-6	13	9
-5	16	15
-4	16	-13
-3	24	-14
-2	39	23
-1	42	36
0	17	17
1	59	-52
2	17	-14
3	56	49
4	26	22
5	17	-11
6	46	-38
7	8	7
8	26	36
12 k -3		
-3	26	-26
-2	16	-14
-1	30	27
0	32	26

k	$\lvert F_o\rvert$	F_o
1	28	-28
2	28	-24
4	19	17
5	4	1
13 k -3		
-1	3	0
0	6	-9
1	7	-13
2	6	4
0 k 4		
-13	10	-8
-11	11	-11
-10	31	31
-9	38	39
-8	51	-49
-7	30	-28
-6	28	23
-5	69	69
-4	11	11
-3	76	-93
-2	7	7
-1	55	70
0	55	69
1	23	-26
2	48	-61
3	39	33
4	30	28
5	19	16
8	17	16
1 k 4		
-14	16	30
-13	21	22
-12	10	-12
-11	49	-49
-10	30	32
-9	61	66
-8	10	8
-7	37	-41
-6	38	-42
-5	64	69
-4	27	31
-1	13	-18
0	33	41
1	8	-7
2	10	14
3	19	21
4	34	32
5	21	19
7	31	37
1 k -4		
-8	41	47
-7	17	16
-6	29	-27
-5	48	-52
-4	31	32
-3	76	81
-2	36	-33
-1	43	-46
0	6	-4
1	33	42
2	28	47
3	31	-42
4	26	-25
9	11	13
10	31	-33
11	24	-22
12	14	14
13	16	17
14	6	-9
2 k 4		
-13	24	31
-12	9	8
-11	19	-18
-8	15	18
-7	9	-10
-6	10	13
-5	8	10
-4	63	-67
-3	9	-7
-2	28	36
-1	30	37

k	$\lvert F_o\rvert$	F_c
0	25	-27
1	67	-85
3	32	42
5	56	-51
6	42	-37
7	23	21
8	12	15
2 k -4		
-9	14	-20
-8	15	16
-7	25	21
-5	36	-35
-4	16	-13
-2	16	-13
-1	11	8
0	14	13
1	12	-8
3	22	-32
4	54	61
5	8	6
6	39	-40
7	79	-83
9	56	65
11	39	-41
12	21	-19
13	22	24
14	8	12
3 k 4		
-12	25	-25
-10	29	28
-8	50	-55
-7	43	-49
-6	28	33
-5	35	40
-4	33	-35
-3	76	-80
-1	51	62
1	35	-43
2	28	-37
3	9	7
4	43	34
3 k -4		
-7	21	-20
-6	31	-26
-5	10	9
-4	40	38
-3	47	-39
-2	84	-77
-1	40	-33
0	98	94
1	75	83
2	60	-101
3	71	-85
4	9	-6
5	100	79
6	49	40
7	56	-49
9	20	17
10	31	28
13	16	19
4 k 4		
-12	29	-31
-11	26	-25
-10	10	11
-9	38	37
-8	10	-12
-7	37	-40
-5	23	23
-4	12	14
-2	13	10
-1	19	19
2	21	21
3	21	20
5	21	-18
6	28	29
4 k -4		
-9	12	14
-8	35	34
-6	60	-62
-5	17	-14
-4	54	54

Table 2. Continued.

k	$\lvert F_o \rvert$	F_c
-3	63	55
-1	59	-57
0	38	36
1	42	43
2	30	31
3	20	21
4	11	5
5	30	28
6	35	-29
7	28	23
8	58	54
9	12	13
10	10	-8
11	31	-29
12	28	24
13	28	30
5 k 4		
-9	11	10
-7	21	20
-6	28	26
-4	18	-17
-2	64	64
-1	29	26
0	40	-43
1	30	-28
2	13	15
3	51	51
5	34	-38
5 k -4		
-9	11	-13
-8	31	33
-7	27	23
-4	16	-15
-3	22	17
-2	18	16
-1	38	30
0	58	60
1	37	-39
2	55	-62
3	13	14
4	65	65
5	14	14
6	81	-75
7	39	-39
8	41	37
9	45	46
10	25	-25
11	62	-62
13	21	21
6 k 4		
-10	29	33
-8	42	-41
-6	33	29
-5	38	36
-4	33	-30
-3	53	-49
-2	17	15
-1	23	20
1	23	-25
2	13	-13
4	10	-7
6 k -4		
-8	9	10
-7	32	-33
-6	34	-31
-5	27	23
-4	40	39
-3	17	-16
-2	66	-62
-1	17	-18
0	42	37
2	65	-66
3	55	-53
4	40	36
5	28	25
6	44	-46
7	39	-35
8	12	-9
9	25	19
11	15	-16
13	7	-6
7 k 4		
-8	20	-18
-7	35	-33
-5	14	11
-1	16	-14
0	24	-23
2	27	30
7 k -4		
-8	30	35
-7	41	-37
-6	13	-9
-5	33	30
-4	25	25
-3	13	-10
-2	13	15
-1	12	-12
1	20	-16
2	14	12
3	23	-21
4	26	-23
5	17	15
7	31	29
8	27	-23
9	55	-54
10	16	-14
12	27	34
8 k 4		
-5	15	-15
-4	23	-25
-2	28	34
8 k -4		
-4	10	11
-3	20	-19
-1	27	28
0	37	31
1	23	-16
2	50	-43
3	43	37
4	49	47
6	46	-38
7	11	-11
8	66	59
9	24	18
10	27	-22
11	24	-19
9 k -4		
-7	18	-22
-6	16	-16
-5	57	56
-4	39	36
-3	37	-36
-2	36	-32
0	70	66
1	10	12
2	54	-46
3	25	-17
4	29	24
5	40	33
6	16	-14
10 k -4		
-6	27	-30
-5	19	16
-4	31	28
-3	10	9
-2	31	-24
-1	11	-10
0	11	7
1	12	-9
2	11	7
5	26	-19
6	30	-23
7	32	22
8	25	20
9	26	-23
11 k -4		
-4	13	-10
-3	21	-19
-1	36	28
1	60	-46
2	29	-23
3	33	23
4	47	34
5	31	-21
6	57	-44
12 k -4		
-3	26	-32
-2	23	-22
-1	32	27
0	26	21
1	12	-8
2	43	-30
4	37	29
5	9	7
0 k 5		
-12	21	-26
-10	24	22
-9	17	16
-8	30	-32
-7	42	-42
-6	17	18
-5	37	34
-4	33	-29
-3	70	-80
-2	6	-2
-1	46	45
0	6	-1
1	44	-42
2	43	-44
3	16	16
4	26	26
5	21	-15
6	21	-18
1 k 5		
-13	7	6
-12	34	-33
-11	61	-47
-10	12	13
-9	48	46
-8	15	-11
-7	48	-43
-6	30	-29
-5	25	22
-4	18	15
-3	27	-19
-2	11	-8
2	22	23
3	22	17
4	22	-20
5	22	-17
6	12	10
1 k -5		
-7	18	22
-6	37	-41
-5	52	-57
-4	17	18
-3	41	44
-2	17	13
-1	51	-51
0	25	-25
1	40	37
2	14	13
3	12	-9
4	22	-27
5	29	28
6	31	32
8	20	23
12	21	15
13	31	-33
2 k 5		
-11	24	-20
-8	12	10
-7	17	13
-6	9	6
-5	11	8
-4	35	-36
-2	54	57
-1	32	28
0	22	-21
1	34	-38
2	24	19
3	56	53
5	29	-28
6	11	-13
2 k -5		
-7	28	33
-3	15	12
-2	16	12
-1	7	-2
0	56	58
1	23	20
2	15	-18
3	4	-7
4	13	17
5	46	63
6	12	-9
7	35	-37
8	28	25
9	45	47
11	49	-45
12	23	-18
13	27	25
3 k 5		
-12	12	-16
-11	13	10
-10	49	44
-8	38	-31
-7	14	-11
-6	40	40
-5	51	53
-4	35	-37
-3	43	-44
-2	13	14
-1	47	49
0	26	22
1	34	-33
2	8	-7
3	11	8
4	9	8
3 k -5		
-8	6	9
-6	19	-19
-5	22	19
-4	36	43
-3	18	13
-2	45	-51
-1	27	-24
0	53	58
1	39	45
2	23	-35
4	5	-4
5	55	72
6	8	9
7	40	-46
8	41	-41
9	7	6
10	22	18
11	22	-16
12	14	-11
13	10	-5
4 k 5		
-11	8	-9
-10	34	35
-9	23	18
-8	18	-13
-7	36	-34
-5	29	24
-3	12	-9
-2	20	-17
0	23	-15
2	29	25
3	12	-11
4	22	-26
4 k -5		
-8	16	27
-6	31	-35
-5	25	-28
-4	23	24
-3	39	42
-2	39	-41
-1	53	-58
1	19	17
2	8	8
3	23	-31
4	22	-27
5	9	-6
6	11	-10
8	19	18
9	15	14
10	41	-38
11	28	-27
12	25	20
13	23	23
5 k 5		
-8	13	-10
-6	16	14
-5	29	-26
-4	37	-30
-2	35	32
-1	15	10
0	46	-45
1	30	-26
2	17	16
5 k -5		
-7	6	7
-5	27	-27
-3	7	7
-2	10	-9
-1	18	20
1	18	-19
2	42	-51
4	54	77
5	17	16
6	33	-33
7	48	-51
8	31	28
9	59	64
10	16	-13
11	37	-32
12	12	-8
13	25	29
6 k 5		
-8	23	-43
-6	28	29
-5	9	12
-4	21	-20
-3	33	-31
-2	22	22
-1	26	26
6 k -5		
-7	9	-10
-6	16	15
-5	11	10
-4	45	52
-3	14	-15
-2	29	-35
-1	7	-7
0	42	48
1	44	54
2	51	-64
3	25	-25
4	30	33
5	45	47
6	22	22
7	43	-43
9	24	20
10	17	10
12	6	-3
7 k -5		
-7	8	11
-6	29	-34
-5	8	-11
-4	40	41
-3	23	26
-1	30	-32
0	22	22
1	23	20
2	10	-8
3	12	13
4	9	-5
5	13	13
8	35	30
9	22	-14
10	35	-27
11	12	-11
12	21	22
8 k -5		
-6	7	-6
-5	10	10
-3	14	-11
0	22	27
1	27	-27
2	44	-50
3	20	15
4	41	39
6	55	-57
7	33	-30
8	35	25
9	32	23
10	20	-18
11	40	-41
9 k -5		
-5	23	27
-4	20	17
-3	26	-25
-2	50	-51
0	45	45
2	46	-47
3	34	-33
4	33	27
5	35	28
6	24	-20
7	24	-16
8	18	-9
9	13	10
10	9	5
10 k -5		
-4	23	25
-3	13	13
-2	26	-24
1	15	10
2	15	11
3	8	6
4	24	23
5	23	-15
6	8	-8
7	32	27
8	29	25
11 k -5		
-3	10	-10
-2	9	6
-1	29	29
0	10	9
1	19	-11
2	26	-22
3	42	32
4	50	42
5	22	-18
6	34	-29
7	11	-8
12 k -5		
0	20	22
2	31	-32
3	9	-7
4	15	16

The unit cell contains sixteen hydrogen atoms, which should be associated with some of the oxygen atoms. From the structural point of view the oxygen atoms differ. O_7 is involved in the bridge between the molybdenum atoms, O_{1-4} and O_{8-11} belong to the peroxido groups, and the Mo_1-O_5 and Mo_2-O_{12} bonds are short enough to be double bonds, making it highly probable that the hydrogen atoms are associated with the oxygen atoms O_6 and O_{13-15}. It has not, of course, been possible to determine the parameters of the hydrogen atoms in this investigation.

Table 3. Atomic coordinates (expressed in fractions of the cell edges) and isotropic thermal parameters with their standard deviations for $K_2Mo_2O_{11}.4H_2O$. The temperature factor $= \exp[-B(\sin^2\theta)/\lambda^2]$. Space group $P\bar{1}$. 2 formula units in the cell. All atoms occupy the twofold position 2*i*.

Atom	x	y	z	B Å^2	$\sigma(x)$ $\times 10^4$	$\sigma(y)$ $\times 10^4$	$\sigma(z)$ $\times 10^4$	$\sigma(B)$ Å^2
Mo_1	0.0288	0.2401	0.0484	1.79	1	1	2	0.03
Mo_2	0.6725	0.1972	0.0180	1.99	1	1	2	0.03
K_1	0.2304	0.0203	0.4957	2.66	3	3	6	0.05
K_2	0.8108	0.5939	0.2956	2.72	3	3	6	0.05
O_1	0.9681	0.3977	0.2130	2.83	10	9	18	0.17
O_2	0.1158	0.4121	0.2037	2.67	10	9	18	0.16
O_3	0.1742	0.2016	0.9006	2.61	10	9	18	0.16
O_4	0.0519	0.1114	0.7746	2.87	10	9	19	0.17
O_5	0.0922	0.1825	0.2728	3.01	10	9	19	0.18
O_6	0.9389	0.3289	0.7289	2.38	10	8	17	0.16
O_7	0.8354	0.1696	0.9210	2.10	9	8	16	0.14
O_8	0.7819	0.1590	0.3097	3.46	11	10	20	0.19
O_9	0.6277	0.1649	0.2736	3.56	12	10	21	0.20
O_{10}	0.5293	0.8434	0.1782	2.97	10	9	19	0.18
O_{11}	0.4433	0.8452	0.3247	3.07	11	9	19	0.18
O_{12}	0.6817	0.3504	0.1135	2.91	11	9	19	0.17
O_{13}	0.6550	0.9693	0.8650	2.56	10	9	18	0.16
O_{14}	0.5716	0.6417	0.4386	3.80	12	11	21	0.21
O_{15}	0.3953	0.4205	0.1441	3.05	11	9	19	0.18

Table 4. Bond distances and angles in the μ-oxido-bis(oxidodiperoxidoaquomolybdenum(VI))-ion.

	Distance (Å)	e.s.d. (Å)		Distance (Å)	e.s.d. (Å)
Mo_1-O_1	1.974	0.010	Mo_2-O_8	1.966	0.012
Mo_1-O_2	1.980	0.009	Mo_2-O_9	1.938	0.015
Mo_1-O_3	1.953	0.012	Mo_2-O_{10}	1.972	0.009
Mo_1-O_4	1.959	0.010	Mo_2-O_{11}	1.976	0.010
Mo_1-O_5	1.664	0.012	Mo_2-O_{12}	1.662	0.010
Mo_1-O_6	2.420	0.009	Mo_2-O_{13}	2.470	0.009
Mo_1-O_7	1.933	0.010	Mo_2-O_7	1.921	0.010
O_1-O_2	1.525	0.016	O_8-O_9	1.498	0.017
O_3-O_4	1.455	0.013	$O_{10}-O_{11}$	1.453	0.019

	Angle (°)	e.s.d. (°)		Angle (°)	e.s.d. (°)
$O_1-Mo_1-O_2$	45.4	0.4	$O_8-Mo_2-O_9$	45.1	0.5
$O_1-Mo_1-O_3$	132.4	0.4	$O_8-Mo_2-O_{10}$	129.8	0.5
$O_1-Mo_1-O_4$	155.8	0.5	$O_8-Mo_2-O_{11}$	154.4	0.4
$O_1-Mo_1-O_5$	100.6	0.5	$O_8-Mo_2-O_{12}$	102.7	0.5
$O_1-Mo_1-O_6$	78.3	0.5	$O_8-Mo_2-O_{13}$	78.9	0.4
$O_1-Mo_1-O_7$	89.2	0.5	$O_8-Mo_2-O_7$	88.0	0.5
$O_2-Mo_1-O_3$	88.8	0.4	$O_9-Mo_2-O_{10}$	87.9	0.5
$O_2-Mo_1-O_4$	129.4	0.5	$O_9-Mo_2-O_{11}$	129.0	0.5
$O_2-Mo_1-O_5$	101.1	0.4	$O_9-Mo_2-O_{12}$	99.3	0.6
$O_2-Mo_1-O_6$	77.5	0.4	$O_9-Mo_2-O_{13}$	81.8	0.4
$O_2-Mo_1-O_7$	132.7	0.5	$O_9-Mo_2-O_7$	132.0	0.5

Table 4. Continued.

$O_3-Mo_1-O_4$	43.7	0.4	$O_{10}-Mo_2-O_{11}$	43.2	0.5
$O_3-Mo_1-O_5$	100.5	0.5	$O_{10}-Mo_2-O_{12}$	101.1	0.4
$O_3-Mo_1-O_6$	79.8	0.4	$O_{10}-Mo_2-O_{13}$	77.8	0.4
$O_3-Mo_1-O_7$	128.1	0.4	$O_{10}-Mo_2-O_7$	129.4	0.4
$O_4-Mo_1-O_5$	103.6	0.5	$O_{11}-Mo_2-O_{12}$	102.9	0.5
$O_4-Mo_1-O_6$	77.6	0.4	$O_{11}-Mo_2-O_{13}$	75.5	0.4
$O_4-Mo_1-O_7$	85.1	0.4	$O_{11}-Mo_2-O_7$	87.5	0.4
$O_5-Mo_1-O_6$	178.6	0.4	$O_{12}-Mo_2-O_{13}$	178.5	0.4
$O_5-Mo_1-O_7$	99.6	0.5	$O_{12}-Mo_2-O_7$	101.0	0.5
$O_6-Mo_1-O_7$	81.2	0.4	$O_{13}-Mo_2-O_7$	79.0	0.4
$Mo_1-O_7-Mo_2$	136.1	0.4			

Table 5. Hydrogen bond distances in $K_2Mo_2O_{11}\cdot 4H_2O$. Values less than 3.1 Å are included. The first atom symbols refer to the coordinates given in Table 3. After the second atom symbols stand within brackets the unit cell translations in the *a*, *b*, and *c* directions and after that the number of the symmetry operation performed on the original coordinates of the atom as given in the *International Tables for X-ray Crystallography* Vol. I.

O_2	$-O_6$ (1 1 1)2	2.93 Å
	$-O_{15}$(0 0 0)1	2.97
O_3	$-O_{13}$(1 1 2)2	2.98
	$-O_{15}$(0 0 1)1	3.04
O_9	$-O_{13}$(1 1 1)2	3.00
O_{10}	$-O_{13}$(1 2 1)2	2.82
O_{11}	$-O_{13}$(1 2 1)2	2.75
O_{12}	$-O_{15}$(0 0 0)1	3.03
O_{14}	$-O_{15}$(0 0 0)1	2.85
	$-O_{15}$(1 1 1)2	2.83

Table 6. Cation environment in $K_2Mo_2O_{11}\cdot 4H_2O$. Distances less than 3.5 Å are included. Symbols are explained in Table 5.

K_1	$-O_3$ (0 0 0)1	2.94 Å
	$-O_4$ (0 0 0)1	2.87
	$-O_4$ (0 0 1)2	2.94
	$-O_5$ (0 0 0)1	2.74
	$-O_7$ (1 0 1)2	2.71
	$-O_8$ (1 0 1)2	2.72
	$-O_9$ (1 0 1)2	3.00
	$-O_{10}$(1 1 1)2	2.72
	$-O_{11}$(0 −1 0)1	3.12
	$-O_{11}$(1 1 1)2	3.34
	$-O_{13}$(1 1 1)2	2.89
K_2	$-O_1$ (0 0 0)1	2.73
	$-O_1$ (2 1 1)2	3.11
	$-O_2$ (1 1 0)2	3.42
	$-O_2$ (1 1 1)2	2.99
	$-O_3$ (1 1 1)2	2.99
	$-O_5$ (1 1 1)2	2.98
	$-O_6$ (2 1 1)2	2.76
	$-O_{12}$(0 0 0)1	2.83
	$-O_{14}$(0 0 0)1	2.83
	$-O_{15}$(1 1 0)2	2.80

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of $K_2Mo_2O_{11}\cdot 4H_2O$ consist of dinuclear complex ions, potassium ions, and lattice water molecules as can be seen from the projection of the unit cell in Fig. 1 which also shows how the complex ion is built. The mean configuration about the molybdenum atoms is illustrated in Fig. 2.

As can be seen from Fig. 1 the anions are dinuclear with a nonlinear oxygen bridge, the Mo—O—Mo angle being 136.1°. The molybdenum atoms are 7-coordinated by a pentagonal bipyramidal arrangement of oxygen atoms, the two bipyramidal pentagons sharing a corner to form the dinuclear anion. The equatorial planes within the anion make an angle of 66.9° with one another (*cf.* 62.1° found for the $[W_2O_{11}(H_2O)_2]^{2-}$ ion using the parameters given in Ref. 14). The five equatorial oxygen atoms in each pyramid are about equally remote from the central molybdenum atom (1.92—1.98 Å), and the bond distances imply that these Mo—O bonds are single bonds. The $Mo_1—O_5$ and $Mo_2—O_{12}$ bonds are 1.66 Å and are thus significantly shorter indicating considerable double bond character, while the $Mo_1—O_8$ and $Mo_2—O_{13}$ distances

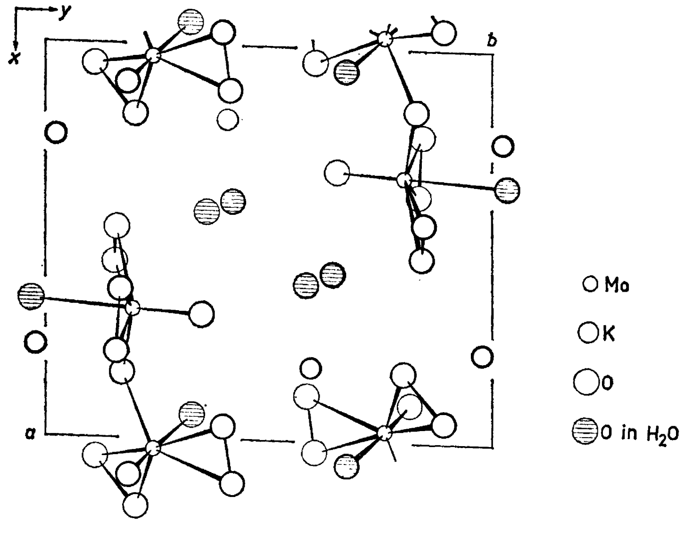

Fig. 1. The crystal structure of $K_2Mo_2O_{11}\cdot 4H_2O$ viewed along the *c*-direction.

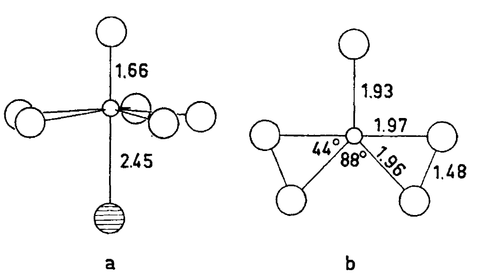

Fig. 2. The mean configuration about the molybdenum atoms viewed a) parallel to the equatorial plane and b) perpendicular to the equatorial plane.

are significantly longer, *i.e.* 2.42 Å and 2.47 Å, respectively. These long bonds are interpreted as being rather weak bonds between molybdenum atoms and water molecules. The same conclusion can be drawn for the "tetraperoxoditungstate" ion.[14] The rational name for the anion is thus μ-oxido-bis(oxidodiperoxidoaquomolybdenum(VI)).

Within the limits of experimental error all five equatorial oxygen atoms lie in a plane within each of the two bipyramids. The equations of these planes as determined by the least-squares method using the procedure of Schoemaker, Waser, Marsch and Bergman,[23] are

A $$0.1202x - 0.8153y + 0.5665z + 0.6094 = 0$$

and

B $$-0.0295x + 0.9996y - 0.0004z - 0.8285 = 0$$

expressed in fractional coordinates and referred to the original axes. The distances of selected atoms from the planes *A* and *B* are:

A—O_1	0.02 Å	**B**—O_8	0.06 Å
O_2	0.01	O_9	0.05
O_3	0.05	O_{10}	0.00
O_4	0.06	O_{11}	0.03
O_7	0.03	O_7	0.04
Mo_1	0.38	Mo_2	0.39

The molybdenum atoms are thus displaced about 0.4 Å from the equatorial planes in the direction of the apical double-bonded oxygen atoms. The effect of this is that the distances from the apically situated oxygen atoms to the respective planes are almost equal, being 2.04 Å and 2.04 Å for **A**—O_5 and **A**—O_6 and 2.05 Å and 2.08 Å for **B**—O_{12} and **B**—O_{13}, respectively. The same phenomenon has been reported for oxidodiperoxido-1,10-phenanthrolinechromium(VI), where chromium is displaced 0.27 Å from the equatorial plane.

The average O—O distance in the $[Mo_2O_{11}(H_2O)_2]^{2-}$ ion is 1.48 Å which does not differ significantly from the value of 1.49 Å found in simple peroxides. For the peroxidochromates, however, distances between 1.40 Å and 1.47 Å have been reported while 1.50 Å was obtained for the $[W_2O_{11}(H_2O)_2]^{2-}$ ion. As the standard deviations for the O—O bonds in all investigations of the transition metal peroxides are 0.01—0.03 Å, it is impossible to decide whether or not the bonds are actually different even if it is claimed that the O—O bonds in the peroxidochromates are shorter than those in the simple peroxides.[12]

Crystals of $K_2Mo_2O_{11}\cdot 4H_2O$ and $K_2W_2O_{11}\cdot 4H_2O$ were not supposed to be isomorphous since the powder photographs were rather different. Furthermore, while some simple oxido-salts of molybdenum and tungsten are isostructural, many oxido-compounds of these two elements of similar formula-type have different crystal structures. This structure analysis has confirmed that the structures of the stoichiometrically similar molybdenum and tungsten peroxido compounds are not isomorphous. (Despite the similar cell volumes, the unit cells differ considerably, and, furthermore, the distance between the symmetry-related O_{12} atoms is 5.10 Å in $K_2Mo_2O_{11}\cdot 4H_2O$ but 3.75 Å in

$K_2W_2O_{11}\cdot 4H_2O$.) The reason why this should be so cannot be answered at present. Although the crystals of the two compounds are not isostructural, they show, however, a certain degree of similarity. They are built up of isomorphous anions (bond distances and angles in the anions $[Mo_2O_{11}(H_2O)_2]^{2-}$ and $[W_2O_{11}(H_2O)_2]^{2-}$ are almost identical), potassium ions, and water molecules, and the relationship between the two structures can be seen more easily if the unit cell of $K_2W_2O_{11}\cdot 4H_2O$ is transformed to a new cell by the matrix

$$\begin{bmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & \bar{1} \end{bmatrix}$$

If the origins, the *ab*-planes and the directions of the *a*-axes of the two unit cells are made to coincide with one another, the rows of anions closest to the origin in the *a*-direction in both cells coincide almost completely (to within 0.1—0.2 Å). To make the next rows of anions coincide the unit cells have to be displaced about 2.7 Å relative to each other in the *a*-direction.

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REFERENCES

1. Wilson, I. A. *Arkiv Kemi, Mineral. Geol.* **B 5** (1942) No. 5.
2. Stomberg, R. and Brosset, C. *Acta Chem. Scand.* **14** (1960) 441.
3. Stomberg, R. *Acta Chem. Scand.* **17** (1963) 1563.
4. Stomberg, R. *Arkiv Kemi* **23** (1965) 401.
5. Mc Laren, E. M. and Helmholz, L. *J. Chem. Phys.* **63** (1959) 1279.
6. Stomberg, R. *Arkiv Kemi* **22** (1964) 49.
7. Stomberg, R. *Arkiv Kemi* **24** (1965) 47.
8. Stomberg, R. *Arkiv Kemi* **22** (1964) 29.
9. Pedersen, B. F. and Pedersen, B. *Acta Chem. Scand.* **18** (1964) 1454.
10. Stomberg, R. *Arkiv Kemi* **24** (1965) 111.
11. Stomberg, R. and Ainalem, I. B. *To be published.*
12. Stomberg, R. *Arkiv Kemi* **24** (1965) 283.
13. Vannerberg, N. G. and Brosset, C. *Acta Cryst.* **16** (1963) 247.
14. Einstein, F. W. B. and Penfold, B. R. *Acta Cryst.* **17** (1964) 1127.
15. Grandjean, D. and Weiss, R. *Compt. Rend.* **261** (2) (1965) 448.
16. Connor, J. A. and Ebsworth, E. A. V. *Advan. Inorg. Chem. Radiochem.* **6** (1964) 279.
17. Vogel, A. I. *Quantitative Inorganic Analysis*, Longmans, London 1961.
18. Abrahamsson, S. and Larsson, K. *Arkiv Kemi* **24** (1965) 383.
19. Abrahamsson, S. *Arkiv Kemi* **24** (1965) 389.
20. Aleby, S. *Arkiv Kemi* **24** (1965) 395.
21. Larsson, K. *Arkiv Kemi* **23** (1964) 17.
22. Abrahamsson, S., Nilsson, B. and Selin, K. *Arkiv Kemi* **24** (1965) 407.
23. Schoemaker, V., Waser, J., Marsch, R. E. and Bergman, G. *Acta Cryst.* **12** (1959) 600.

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