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Multicomponent Polyanions

IV. The Molecular and Crystal Structure of $Na_6Mo_5P_2O_{23}(H_2O)_{13}$, a Compound Containing Sodium-coordinated Pentamolybdodiphosphate Anions

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The crystal structure of $Na_6Mo_5P_2O_{23}(H_2O)_{13}$ has been determined from three-dimensional X-ray data, collected by the equi-inclination Weissenberg method using Cu$K\alpha$-radiation. There are four formula units in the orthorhombic unit cell, and the cell dimensions are $a = 15.423$ Å, $b = 16.896$ Å, and $c = 12.394$ Å. The space group is *Pbcn*. The structure is built up of sodium coordinated $Mo_5P_2O_{23}^{6-}$-groups. These groups are coupled together through bonds O – Na – O and O – Na – H_2O – Na – O. Final refinement by least squares analysis with isotropic temperature factors, using 2681 (visually estimated) independent reflections, resulted in an R-value of 9.4 %.

In a recent emf-investigation [1] aqueous equilibria

$$p\mathrm{H}^+ + q\mathrm{MoO_4}^{2-} + r\mathrm{HPO_4}^{2-} \rightleftharpoons (\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q(\mathrm{HPO_4}^{2-})_r$$

were studied at 25°C in a 3.0 M $NaClO_4$-medium. It was found that with excess phosphate ions the main complexes were: $(H^+)_8(MoO_4^{2-})_5(HPO_4^{2-})_2^{6-}$, $(H^+)_9(MoO_4^{2-})_5(HPO_4^{2-})_2^{5-}$, and $(H^+)_{10}(MoO_4^{2-})_5(HPO_4^{2-})_2^{4-}$ (removal of five water gives, respectively, $Mo_5P_2O_{23}^{6-}$, $HMo_5P_2O_{23}^{5-}$, and $H_2Mo_5P_2O_{23}^{4-}$), with the formation constants log $\beta_{8,5,2} = 61.97$, log $\beta_{9,5,2} = 67.07$, and log $\beta_{10,5,2} = 70.86$. In close connection with this equilibrium investigation, attempts were made to obtain crystals, which could contain the complexes. The crystallization experiments were carried out by slow evaporation of equilibrium solutions of known compositions at 25°C. Hitherto the phases given in Table 1 have been prepared and characterized.

Complete structure determination has been carried out for the phases (1) and (4). The phase (4) investigation will be published in a forthcoming paper and structure (1) is the topic of the present report. Intensity data are being collected for phases (2) and (3).

Table 1. Crystal data for sodium-pentamolybdo-diphosphates under investigation.

Formula	System	Cell-dimensions	Space group	Density (g/cm³)	Z
(1) $Na_6Mo_5P_2O_{23}(H_2O)_{13}$	Orthorhombic	$a=15.423$ $b=16.896$ $c=12.394$	*Pbcn*	2.62	4
(2) $Na_6Mo_5P_2O_{23}(H_2O)_x$	»	$a=10.7$ $b=15.8$ $c=19.9$	$P2_12_12_1$	2.63	4
(3) $Na_5HMo_5P_2O_{23}(H_2O)_{7-9}$	Triclinic	$a=10.45$ $b=18.65$ $c=8.32$ $\alpha=89.8$ $\beta=108.7$ $\gamma=101.3$		2.66	2
(4) $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$	Monoclinic	$a=26.388$ $b=13.661$ $c=8.041$ $\beta=91.37°$	$P2_1/n$	2.71	4

EXPERIMENTAL

In a typical preparation of the crystals a solution with the composition $[MoO_4^{2-}]_{tot}=2.04$ M, $[H_2PO_4^-]_{tot}=0.82$ M, and $[HClO_4]_{tot}=2.442$ M was placed for crystallization at room temperature. After a few days (sometimes weeks) colourless ball-shaped crystals were obtained. Sometimes the crystals grew to a radius of about 0.4 cm. They are not stable in air, and during the X-ray exposures they were enclosed together with part of the mother liquid in a sealed glass capillary.

The contents of Na, P, and Mo in the crystals were determined by analysis (carried out at the Department of Analytical Chemistry, Umeå University). (Found: Na 10.8; P 4.7; Mo 38.0. Calc. for $Na_6Mo_5P_2O_{23}(H_2O)_{13}$: Na 10.8; P 4.8; Mo 37.4.) Water analysis was performed with the Karl-Fisher method and gave 18.0 % H_2O (calc. 18.3). In some experiments we also measured the loss of water in a thermo-balance analysis. The results found were in very good agreement with those mentioned above. Here we also observed that the loss of water occurred in three steps at the following temperatures: 95°C (loss of 7 H_2O); 143°C (another 4), and 330°C (the last 2).

From rotation photographs (around [001], [010], and [100]) and the corresponding Weissenberg photographs (zero, first and second layer lines) taken with Cu$K\alpha$-radiation it was concluded that the crystals are orthorhombic. The dimensions were refined from powder data. Systematic extinctions gave the unique space group *Pbcn*. Precession photographs were taken to confirm the space group.

Equi-inclination Weissenberg films, $hk0-hk11$, were taken with Cu$K\alpha$-radiation. The intensities of 2681 independent reflections were estimated visually with the multiple film technique. No correction was applied for absorption as the crystal was spherical with a radius of 0.06 mm.

The computer programs used were the same as those given in Ref. 2.

CRYSTAL DATA

$Na_6Mo_5P_2O_{23}(H_2O)_{13}$ F.W. = 1281.8
Orthorhombic *Pbcn* $Z=4$
$a=15.423$ (1) Å
$b=16.896$ (1) Å $d_{calc}=2.64$ g/cm³
$c=12.394$ (1) Å $d_{exp}=2.62$ g/cm³ (flotation method)
$V=3229.7$ Å³

STRUCTURE DETERMINATION AND REFINEMENT

From a three-dimensional Patterson synthesis the approximate coordinates for the Mo-atoms were readily found. With 20 Mo in the unit cell at least one must be in a special four-fold position and this provided a starting point.

The remaining Mo-atoms were found to be in two general eightfold positions. A refinement at this stage gave an R-value of 37 %.

A three-dimensional Fourier synthesis was performed with the known Mo-atoms. This gave the coordinates of P and oxygens bound to P and Mo. The R-value decreased to 28 %.

In a second electron density calculation the remaining atoms, Na and water oxygens, appeared.

By using the least squares method with block-diagonal matrix approximation, the various atomic parameters were refined and the resulting R-value was 9.4 %

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

The scattering factors for Mo^+, P, O^-, and Na^+ were used [3] and account was taken of the real part of the dispersion correction. The weighting scheme used was that proposed by Cruickshank: $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ with the values for the constants $a = 20$, $c = 0.004$, and $d = 0.0001$.

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given in Table 2, and a comparison between the observed and calculated structure factors is reported in Table 3.

Table 2. Fractional atomic coordinates and isotropic thermal parameters. The standard deviations in parentheses are for the last decimal place given. For the oxygen atoms indexed O(ij) or OP(ij) the (ij) means that the atom is bonded to the molybdenum atoms i and j. When the oxygen atoms are denoted Aq(ij) they are water oxygens and (ij) means that the atom is bonded to the sodium atoms i and j.

	x	y	z	B
Mo1	0.50000(0)	0.55505(8)	0.25000(0)	0.69(2)
Mo2	0.54308(6)	0.67007(6)	0.03499(8)	0.76(1)
Mo3	0.54863(6)	0.85956(6)	0.11588(9)	1.00(2)
P	0.6195 (2)	0.7243 (2)	0.2909 (2)	0.76(4)
O(1)	0.5880 (6)	0.4931 (6)	0.2355 (8)	1.6 (2)
O1(2)	0.6360 (6)	0.6195 (6)	−0.0029 (8)	1.7 (2)
O2(2)	0.4818 (7)	0.6740 (6)	−0.0809 (9)	1.8 (2)
O1(3)	0.6261 (7)	0.9307 (6)	0.0935 (9)	2.2 (2)
O2(3)	0.4682 (7)	0.8898 (7)	0.0283 (9)	2.2 (2)
O(12)	0.4776 (6)	0.5866 (5)	0.1023 (7)	1.2 (1)
O(23)	0.5930 (6)	0.7735 (6)	0.0294 (8)	1.5 (1)
O(33′)	0.5000 (0)	0.8916 (8)	0.2500 (0)	1.5 (2)
OP	0.6956 (6)	0.6951 (5)	0.3540 (7)	1.3 (1)
OP(3)	0.6398 (5)	0.7993 (5)	0.2276 (7)	1.1 (1)
OP(12)	0.5909 (5)	0.6579 (5)	0.2119 (7)	0.9 (1)
OP(23)	0.4582 (5)	0.7447 (5)	0.1322 (7)	1.0 (1)
Aq(2)	0.3842 (8)	0.0317 (8)	0.131 (1)	2.9 (2)
Aq1(12)	0.3310 (7)	0.4544 (6)	0.4977 (9)	2.0 (2)
Aq2(12)	0.2498 (7)	0.4107 (6)	0.1860 (8)	1.9 (2)
Aq1(13)	0.2861 (7)	0.2675 (6)	0.4355 (9)	2.3 (2)
Aq2(13)	0.3572 (7)	0.2519 (7)	0.2166 (9)	2.3 (2)
Aq(23)	0.2879 (7)	0.0801 (6)	0.3608 (9)	2.2 (2)
Aq(33′)	0.0000 (0)	0.624 (1)	0.2500 (0)	2.8 (3)
Na1	0.3469 (4)	0.3732 (4)	0.3335 (5)	2.6 (1)
Na2	0.2362 (5)	0.0582 (4)	0.1790 (5)	3.0 (1)
Na3	0.3971 (4)	0.1828 (4)	0.3766 (5)	2.3 (1)

Table 3. Observed and calculated structure factors.

0 K 0			9 K 0			16 55 -50			17 37 -39			12 K 1			12 184 177		
4 226 -316			19 34 25			15 39 -34			15 52 32			17 28 -24			8 36 -35		
6 87 104			17 99 -82			14 51 45			14 52 46			16 57 -52			6 241 268		
8 77 -88			15 197 187			13 184 175			13 35 30			14 141 135			4 208 -237		
10 287 -312			13 92 90			12 133 123			12 75 66			12 122 124					
12 66 66			11 287 -311			11 155 149			11 129 -140			8 126 -128			1 K 2		
14 49 25			9 77 69			10 142 -145			9 104 100			6 42 36			21 131 -122		
16 77 62			5 108 -99			9 81 -72			7 219 240			5 102 103			20 26 -23		
18 97 99			3 40 38			8 20 7			6 42 -42			4 80 -83			19 61 -50		
20 48 -47			1 74 69			7 46 -40			5 350 -435			3 37 -36			18 40 -25		
						6 120 -124			4 165 -168			2 87 -87			16 29 22		
1 K 0			10 K 0			4 49 -58			3 34 -20			1 107 -108			15 163 -148		
21 158 -148			18 108 91			3 136 -147			2 20 -3						14 55 44		
19 153 127			12 93 -82			2 46 -43			1 150 164			13 K 1			13 55 -47		
17 301 279			10 141 134									16 95 96			12 28 21		
15 245 -242			8 154 -152			2 K 1			7 K 1			15 86 88			11 264 253		
13 48 46			6 206 -203			21 30 -23			20 124 143			14 38 -41			10 52 -47		
11 194 179			4 270 302			20 86 -74			19 66 -57			13 28 26			9 143 -144		
9 258 -276			2 147 152			19 33 31			18 63 54			12 74 -66			8 53 54		
7 161 -177			0 201 -225			16 161 147			17 73 66			11 30 17			7 133 145		
5 219 271						15 55 44			16 228 -200			10 76 80			6 103 106		
			11 K 0			11 105 -94			15 42 31			9 85 80			5 78 80		
2 K 0			17 154 -159			10 95 86			14 132 124			7 89 -97			4 179 -191		
18 92 94			15 265 261			9 101 103			13 39 40			6 68 -69			3 256 -304		
12 104 100			11 221 -209			8 49 46			12 82 80			5 120 -138			2 73 -68		
10 245 -243			7 64 64			7 55 61			11 29 -8			4 35 -13					
8 28 20			5 139 -137			6 128 -150			10 138 -151			3 102 -102			2 K 2		
6 274 373			3 117 117			5 177 -196			9 144 150			1 117 127			21 93 -85		
4 245 -351			1 118 121			4 101 -104			8 25 17						20 133 -118		
2 132 -160						3 70 77			7 52 -54			14 K 1			19 64 53		
			12 K 0			1 157 164			6 137 136			14 80 71			17 79 60		
3 K 0			16 69 67						5 235 -252			12 74 77			16 76 -68		
21 95 -88			12 119 -113			3 K 1			4 81 -74			11 75 77			15 118 -103		
19 96 79			10 73 63			21 30 -31			3 59 -46			9 56 -59			14 95 -90		
17 155 138			8 81 -72			20 135 115			2 22 -16			8 53 -44			13 84 -68		
15 140 -128			6 174 -186			19 39 31			1 62 58			7 93 -86			12 194 190		
11 264 279			4 141 141			18 62 49						5 148 165			11 90 76		
9 328 -392			2 261 280			17 35 -29			8 K 1			4 173 -131			10 62 59		
7 230 -252			0 243 -273			16 223 -201			19 45 51			3 110 -121			8 70 -67		
5 176 209						15 80 76			14 75 69			2 35 -31			7 85 88		
3 106 114			13 K 0			14 39 37			13 43 46			1 140 -159			6 188 195		
1 55 45			15 190 204			13 69 50			12 194 204						4 188 -197		
			13 45 -38			12 176 169			11 121 -122			15 K 1			3 163 169		
4 K 0			11 191 -193			11 129 127			10 109 -111			14 72 -78			2 214 -235		
20 85 60			7 66 55			10 190 -216			8 88 -90			13 64 71			1 110 -94		
18 53 47			5 167 -178			9 159 -169			7 160 166			12 105 -102			0 192 178		
16 60 47			3 142 139			8 76 79			6 55 -60			10 137 144					
14 38 -31			1 130 136			7 39 36			5 219 -228			9 47 38			3 K 2		
12 106 99						6 86 94			4 101 -94			7 96 -53			21 110 -108		
10 155 -156			14 K 0			5 34 -29			3 22 -8			6 81 -77			19 83 -67		
8 165 -178			14 43 43			4 169 -193			2 124 -129			5 65 -74			18 65 -47		
6 47 -32			12 123 -123			3 216 -268			1 191 202			4 85 80			16 53 41		
4 240 -293			6 160 -176			1 174 -180						3 34 -34			15 148 -143		
2 155 179			4 92 87						9 K 1						14 105 82		
0 175 178			2 130 135			4 K 1			19 89 -86			16 K 1			13 102 97		
			0 125 -134			21 74 -71			17 110 99			12 61 61			11 164 155		
5 K 0						20 77 -66			16 134 -126			11 83 94			10 123 -116		
17 101 87			15 K 0			19 25 33			15 82 69			10 54 -53			8 69 -66		
13 86 -80			13 44 -39			18 38 29			14 58 53			9 33 -40			7 124 127		
9 252 -271			11 109 -107			15 48 40			13 86 79			7 101 -100			6 263 293		
7 203 -213			9 60 51			14 164 160			12 79 78			6 89 -96			5 116 122		
5 153 156			7 65 -63			12 50 45			10 54 -54			5 172 192			4 305 -340		
3 24 -20			3 65 63			11 155 -150			9 79 79			4 48 -50			3 255 -278		
1 174 190						10 105 103			6 32 28			3 34 -41			2 83 -70		
			16 K 0			9 128 130			5 244 -258			1 148 -162			1 86 -67		
6 K 0			12 96 -110			8 36 -33			4 109 -111						0 340 392		
20 53 47			10 44 -42			7 194 205			3 39 -41			17 K 1					
18 65 53			8 36 -36			6 124 -121			2 42 33			10 152 179			4 K 2		
16 97 90			6 91 -94			5 218 -252			1 53 49			9 48 -46			20 100 -94		
14 81 -71			2 69 72			4 218 -256						8 37 -39			19 91 79		
12 123 -115						3 69 66			10 K 1			6 83 -89			17 127 109		
10 38 -30			17 K 0			2 73 -66			18 31 29			5 81 -77			16 110 -96		
8 70 -61			7 158 -173			1 297 390			16 87 -76			4 91 94			15 155 -132		
6 130 -126			3 93 90						14 110 109			3 46 -55			14 34 -30		
4 57 -50						5 K 1			12 136 135			2 45 -39			13 72 -65		
2 98 89			18 K 0			20 138 135			10 63 -58			1 79 -81			12 143 139		
0 43 40			4 34 -40			19 27 22			9 30 24						11 241 246		
			0 126 129			18 50 41			8 58 -56			18 K 1			10 81 77		
7 K 0						17 38 -26			7 99 107			8 30 32			9 118 -114		
15 117 96			19 K 0			16 221 -215			5 76 -76			7 94 -103			8 98 99		
11 211 -219			5 49 43			15 138 130			3 52 43			6 103 -121			7 187 -185		
5 169 -178			3 63 67			14 105 106			2 243 -270			5 129 137			6 218 226		
1 140 141						13 34 25						4 58 -63			5 133 133		
			0 K 1			12 165 162			11 K 1			1 129 -138			4 67 61		
8 K 0			20 128 -104			10 226 -233			17 71 61						3 146 138		
18 141 117			16 231 210			8 52 55			15 89 88			19 K 1			2 335 -366		
16 48 39			12 48 37			7 150 -149			9 60 62			4 57 59			1 67 -65		
12 105 -103			10 181 187			6 162 170			8 76 68			3 53 -60			0 84 77		
10 70 67			8 327 -430			5 108 -118			6 63 -57			2 68 -71					
8 135 -133			4 112 -120			4 75 -72			5 155 -168			1 41 -44			5 K 2		
6 291 -328						3 159 -168			3 44 -41						19 61 -52		
4 176 179			1 K 1			2 69 65			2 55 56			0 K 2			18 63 -41		
2 170 170			21 27 -22						1 116 116			20 149 -139			16 60 -51		
0 97 88			20 53 46			6 K 1						16 82 -70			15 118 -115		
			17 48 48			19 45 49						14 172 -164			14 98 91		

Table 3. Continued.

13 128 120	11 41 37	6 96 -101
11 49 45	10 107 110	4 119 130
10 171 -165	9 33 -29	2 57 54
9 124 122	8 129 128	1 52 -53
8 86 88	7 68 66	0 169 -190
7 67 63	6 164 -162	
6 293 310	5 64 65	18 K 2
5 143 140	4 111 107	8 22 25
4 165 -165	3 27 -20	7 54 61
3 164 -152	2 41 -39	6 71 72
2 178 -172	1 57 -53	5 31 -32
1 22 18	0 263 -268	2 49 -43
0 229 225		0 31 -36
	11 K 2	
6 K 2	17 121 -123	19 K 2
20 34 -31	16 25 19	4 50 56
19 76 63	15 76 70	3 47 -49
18 49 -37	14 40 -42	2 26 31
17 205 170	12 72 71	1 21 -28
16 71 -68	11 76 -70	0 85 -94
15 193 -181	9 173 190	
13 53 -29	8 84 -94	0 K 3
12 86 79	5 137 -141	20 63 -50
11 194 192	3 117 121	18 38 -29
10 76 73	1 136 -145	16 93 77
9 50 -47	0 34 -33	14 146 -135
8 41 35		12 348 -376
7 179 -182	12 K 2	10 214 238
6 90 83	16 58 -55	8 62 59
5 173 196	15 47 41	6 89 -88
4 24 -20	14 85 76	4 112 127
3 25 22	12 105 -103	
2 81 71	11 77 -76	1 K 3
1 163 -163	10 152 100	21 78 76
0 58 -51	9 31 -37	20 22 21
	8 109 111	19 57 46
7 K 2	7 77 85	18 41 33
20 32 -31	6 130 -133	17 113 -90
19 38 -35	5 44 -39	15 130 -109
18 31 -11	4 142 156	14 65 -59
17 104 -93	2 56 -55	13 82 -74
16 51 -45	1 45 43	12 42 -34
15 40 35	0 236 -277	11 97 87
14 109 96		10 79 75
13 34 -33	13 K 2	9 162 -163
12 53 -40	15 47 44	8 62 63
11 63 61	14 100 -90	7 118 118
10 161 -169	11 64 -57	6 33 -30
9 129 127	10 78 69	5 267 315
8 92 84	9 233 234	4 105 -102
7 106 99	8 47 -49	3 62 -59
6 160 162	7 31 -29	2 153 163
4 193 -204	5 53 -51	
3 37 -34	4 123 137	2 K 3
2 21 11	3 47 41	21 53 -55
1 24 -27	2 35 -34	20 68 -53
0 237 242	1 123 -129	19 150 135
	0 127 -140	18 64 -47
8 K 2		17 53 -47
19 37 24	14 K 2	16 127 114
18 133 -127	14 64 64	15 49 -49
17 131 118	13 51 46	14 179 -173
15 91 -80	12 36 -38	13 82 73
13 77 -69	11 126 -133	12 195 -186
11 136 146	10 83 85	10 116 114
10 124 127	9 44 43	9 100 -109
9 72 -75	8 123 120	8 89 85
8 135 131	7 98 105	7 17 -7
7 110 -102	6 76 -79	6 66 -72
5 108 82	5 29 -33	5 66 -59
4 26 -22	4 50 50	4 109 108
3 45 -45	3 104 -123	3 103 -104
2 48 34	1 68 72	2 189 200
0 325 -364	0 192 -209	1 190 207
9 K 2	15 K 2	3 K 3
19 73 -79	10 87 93	20 33 -17
18 21 -13	9 138 157	19 28 19
17 147 -132	8 38 -36	18 28 21
16 28 25	7 34 42	17 34 -18
15 88 81	6 126 -121	15 126 -124
14 36 25	4 47 158	14 89 93
13 44 -47	1 64 -69	13 64 -58
12 39 -37	0 83 -91	12 40 -33
11 34 25		10 36 29
10 52 -41	16 K 2	9 79 -71
9 196 208	11 135 -142	8 59 63
7 115 112	10 48 49	7 45 43
6 176 181	9 28 31	6 134 -140
5 145 -145	8 77 81	5 234 267
4 124 -130	7 92 96	4 65 -69
3 39 35	6 41 43	3 55 63
2 57 -50	5 42 -41	2 281 299
1 170 -172	4 28 -23	1 252 -246
0 32 31	3 69 -75	
	1 54 54	4 K 3
10 K 2	0 155 -155	20 24 -14
18 144 -157		19 137 126
15 43 -43	17 K 2	17 131 -115
14 62 55	10 56 59	16 27 26
13 51 -48	9 49 55	15 78 -81
12 64 -61	7 89 91	14 192 -181

13 213 210	5 84 -78	18 K 3
12 49 -39	4 97 -96	7 73 -83
11 103 -98	3 80 80	6 25 23
10 48 41	2 229 248	5 40 39
9 99 -95	1 305 340	4 39 37
8 140 141		3 25 20
7 147 155	10 K 3	2 84 91
6 70 67	18 30 27	1 46 -44
5 108 108	17 56 -51	
4 48 46	16 207 -204	19 K 3
3 224 -225	14 34 30	3 29 34
2 88 75	13 33 25	2 73 -88
1 61 47	11 69 -64	1 45 -52
	10 118 -136	
5 K 3	7 60 53	0 K 4
19 24 18	6 191 211	20 39 -38
16 60 -55	1 96 94	18 359 336
15 81 -71		14 184 -172
14 43 47	11 K 3	12 48 42
13 97 -84	16 42 -41	10 44 33
12 61 -59	15 50 -53	8 159 -155
11 69 -70	14 51 48	6 23 -29
10 135 -141	13 43 -35	4 204 212
9 26 18	11 163 -182	
8 228 257	9 98 107	1 K 4
6 25 -7	8 40 -37	20 33 -32
5 193 202	7 117 127	18 53 43
4 133 -133	6 67 67	17 50 50
3 122 117	5 136 -148	16 30 -22
2 208 204	3 144 156	15 68 50
1 54 -50	1 206 233	13 104 97
		12 58 51
6 K 3	12 K 3	11 176 -155
20 53 51	16 144 -159	10 64 -60
19 80 74	15 42 38	9 293 -305
18 39 29	12 72 61	8 67 -72
17 69 -55	10 171 -186	7 199 199
16 89 -76	8 75 76	6 108 -103
15 87 -82	6 129 151	5 112 112
14 81 -79	3 79 -84	4 116 117
13 207 221	2 32 23	3 176 -196
11 128 -139	1 54 51	2 98 -98
10 76 -76		
9 155 -160	13 K 3	2 K 4
8 65 67	15 59 -55	20 42 -38
7 218 228	13 45 -38	18 269 239
6 115 115	12 38 36	17 73 59
5 76 71	11 118 -126	16 45 38
4 126 120	9 37 35	15 101 -100
3 53 -52	8 68 -67	14 143 -134
2 31 28	7 105 113	12 67 60
1 44 34	5 78 -85	11 59 68
	4 103 108	10 58 52
7 K 3	3 125 142	9 35 -26
18 37 29	2 125 -144	8 251 -255
17 30 -26	1 136 157	7 106 -111
15 38 -31		6 29 -26
14 74 69	14 K 3	5 168 157
13 110 -112	13 97 -101	4 59 62
12 32 25	10 118 -117	3 89 -91
11 30 -18	9 72 73	2 116 110
10 112 -118	8 57 66	1 35 -34
9 59 56	7 56 -61	0 132 125
8 118 126	6 92 101	
7 141 143	4 32 31	3 K 4
6 155 -150	3 69 82	20 88 -88
5 54 -48	2 51 58	19 45 42
4 263 -279	1 36 -33	18 64 61
3 73 74		17 39 19
2 276 309	15 K 3	16 44 -36
1 150 146	13 26 -25	15 100 93
	12 70 76	14 27 -27
8 K 3	11 46 -47	13 28 25
19 89 93	8 81 -87	12 71 66
18 63 51	7 47 50	11 115 -107
17 67 -61	5 36 35	10 64 -62
16 186 -173	4 128 129	9 182 -202
15 61 -51	3 51 52	8 22 -19
13 141 143	2 129 -141	7 112 110
12 28 -30	1 79 86	6 124 126
11 62 -61		5 107 101
10 108 -116	16 K 3	3 185 -184
7 62 63	11 68 67	2 186 -186
6 206 219	10 31 -31	1 64 65
5 125 -126	9 63 74	0 101 92
4 72 74	8 29 31	
3 43 -33	7 82 -85	4 K 4
1 26 19	6 61 69	18 145 120
	4 29 39	17 118 97
9 K 3	3 84 85	16 68 68
18 40 38	2 79 88	15 113 -111
17 30 -32	1 62 -56	14 119 -113
16 72 -70		13 34 -26
15 23 -24	17 K 3	11 113 111
14 43 37	10 45 48	10 55 -45
13 73 -74	9 20 -26	9 98 -107
12 56 -52	8 94 -109	8 193 -202
11 121 -133	6 57 63	7 66 70
9 121 118	5 117 132	6 50 51
8 68 72	4 81 87	5 43 40
7 119 124	2 99 -115	4 46 -49
6 25 -26		3 133 -124

Table 3. Continued.

2	179	172		10 K 4		6	89	-96	10	88	94		10 K 5		5	90	-106
1	16	11	17	59	62	4	40	40	9	156	-155	17	18	20	4	89	95
0	26	-12	16	47	41	3	21	-21	8	143	-146	15	47	-49	2	79	-90
			15	77	-71	2	57	56	7	137	145	14	125	122			
	5 K 4		14	198	201	1	84	94	6	122	-129	13	83	74		18 K 5	
20	39	-48	13	37	43	0	93	-88	5	89	88	12	62	58	5	50	-60
19	65	62	12	141	-153				4	29	19	10	47	-49	3	58	67
18	39	44	10	168	-195		18 K 4		3	58	-56	9	29	-24	2	77	-89
17	50	40	8	161	180	6	59	-71	2	149	-136	8	92	102	1	46	-42
15	34	28	7	28	-22	5	25	-28	1	22	-10	7	37	34			
14	57	-55	6	85	-80	4	64	70				6	102	-109		0 K 6	
12	75	77	5	92	93	3	46	45		5 K 5		5	58	-52	20	80	-77
11	110	-103	4	74	-80	2	49	52	19	40	-36	4	239	-256	16	34	-39
10	81	-77	3	104	-111	1	19	-15	18	24	-15	2	175	197	14	103	-95
9	136	-144	2	103	104				17	44	34				12	23	14
8	92	-91	1	73	69		19 K 4		16	56	37		11 K 5		10	84	77
7	91	-85	0	118	131	1	90	123	15	65	56	16	20	-18	8	38	24
6	181	195				0	36	-47	14	58	59	14	31	-24	6	22	6
5	56	-65		11 K 4					13	42	32	13	185	196	4	41	-49
4	178	-181	17	59	63		0 K 5		12	104	-97	12	55	47	2	34	-39
3	129	120	15	26	24	20	45	-56	11	69	70	10	52	-53			
2	80	-72	13	101	-90	16	95	91	10	47	37	9	100	-115		1 K 6	
1	40	-28	11	37	28	14	24	3	8	126	119	8	41	39	19	74	-68
0	266	289	7	173	-208	12	147	148	7	29	-26	7	95	100	18	45	38
			6	40	42	10	101	97	6	115	-117	5	152	-157	17	82	-57
	6 K 4		5	28	23	8	278	-288	5	55	-51	4	61	64	14	82	-76
18	35	21	4	55	42	6	168	160	4	214	-218	3	75	-78	12	43	32
17	128	113	3	262	293	4	83	90	3	213	-202	1	37	21	10	37	27
16	77	74	2	104	-101	2	205	-231	2	342	338				9	54	53
15	100	-100	1	70	-59				1	89	80		12 K 5		8	68	-46
12	105	-105	0	76	71		1 K 5					15	35	27	7	152	153
11	136	139				20	18	-18		6 K 5		14	122	126	6	111	114
10	125	-127		12 K 4		19	175	-172	19	145	149	13	34	-33	5	39	-36
9	179	-184	16	59	65	17	188	162	18	36	-31	12	33	29	4	62	63
8	90	-92	14	139	142	16	53	37	17	124	-117	11	45	-41	3	163	-204
7	37	36	12	118	-116	15	137	130	16	62	53	10	54	-54	2	29	-31
6	54	-55	10	132	-148	14	50	33	15	33	-21	9	28	25	1	18	-14
5	70	59	9	32	35	13	95	-87	14	90	84	8	105	113	0	39	-56
4	56	-51	8	60	63	11	95	87	13	149	160	7	37	29			
3	148	-141	7	35	37	10	43	-31	12	78	76	6	69	-81		2 K 6	
2	105	94	6	68	-70	9	147	144	11	47	-43	5	75	-86	19	27	-20
1	143	142	4	31	-33	8	67	59	9	156	-158	4	185	-225	18	79	-68
0	200	193	3	36	-38	7	238	-249	8	37	-33	3	71	74	15	38	21
			2	124	136	6	161	-167	7	66	66	2	79	84	14	78	-69
	7 K 4		0	145	170	5	22	-20	6	111	-112	1	54	53	13	39	28
19	72	70				4	15	-12	5	171	172				12	93	86
18	30	30		13 K 4		3	97	-107	4	146	-140		13 K 5		11	94	90
17	105	100	15	37	43	2	78	80	3	117	-113	14	34	39	10	103	91
14	79	-84	13	64	-62	1	195	-202	2	64	-57	13	161	178	9	193	-198
13	60	-58	12	40	-35				1	17	-11	12	61	64	8	96	91
12	117	124	10	40	45		2 K 5					11	34	-29	7	210	214
11	76	-74	7	127	-150	20	37	-40		7 K 5		10	43	-44	6	71	70
10	79	-72	6	45	-42	19	40	30	19	34	36	9	53	-57	5	27	-20
9	49	-48	5	39	-42	18	28	-20	18	36	36	8	92	-96	4	104	103
8	67	-66	3	197	231	17	35	-17	17	23	-24	7	73	81	3	217	-249
7	192	-219	2	49	46	16	78	73	15	47	39	6	50	54	2	165	-196
6	270	297	1	51	-50	15	102	-95	14	51	48	5	91	-98	1	127	170
4	112	-100	0	82	-80	14	41	31	13	154	167	4	33	37	0	241	-321
3	207	223				13	180	171	12	97	-97	3	71	-78			
2	118	-115		14 K 4		12	159	139	11	27	-25	2	80	-93		3 K 6	
1	40	-37	14	49	55	11	31	-31	10	23	18	1	42	35	19	59	-57
0	68	58	13	34	-35	10	146	146	9	65	-64				18	137	126
			12	99	-98	9	136	-129	8	72	66		14 K 5		17	84	-66
	8 K 4		11	38	-29	8	196	-201	6	40	-31	13	85	-91	16	37	-29
19	34	37	10	75	-69	7	54	51	5	112	-107	12	43	41	15	73	-64
18	51	-48	9	59	-59	6	120	-120	4	204	-215	11	22	-20	14	170	-158
17	73	65	5	75	-80	5	49	-50	3	102	-106	10	50	-56	13	91	81
16	66	60	3	73	85	4	69	64	2	242	244	9	79	78	12	184	190
15	120	-112	2	49	54	3	146	-144	1	76	-77	8	35	33	11	61	53
14	139	143	1	24	-21	2	261	-312				7	46	-46	10	36	31
12	151	-162	0	89	96	1	38	36		8 K 5		6	53	-53	9	83	86
11	122	127							17	56	-48	5	59	-56	8	167	-172
10	115	-122		15 K 4			3 K 5		15	60	-48	4	139	-162	7	139	138
9	112	-122	12	49	-45	20	21	-21	14	93	86	2	53	56	6	60	48
8	116	111	11	78	-86	19	104	-103	13	116	125	1	100	103	5	41	41
7	59	59	10	34	26	17	131	113	12	45	51				4	70	66
6	80	-86	8	37	27	16	64	52	11	29	-25		15 K 5		3	67	-59
5	125	132	7	89	-90	15	120	124	10	43	-43	12	34	38	2	60	64
4	85	-81	6	68	-68	14	29	-22	9	101	-108	9	25	-21	1	162	-187
3	123	-122	5	83	-84	13	72	-67	8	101	114	8	107	-119	0	43	37
2	38	-32	4	63	70	12	95	-92	7	40	41	7	28	25			
1	32	19	3	99	114	11	117	110	6	106	-106	6	92	105		4 K 6	
0	208	217	2	49	50	10	58	-50	5	98	101	5	121	-140	19	25	-18
			1	26	25	9	91	89	4	174	-178	4	45	42	18	52	-46
	9 K 4		0	145	-185	8	223	236	3	76	-71	3	73	-76	16	47	-44
18	59	62				7	171	-174	2	103	93	2	112	-126	13	76	78
17	106	89		16 K 4		6	168	-173	1	23	-24	1	55	51	12	110	106
16	30	-24	11	40	-48	5	80	-83							10	99	89
14	34	-28	9	60	65	3	40	-35		9 K 5			16 K 5		9	171	-184
13	61	-61	8	36	-41	2	254	270	17	49	-46	10	30	-31	8	40	-32
12	112	119	6	92	-94	1	57	-52	14	35	32	9	85	94	7	239	273
11	36	21	5	45	-48				13	170	175	8	29	30	6	34	23
10	74	-81	4	25	28		4 K 5		10	47	-47	7	51	-58	5	41	40
8	74	-74	3	57	56	20	26	-33	9	70	-70	6	58	-59	4	77	76
7	227	-258	2	48	43	19	121	110	8	42	43	4	77	-90	3	333	-363
6	83	82	1	50	-44	17	111	-102	7	53	46	3	46	57	2	55	-42
5	26	25	0	28	32	16	64	50	6	70	-73	1	77	80	1	234	239
4	38	-24				15	108	-96	5	136	-148				0	134	-126
3	245	246		17 K 4		14	41	40	3	95	-95		17 K 5				
2	39	-30	9	28	-34	13	167	169	2	149	154	8	72	-91		5 K 6	
1	30	-25	8	31	32	12	42	28	1	73	-12	7	30	-31	19	35	-33
0	165	164	7	50	-44	11	52	-53				6	49	53	18	218	207

Table 3. Continued.

17	53	-47	0	143	-155	2	166	-207	4	132	131	8	132	141	16	28	23
16	38	-28							3	40	34	7	23	16	15	69	-60
15	37	-22		11 K 6			1 K 7		2	135	132	6	27	22	14	93	79
14	202	-210	15	49	-49	19	174	-192	1	31	23	5	35	34	13	49	34
12	211	231	13	28	-23	18	34	33				4	44	-43	12	75	-66
11	41	39	12	32	27	17	153	132		7 K 7		2	133	153	11	58	57
10	32	25	11	73	70	16	28	-21	17	59	-63	1	56	-61	10	108	-110
9	96	96	10	44	-43	15	64	54	16	26	-22				9	142	-139
8	158	-153	9	102	105	14	50	36	15	109	-99		15 K 7		8	44	35
7	115	106	8	37	37	13	300	-325	14	35	24	9	34	-36	7	81	70
6	42	40	5	26	-5	9	174	165	12	66	65	8	37	42	6	79	-72
5	67	62	4	45	-47	8	101	-104	11	48	-50	7	99	118	5	57	37
4	178	180	3	47	42	7	160	-169	10	77	-74	6	39	-38	4	51	-39
3	34	-25	2	27	26	6	45	46	9	97	-101	3	47	52	3	209	-209
2	193	-182	1	147	-161	5	102	105	8	29	23	2	40	39	2	28	21
1	79	-70	0	27	29	4	29	-23	7	111	109	1	90	100	1	126	124
0	69	49				3	165	238	6	22	-26				0	68	57
				12 K 6		1	29	-33	5	130	131		16 K 7				
	6 K 6		14	56	54				4	58	54	8	54	65		5 K 8	
18	68	-63	13	59	-56		2 K 7		3	97	92	6	47	62	17	39	34
16	33	-26	11	95	94	19	43	48	2	82	-74	4	33	31	16	27	-26
15	77	-74	8	75	79	18	29	-22	1	68	62	2	33	27	14	131	-123
13	121	128	7	62	-59	17	39	-41				1	43	-49	13	36	-32
11	88	-86	3	45	35	16	54	-32		8 K 7					12	161	156
10	62	61	2	44	-44	15	70	69	17	20	13		17 K 7		11	63	-60
9	55	-56	1	24	-17	14	150	-148	15	30	25	3	53	63	10	49	44
8	150	152	0	59	-56	13	61	-46	12	81	-84	2	36	43	9	98	-98
7	110	119				12	26	-16	11	34	-30	1	45	54	8	190	-218
6	110	111		13 K 6		11	45	40	10	47	-47				7	101	-101
5	105	95	14	103	120	10	37	32	9	37	-33		0 K 8		6	124	133
4	28	-20	13	28	-26	9	79	74	8	165	175	18	87	-87	5	58	55
3	379	-379	12	48	-48	8	184	-186	7	67	58	16	108	93	4	19	-10
2	67	-58	11	29	29	7	62	-58	6	50	-47	14	95	84	3	33	27
1	260	266	10	73	-73	6	198	214	5	131	-134	12	118	-120	2	47	-35
0	118	-109	9	104	102	4	274	342	4	61	-52	10	135	-130	1	79	68
			8	103	112	2	149	-197	3	81	75	8	55	45	0	30	21
	7 K 6		6	28	-21	1	19	-19	2	242	253	6	56	54			
18	155	165	5	41	-39							4	106	-117		6 K 8	
17	31	-29	4	47	-52		3 K 7			9 K 7		2	89	94	17	35	38
16	25	-13	3	26	10	19	105	-117	16	27	-22				16	29	23
14	186	-179	1	71	-72	18	76	23	15	131	-123		1 K 8		15	92	-83
12	176	185	0	53	64	17	56	55	13	135	129	18	66	57	14	26	-15
11	46	42				16	49	-40	11	84	-88	17	105	98	13	48	34
10	60	65		14 K 6		15	45	33	9	134	-152	16	30	-31	12	47	-45
9	151	168	11	23	27	13	191	-201	7	133	148	14	47	-33	11	71	78
8	212	-233	10	54	51	12	62	63	6	43	44	13	68	-59	10	58	-59
7	60	55	9	96	101	11	27	-22	5	97	100	12	41	38	9	153	-165
6	40	27	8	81	92	10	31	-19	4	65	-53	11	57	42	8	109	-113
5	26	-22	7	113	-127	9	96	91	2	47	37	10	23	-17	7	175	197
4	104	100	6	34	32	8	91	-88	1	27	-24	9	40	-34	6	123	-132
3	35	-34	4	42	-44	7	53	-54				8	43	33	5	22	7
2	157	-151	3	126	148	6	84	89		10 K 7		7	202	-205	4	30	26
1	51	-45	2	39	-34	5	150	164	13	23	-20	6	43	-30	3	197	-188
0	130	122	1	76	-82	4	45	-38	12	136	-136	5	34	-24	2	119	107
			0	99	-109	3	119	117	10	88	-91	4	25	19	1	111	91
	8 K 6					2	19	-19	9	29	30	3	191	307	0	116	100
17	34	32		15 K 6		1	24	-17	8	176	217	2	56	-71			
16	60	-45	11	52	56				6	34	34	1	48	-58		7 K 8	
15	65	-65	10	35	-35		4 K 7		4	127	-123	0	21	28	17	23	21
14	50	41	9	96	106	18	33	-32	3	24	-21				15	55	55
13	71	68	8	113	125	17	40	33	2	263	298		2 K 8		14	121	-117
11	54	-51	7	37	36	15	37	32	1	75	66	18	38	-32	13	29	26
10	38	36	6	44	-43	14	60	-59				17	32	31	12	153	163
9	82	-82	4	38	-43	13	69	-61		11 K 7		16	76	63	11	106	-114
8	135	152	3	39	-39	12	46	-38	15	117	-140	15	37	-33	9	105	-120
7	106	112	1	56	-60	11	31	16	14	38	33	14	119	104	8	140	-152
6	49	35	0	68	72	9	33	21	13	125	136	13	37	28	6	179	140
4	55	-54				8	136	-136	12	56	-50	12	93	-84	5	58	-63
3	203	-192		16 K 6		7	35	33	11	95	-102	11	36	-32	4	72	-65
2	31	-28	9	102	115	6	104	98	9	123	-137	10	161	-163	3	27	-19
1	145	130	8	44	45	5	34	-32	8	41	-38	9	43	-33	2	35	27
0	111	-109	7	131	-148	4	229	233	7	158	181	8	77	61	1	149	142
			6	20	27	3	70	70	6	24	17	7	21	14	0	95	78
	9 K 6		5	33	-33	2	82	-78	5	77	84	6	78	-73			
17	37	-41	3	168	205	1	79	74	4	24	-19	5	32	24		8 K 8	
15	25	-18	2	39	-40				3	37	31	4	79	-85	16	49	49
14	120	-115	1	85	-99		5 K 7		2	74	72	3	136	-164	15	65	-50
12	93	102	0	78	-83	16	61	-46	1	24	16	2	56	70	14	108	-96
11	90	91				15	38	-26				1	79	110	13	57	47
10	26	26		17 K 6		13	82	-73		12 K 7		0	191	308	11	51	45
9	98	97	7	35	42	12	75	72	13	23	14				10	25	22
8	118	-137	6	30	-29	10	61	-57	12	116	-117		3 K 8		9	81	-92
6	91	91	4	48	-56	9	25	20	10	82	-81	18	118	123	8	119	-124
4	24	-10	3	23	-23	8	30	19	8	148	168	17	83	77	7	82	82
3	43	45	2	50	51	6	50	37	5	58	59	16	39	-38	6	43	-37
1	147	-147	0	33	-28	5	136	135	4	102	-112	14	110	-93	5	45	38
0	26	-31				4	75	70	3	37	-32	13	28	-5	4	60	63
				18 K 6		3	42	38	2	231	285	12	83	80	3	203	-201
	10 K 6		3	137	179	2	81	-68				9	55	-37	2	91	81
16	64	-51	2	22	-28	1	70	57		13 K 7		8	100	-99	1	172	170
15	28	-28	1	85	-110				13	81	95	7	191	-205	0	40	-42
14	64	59	0	62	-73		6 K 7		11	64	-59	6	32	24			
11	73	78				17	55	47	9	91	-88	5	34	30		9 K 8	
10	54	50		0 K 7		14	105	-92	8	41	47	4	69	62	15	98	105
9	69	-79	18	25	-21	13	26	-17	7	134	150	3	148	153	14	64	-59
8	75	76	16	60	-40	12	109	-111	6	39	-42	2	123	-134	13	32	27
7	52	46	14	128	-116	11	48	-53	4	32	-24	1	18	12	12	100	99
6	45	44	12	67	56	9	41	35	1	89	92	0	66	80	11	107	-109
5	45	-40	10	95	87	8	96	92							10	26	-14
3	76	-71	8	248	-264	7	49	44		14 K 7			4 K 8		9	89	-90
2	95	-97	6	119	120	6	21	8	10	56	-66	18	23	22	8	44	-41
1	44	34	4	248	332	5	117	-121	9	61	-67	17	22	30	7	107	116

Table 3. Continued.

6 93 95	1 K 9	1 78 64	6 26 -32	8 26 19	5 48 -41
5 69 -71	17 58 62		5 60 64	7 61 63	2 69 -80
3 69 -69	16 40 -28	7 K 9	4 115 -136	6 156 155	1 22 28
2 72 -66	15 135 112	16 34 -31	3 76 -73	5 74 -66	0 65 -61
1 103 102	14 43 -31	15 63 58	2 20 19	4 166 -172	
0 95 95	13 54 -43	13 67 57	1 24 -26	3 46 33	13 K 10
	12 44 35	12 70 60		2 70 -54	9 41 -39
10 K 8	11 133 143	11 31 21	15 K 9	1 67 -54	7 97 112
15 51 -53	10 29 -16	10 40 41	6 55 -67	0 264 298	6 68 -80
14 89 -95	9 23 -22	8 127 -158	5 77 -92		5 22 19
13 57 50	8 21 -14	7 40 -33	4 76 -84	6 K 10	4 88 100
12 39 30	7 144 -144	6 90 93	3 53 -58	15 120 -137	3 110 -129
10 58 53	6 24 -20	5 98 -102	2 122 147	14 30 -29	0 56 -60
8 161 -189	5 90 86	4 84 77	1 41 41	13 35 -33	
7 31 -23	4 15 18	3 110 -102		12 56 53	14 K 10
6 51 -62	3 41 -48	2 185 -191	16 K 9	11 137 141	6 60 79
5 60 60	2 19 -23	1 52 48	3 63 -76	10 74 69	5 40 -41
4 75 82	1 159 -218		1 23 10	9 73 -63	2 56 -67
3 89 -91		8 K 9		8 68 46	1 31 32
2 102 111	2 K 9	15 35 34	0 K 10	7 78 -87	0 48 -62
1 74 71	17 87 85	14 105 103	16 81 -72	6 30 23	
0 75 21	16 172 168	13 107 -105	14 142 120	5 113 118	15 K 10
	15 31 20	12 70 64	12 67 -54	4 45 39	3 56 -76
11 K 8	14 25 17	11 57 52	8 148 150	3 79 -63	2 33 39
14 37 33	13 118 -96	10 27 -21	6 57 -51	2 38 -30	1 31 -35
13 45 49	12 40 24	9 90 87	4 52 -52	0 104 -107	0 90 -130
12 27 20	10 165 158	8 40 -37	2 32 -34		
11 139 -138	9 115 110	7 61 -65		7 K 10	0 K 11
9 95 -97	8 166 -168	5 82 -79	1 K 10	15 29 -35	14 163 -175
7 39 37	7 79 -69	4 154 -162	15 59 -47	14 35 32	12 165 -147
6 23 -11	6 136 -138	3 75 20	14 25 19	13 28 20	10 107 103
3 54 -52	5 102 -108	2 22 -11	13 30 -16	12 31 27	8 62 56
2 31 -29	4 57 48	1 60 52	12 46 34	11 31 23	6 92 -88
1 149 172	3 87 95		11 50 39	10 106 -104	4 138 169
0 43 42	2 85 -97	9 K 9	9 184 188	9 87 89	2 40 54
	1 53 71	14 39 -43	8 73 -70	7 87 83	
12 K 8		13 104 106	7 87 -76	6 141 149	1 K 11
9 26 25	3 K 9	12 40 35	6 83 75	5 52 43	15 110 -121
8 114 -125	17 71 75	11 46 -42	5 38 -29	4 112 -111	13 36 -29
7 47 -53	16 58 -49	10 30 29	4 61 -68	3 130 -121	12 25 15
6 48 -48	15 93 71	8 26 -23	3 68 78	2 71 -63	11 65 53
5 40 -36	14 21 -20	7 38 39	2 15 15	1 19 -12	10 77 69
4 109 125	13 125 118	6 20 -11	1 97 -134	0 130 126	9 110 -118
3 71 72	12 122 128	5 129 -144	0 62 91		8 57 -52
2 49 48	11 58 -57	4 85 92		8 K 10	7 23 17
1 28 -25	9 71 -65	3 56 -51	2 K 10	14 52 -47	6 17 -6
	7 135 -136	2 104 -102	16 43 -41	12 88 95	5 225 262
13 K 8	6 31 16	1 136 143	15 88 -80	11 104 112	4 24 -20
12 54 -67	5 28 3		14 114 99	10 105 101	3 18 17
11 82 -91	4 70 61	10 K 9	13 71 -13	9 62 -58	2 34 -35
9 67 -75	3 115 -108	14 124 160	12 39 -32	7 70 -73	1 191 -237
8 38 46	2 140 -158	13 28 -30	11 118 121	6 22 6	
7 23 25	1 149 -199	12 65 70	10 53 53	5 82 78	2 K 11
6 42 -45		10 75 -65	9 99 -102	4 43 46	15 15 8
5 25 14	4 K 9	9 25 23	8 130 129	3 50 -42	14 121 -128
4 24 -14	17 50 52	8 23 14	7 22 15	2 112 -115	13 27 -29
3 44 -42	16 107 104	6 40 -30	5 23 13	1 20 -24	12 173 -166
2 28 22	15 93 82	5 26 21	4 56 -50		11 38 36
1 108 115	14 36 -24	4 138 -153	3 83 98	9 K 10	10 146 144
0 31 -21	13 160 -141	3 40 40	2 54 -61	13 67 69	9 29 -23
	12 84 71	1 26 -27	1 22 -18	12 24 20	8 38 33
14 K 8	11 23 -14		0 68 -87	10 39 -32	7 77 -71
9 57 58	10 57 48	11 K 9		9 44 46	6 66 -58
8 82 -91	9 144 144	13 111 149	3 K 10	8 62 -62	5 60 55
7 47 -44	8 29 -23	12 18 11	14 32 23	7 105 113	4 109 108
6 48 -49	7 37 -30	11 45 -53	13 62 -31	6 85 88	2 65 69
5 78 -77	6 131 -113	9 29 30	12 57 49	5 32 29	1 62 -57
3 119 123	5 114 -103	8 43 40	11 109 103	4 77 -74	
2 63 65	4 69 51	7 56 60	10 71 -68	3 164 -191	3 K 11
1 72 -79	3 107 96	6 22 -18	9 121 123	1 38 24	15 42 -43
0 36 39	2 115 -112	5 189 -215	8 198 227	0 50 45	14 61 -46
	1 16 -5	4 28 -15	5 49 -42		13 94 -84
15 K 8		3 53 -63	4 128 -123	10 K 10	12 54 -52
8 68 84	5 K 9	1 98 107	3 56 44	12 94 110	11 45 29
7 24 -19	16 71 -65		2 106 -114	11 37 37	10 126 119
6 79 -88	15 74 70	12 K 9	1 113 -129	10 68 64	9 41 -38
4 31 -31	13 23 20	12 70 89	0 140 170	9 56 -57	8 59 -52
3 21 -13	12 74 63	10 108 -112		8 37 -23	7 41 -39
2 76 72	11 49 42	9 45 -46	4 K 10	7 22 20	5 204 217
1 68 74	10 37 -27	8 70 65	16 34 -28	6 75 76	4 102 99
0 56 -56	8 139 -139	7 37 30	15 123 -123	5 25 -15	2 69 -61
	7 109 -117	6 23 -6	14 31 27	4 28 21	1 83 -92
16 K 8	6 200 215	5 27 29	13 25 -23	2 94 -100	
5 60 -68	5 44 -37	4 143 -140	12 24 15	1 29 17	4 K 11
4 24 -30	4 117 103	3 34 -30	11 167 161	0 88 -89	15 12 -10
3 126 149	3 40 -36	2 47 38	10 79 76		14 79 -80
2 38 39	2 218 -222	1 108 -102	9 69 -65	11 K 10	13 68 -61
1 77 -80	1 141 -137		8 87 86	11 32 31	12 114 -113
0 54 63		13 K 9	7 48 -41	9 47 -36	11 63 63
	6 K 9	8 69 72	6 55 47	8 20 -20	10 89 77
17 K 8	16 35 33	7 58 53	5 87 77	7 123 139	9 36 39
0 63 -79	15 97 93	6 37 -40	4 57 -45	6 35 27	7 83 -85
	14 64 60	5 159 -178	3 16 -9	5 29 17	6 44 38
0 K 9	13 165 -154	4 84 -88	2 29 17	3 159 -163	5 117 119
16 144 146	12 102 101	3 31 -34	0 153 -169	0 59 -51	4 70 60
14 22 -2	9 113 122	2 99 97			3 21 -13
12 52 -53	8 51 -48	1 81 76	5 K 10	12 K 10	2 94 97
10 249 257	7 52 -47		14 54 45	10 51 55	1 100 -95
8 166 -151	6 92 -88	14 K 9	12 54 51	9 30 25	
6 134 -139	5 67 -59	9 52 -66	11 103 93	8 54 -53	5 K 11
4 53 44	4 57 -68	8 55 49	10 127 -138	7 60 56	14 48 -43
2 105 -149	2 65 -56	7 22 21	9 46 53	6 83 83	13 95 -96

Table 3. Continued.

12	49	-45	9	24	15	6	26	-29	1	101	-107	9	22	20	12	K	11		
11	25	-18	8	26	26	4	68	61				7	58	-61	8	21	-24		
10	108	98	7	97	-99	3	80	81		9	K 11	6	122	140	7	22	17		
8	60	-53	6	93	105	2	85	-82	11	73	-90	5	47	42	6	145	175		
7	22	20	5	104	114	1	87	90	10	61	67	4	47	46	5	21	-18		
6	50	-45	4	54	51				9	75	80	3	25	-25	2	19	4		
5	121	117	3	53	-37		8 K 11		8	51	-49	1	34	-20	1	34	32		
4	116	104	2	21	14	13	45	-59	7	99	105								
3	25	22	1	92	-95	12	45	44	6	21	-20		11 K 11		13	K	11		
2	102	-90				11	44	40	5	132	-128	10	38	52	5	25	-24		
1	27	26		7 K 11		10	116	-130	4	46	37	9	55	69	3	62	52		
			13	54	-58	9	38	35	3	136	150	7	84	85	1	123	152		
	6 K 11		12	40	-40	8	39	33	2	55	-45	6	22	21					
14	37	-43	11	90	-87	7	89	-91	1	122	131	5	89	-93	14	K	11		
13	57	-53	10	70	57	6	94	99				3	91	93	2	35	43		
12	26	-22	9	85	74	5	80	80		10 K 11		2	30	-30					
11	78	75	8	51	-40	4	99	93	11	17	17	1	168	188					
10	49	-44	7	59	58	2	28	-34	10	100	-125								

Finally a difference Fourier synthesis was calculated in which no abnormalities could be detected. No attempt was made to locate hydrogen atoms.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up of $Mo_5P_2O_{23}^{6-}$-groups linked together by sodium-oxygen octahedra. The $Mo_5P_2O_{23}^{6-}$ groups are oriented with their pentagon of Mo-atoms approximately parallel to the *yz*-plane and connected through Na^+-ions (O – Na1 – O) forming two symmetry related zig-zag chains directed along the *c*-axis (see Fig. 1).

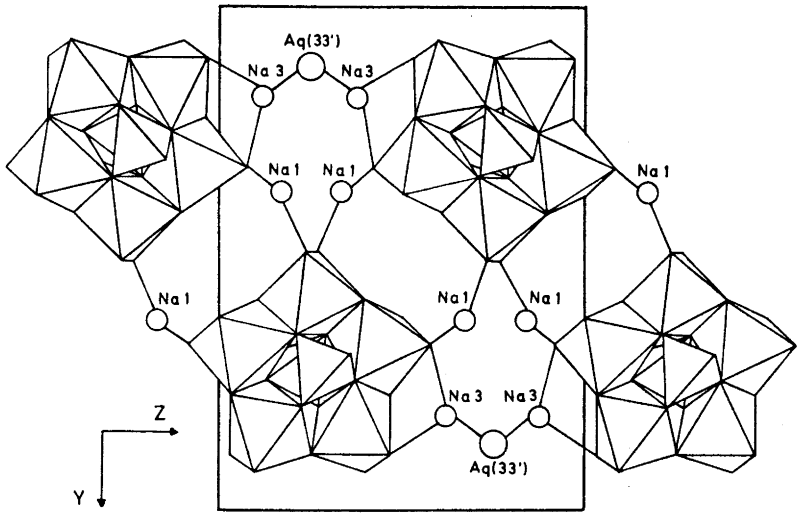

Fig. 1. The zig-zag arrangement of $Mo_5P_2O_{23}^{6-}$-groups in the *yz*-plane and the two types of Na^+-linking between the groups.

The connection within the chains is strengthened by bridges O – Na3 – H_2O – Na3 – O. The symmetry related chains are then coupled together through bridges O – Na2 – H_2O – Na3 – O as shown in Fig. 2.

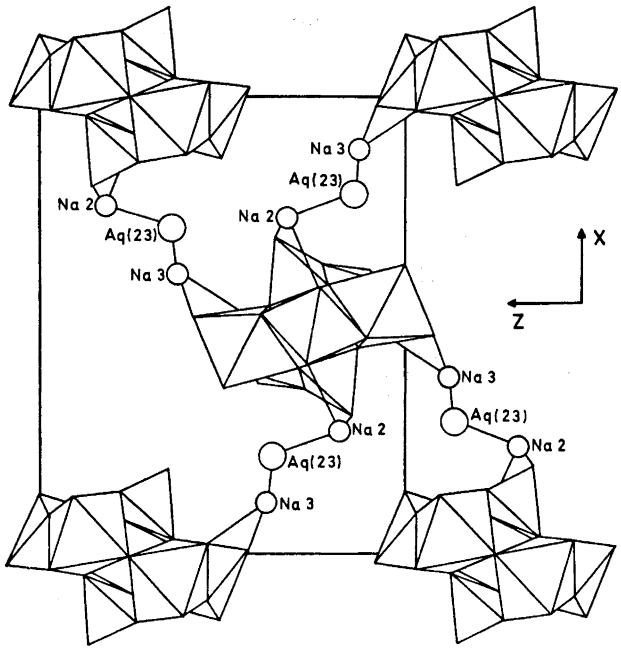

Fig. 2. The Na^+-coupling between symmetry related zig-zag chains.

The $Mo_5P_2O_{23}^{6-}$-group. In this group, five MoO_6-octahedra are coupled together forming a ring. The octahedra are joined together by sharing edges except for in one contact where only a corner is shared. Two PO_4-tetrahedra are attached to the ring, one above and the other below, each having three oxygen atoms in common with the ring. This configuration implies that each MoO_6-octahedron has four shared and two unshared oxygens and each PO_4-tetrahedron has one oxygen unshared. In this way the group becomes ball-shaped with the twelve unshared oxygen atoms protruding from the ball. The symmetry in the group is a twofold rotation axis. The arrangement in the group is shown in Fig. 3.

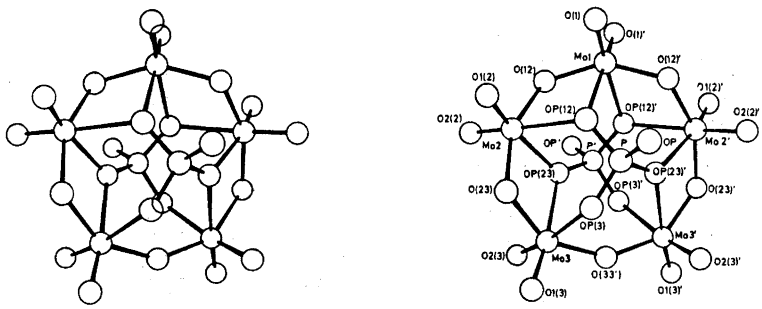

Fig. 3. Stereoscopic view of the $Mo_5P_2O_{23}^{6-}$-group.

Table 4. Distances (Å) and angles (degrees) within the $Mo_5P_2O_{23}^{6-}$-group. The numbering of the atoms is in accordance with that shown in Table 2, with primes indicating atoms in a symmetry related position. The estimated standard deviations are given in parentheses and refer to the last decimal place given.

		Mo, P	
Mo1 – Mo2	3.364(1)	P – Mo1	3.439(3)
Mo2 – Mo3	3.356(1)	P – Mo2	3.505(3)
Mo3 – Mo3′	3.647(2)	P – Mo3	3.335(3)
Mo1 – Mo3	5.459(2)	P – Mo2′	3.432(3)
Mo2 – Mo2′	5.493(2)	P – Mo3′	3.644(3)
Mo2 – Mo3′	5.566(1)	P – P′	3.822(6)
Mo2′ – Mo1 – Mo2	109.44(5)		
Mo1 – Mo2 – Mo3	108.63(4)		
Mo2 – Mo3 – Mo3′	105.18(3)		
		MoO_6-octahedra	
Mo1 – O(1)	1.72(1)	O(1) – Mo1 – O(12)	102.0(4)
Mo1 – O(12)	1.937(9)	O(1) – Mo1 – OP(12)	87.5(4)
Mo1 – OP(12)	2.281(8)	O(1) – Mo1 – O(1)′	105.2(5)
O(1) – O(1)′	2.74(2)	O(1) – Mo1 – O(12)′	97.2(4)
O(1) – O(12)	2.85(1)	O(12) – Mo1 – OP(12)	72.8(3)
O(1) – O(12)′	2.75(1)	O(12) – Mo1 – OP(12)′	82.9(3)
O(1) – OP(12)	2.80(1)	OP(12) – Mo1 – OP(12)′	80.8(3)
OP(12) – O(12)	2.52(1)		
OP(12) – O(12)′	2.81(1)		
OP(12) – OP(12)′	2.96(2)		
Mo2 – O(23)	1.91(1)	O(23) – Mo2 – O1(2)	96.2(4)
Mo2 – O(12)	1.925(9)	O(23) – Mo2 – O2(2)	99.0(4)
Mo2 – O1(2)	1.73(1)	O(23) – Mo2 – OP(23)	74.5(4)
Mo2 – O2(2)	1.72(1)	O(23) – Mo2 – OP(12)	89.3(3)
Mo2 – OP(23)	2.181(9)	O(12) – Mo2 – O1(2)	101.0(4)
Mo2 – OP(12)	2.322(9)	O(12) – Mo2 – O2(2)	95.9(4)
O(23) – O1(2)	2.72(1)	O(12) – Mo2 – OP(23)	82.5(4)
O(23) – O2(2)	2.76(1)	O(12) – Mo2 – OP(12)	72.1(3)
O(23) – OP(23)	2.49(1)	O1(2) – Mo2 – O2(2)	104.3(5)
O(23) – OP(12)	2.99(1)	O1(2) – Mo2 – OP(12)	87.1(4)
O(12) – O1(2)	2.83(1)	O2(2) – Mo2 – OP(23)	96.2(4)
O(12) – O2(2)	2.71(1)	OP(23) – Mo2 – OP(12)	73.8(3)
O(12) – OP(23)	2.72(1)		
O(12) – OP(12)	2.52(1)		
O1(2) – O2(2)	2.73(1)		
O1(2) – OP(12)	2.83(1)		
OP(23) – O2(2)	2.92(1)		
OP(23) – OP(12)	2.71(1)		
Mo3 – O2(3)	1.73 (1)	O2(3) – Mo3 – O(23)	97.4(5)
Mo3 – O(23)	1.932(9)	O2(3) – Mo3 – O(33′)	100.5(4)
Mo3 – O(33′)	1.902(4)	O2(3) – Mo3 – O1(3)	101.0(5)
Mo3 – O1(3)	1.72 (1)	O2(3) – Mo3 – OP(23)	82.8(4)
Mo3 – OP(23)	2.398(9)	O(23) – Mo3 – O1(3)	101.0(5)
Mo3 – OP(3)	2.220(9)	O(23) – Mo3 – OP(23)	69.1(3)
O2(3) – O(23)	2.75(2)	O(23) – Mo3 – OP(3)	77.1(4)
O2(3) – O(33′)	2.79(1)	O(33′) – Mo3 – O1(3)	102.5(5)
O2(3) – O1(3)	2.66(2)	O(33′) – Mo3 – OP(23)	85.8(4)
O2(3) – OP(23)	2.77(1)	O(33′) – Mo3 – OP(3)	80.5(3)
OP(3) – O(23)	2.60(1)	O1(3) – Mo3 – OP(3)	88.9(4)
OP(3) – O(33′)	2.67(1)	OP(23) – Mo3 – OP(3)	86.8(3)

Table 4. Continued.

OP(3) – O1(3)	2.78(1)		
OP(3) – OP(23)	3.18(1)		
O(23) – O1(3)	2.82(1)		
O(23) – OP(23)	2.49(1)		
O(33′) – O1(3)	2.83(1)		
O(33′) – OP(23)	2.95(2)		
		PO_4-tetrahedron	
P – OP	1.495(9)	OP(23) – P – OP	110.8(5)
P – OP(3)	1.524(9)	OP(23) – P – OP(3)	106.6(5)
P – OP(12)	1.553(9)	OP(23) – P – OP(12)	109.0(5)
P – OP(23)	1.570(9)	OP – P – OP(3)	112.5(5)
OP(23) – OP	2.52(1)	OP – P – OP(12)	108.3(5)
OP(23) – OP(3)	2.48(1)	OP(3) – P – OP(12)	109.6(5)
OP(23) – OP(12)	2.54(1)		
OP – OP(3)	2.51(1)		
OP – OP(12)	2.47(1)		
OP(3) – OP(12)	2.51(1)		

Distances and angles between the Mo-atoms in the group are collected in Table 4. It can be seen that when the MoO_6-octahedra share edges the Mo – Mo distances are 3.364 Å (Mo1 – Mo2) and 3.356 Å (Mo2 – Mo3) and when the octahedra only share a corner the distance increases to 3.647 Å (Mo3 – Mo3′). These distances are quite normal. For comparison it may be mentioned that the Mo – Mo distances when octahedra share edges in the structures $Na_3(CrMo_6O_{24}H_6).8H_2O$ [4] and $(NH_4)_6Mo_7O_{24}.4H_2O$ [5] are 3.309 – 3.351 Å and 3.20 – 3.44 Å, respectively. Cross distances within the ring are 5.459, 5.493, and 5.566 Å. These cross distances would be of particular interest as characteristic fingerprints in, for instance, solution X-ray studies.

The sodium coordination around the $Mo_5P_2O_{23}^{6-}$-groups. As mentioned above the $Mo_5P_2O_{23}^{6-}$-group has twelve unshared oxygens. To eight of these, Na^+-ions are coordinated (see Fig. 4). There are three kinds of crystallographically

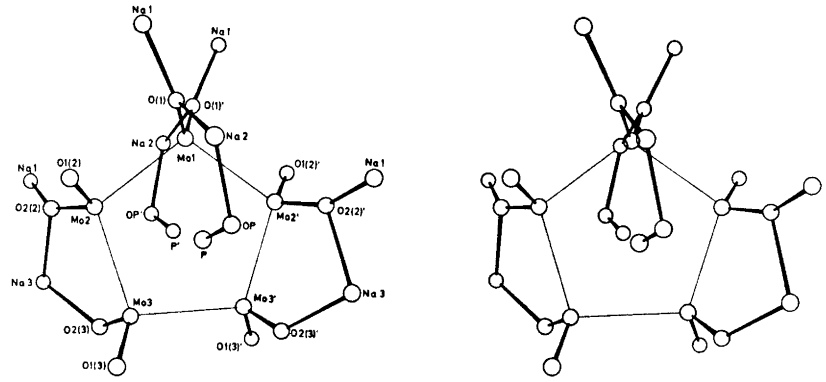

Fig. 4. Stereoscopic view of the sodium coordination to the $Mo_5P_2O_{23}^{6-}$-group (for clarity only the twelve unshared oxygens in the group have been drawn).

different sodium atoms, Na1, Na2, and Na3. Each of these atoms is always coordinated to two $Mo_5P_2O_{23}^{6-}$-oxygens, Na1 to oxygens (the Mo-oxygens O(1) and O2(2)) in two different groups, Na2 and Na3 to oxygens in one and the same group. Na2 binds to one Mo- and one P-oxygen (O(1) and OP) and Na3 to the two Mo-oxygens O2(2) and O2(3). The fact that the sodium ion Na1 is directly bound to oxygens in adjacent $Mo_5P_2O_{23}^{6-}$-groups gives rise to a chain-formation where Na1 acts as a link between the groups. Owing to the symmetry each link consists of a double O – Na1 – O bond (see Fig. 1).

It may be worth mentioning that there are, on average, six Na^+ coordinated per $Mo_5P_2O_{23}^{6-}$, and thus the charge of the group actually has been completely neutralized by the Na^+-ions. If this behaviour is extrapolated to the conditions in aqueous solution one may propose, that also aqueous $Mo_5P_2O_{23}^{6-}$-ions may be thought of as uncharged $Mo_5P_2O_{23}^{6-}$ $(Na^+)_6(H_2O)_x$-molecules, more or less coupled together through the Na^+-ions.

The coupling of the sodium-oxygen octahedra. Besides binding to two $Mo_5P_2O_{23}^{6-}$-oxygens, every sodium also binds to four water oxygens thus forming an octahedral oxygen configuration around each Na^+-ion. The different octahedra [$NaO_6(1)$, $NaO_6(2)$, and $NaO_6(3)$] are more or less coupled together. $NaO_6(1)$ has a surface in common with $NaO_6(3)$ [through the oxygens Aq1(13), Aq2(13), and O2(2)] and an edge in common with $NaO_6(2)$ [through the oxygens Aq2(12) and O(1)]. The remaining oxygen around Na1(Aq1(12)) is shared with a corner of a $NaO_6(2)$ octahedron. $NaO_6(2)$ and $NaO_6(3)$ share a corner through the water oxygen Aq(23). The fourth water-oxygen around Na3, (Aq(33')), is shared with a symmetry-related $NaO_6(3)$ octahedron. This sharing of oxygens between different octahedra binds the $Mo_5P_2O_{23}^{6-}$-groups together forming a three-dimensional network. The smallest unit of coupled NaO_6-octahedra in this network is shown in Fig. 5.

The MoO_6-octahedra. The octahedra are somewhat distorted and the Mo – O distances range from 1.72 Å to 2.40 Å depending on the oxygen coordination. The shortest distances, 1.72 Å, are to oxygens coordinated to only one Mo-atom and the longest, on average 2.30 Å, are to oxygens coordinated

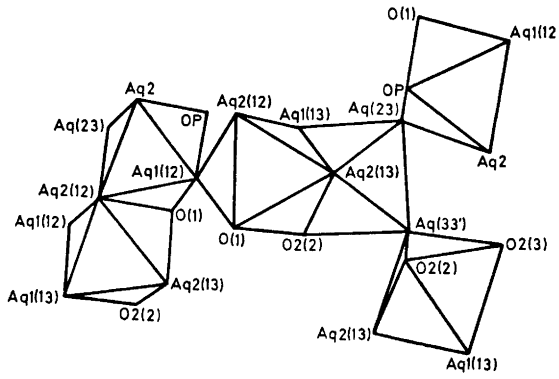

Fig. 5. The smallest unit of coupled NaO_6-octahedra (for clarity the octahedra are idealized).

to one P- and two Mo-atoms. This trend of increasing distances by increasing coordination numbers has been found also in other heteropolyanions containing molybdenum, and a comparison is made in Table 5.

Table 5. Distances (average) Mo—O in relation to the bond number of the oxygen. A comparison with other structures.

Bond number of oxygen	Distances Mo—O (Å)				Coordinating atoms
	$Mo_5P_2O_{23}^{6-}$	$CrMo_6O_{24}H_6^{3-}$	$TeMo_6O_{24}^{6-}$	$CeMo_{12}O_{42}^{8-}$	
1	1.72	1.707	1.714	1.68	Mo
2	1.92	1.939	1.943	1.98	Mo, Mo
3	2.30	2.292	2.299	2.28	Mo, Mo and, respectively, P, Cr, Te or Ce

Table 6. Distances within the NaO_6-octahedra (Å).

Na1 – O2(2)	2.47(1)	O(1) – O2(2)	3.58(1)
Na1 – O(1)	2.42(1)	O(1) – Aq1(12)	3.22(2)
Na1 – Aq1(13)	2.38(1)	O(1) – Aq2(12)	3.02(1)
Na1 – Aq2(13)	2.51(1)	O(1) – Aq2(13)	4.20(2)
Na1 – Aq1(12)	2.47(1)	Aq1(13) – O2(2)	3.18(2)
Na1 – Aq2(12)	2.45(1)	Aq1(13) – Aq1(12)	3.32(2)
		Aq1(13) – Aq2(12)	3.97(1)
		Aq1(13) – Aq2(13)	2.94(2)
		Aq2(13) – O2(2)	3.40(2)
		Aq2(13) – Aq2(12)	3.17(2)
		Aq1(12) – O2(2)	3.33(2)
		Aq1(12) – Aq2(12)	4.13(1)
Na2 – OP	2.43(1)	OP – O(1)	4.07(1)
Na2 – O(1)	2.75(1)	OP – Aq(23)	3.59(1)
Na2 – Aq(23)	2.42(1)	OP – Aq1(12)	3.15(1)
Na2 – Aq1(12)	2.48(1)	OP – Aq(2)	4.01(2)
Na2 – Aq2(12)	2.50(1)	Aq2(12) – O(1)	3.02(1)
Na2 – Aq(2)	2.40(1)	Aq2(12) – Aq(23)	3.64(2)
		Aq2(12) – Aq1(12)	3.49(1)
		Aq2(12) – Aq(2)	2.99(2)
		O(1) – Aq(23)	3.62(1)
		O(1) – Aq1(12)	3.64(2)
		Aq(2) – Aq(23)	3.31(2)
		Aq(2) – Aq1(12)	3.72(2)
Na3 – O2(3)	2.50(1)	O2(3) – Aq(23)	3.51(2)
Na3 – O2(2)	2.80(1)	O2(3) – Aq(33′)	3.49(1)
Na3 – Aq(23)	2.43(1)	O2(3) – O2(2)	3.89(2)
Na3 – Aq1(13)	2.35(1)	O2(3) – Aq1(13)	4.03(2)
Na3 – Aq2(13)	2.38(1)	Aq2(13) – Aq(23)	3.57(2)
Na3 – Aq(33′)	2.44(1)	Aq2(13) – Aq(33′)	3.11(2)
		Aq2(13) – O2(2)	3.40(2)
		Aq2(13) – Aq1(13)	2.94(2)
		O2(2) – Aq(33′)	4.01(2)
		O2(2) – Aq1(13)	3.18(2)
		Aq(23) – Aq(33′)	3.63(1)
		Aq(23) – Aq1(13)	3.30(2)

The NaO_6-octahedra. Distances are collected in Table 6. The distances Na – O range between 2.35 Å and 2.80 Å. There is no significant difference between the distances regardless of whether the oxygens arise from water or from the $Mo_5P_2O_{23}^{6-}$-groups, but two distances are considerably long. These distances are Na2 – O(1) = 2.75 Å and Na3 – O2(2) = 2.80 Å, no other Na – O distance being longer than 2.51 Å. The cause of these long distances is probably that O(1) and O2(2) are in contact also with Na1.

The configuration with four water-oxygens and two "oxide"-oxygens, which characterized the $Na^+ - O$ coordination in the present structure, has also been reported for other structures, for instance in $NaNH_4CrO_4(H_2O)_2$[6] and $Na_3CrMo_6O_{24}H_6(H_2O)_8$.[4] Concerning the distortion of the octahedra it is difficult to find any systematic effects and the octahedra are all far from regular.

The PO_4-tetrahedron. Distances and angles within the group are collected in Table 4. The distances P – O range between 1.50 Å and 1.57 Å and agree well with distances found in other compounds containing phosphate groups. One of the oxygens (OP) in the group is not shared with any Mo-atom and this gives rise to a short distance P – OP (1.50 Å). The O – O distances are 2.47 – 2.54 Å and these are also in agreement with those found in other structures. As can be seen from the distances and angles this group is almost regular.

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