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Multicomponent Polyanions. VIII. On the Crystal Structure of $Na_3H_6Mo_9PO_{34}(H_2O)_x$, a Compound Containing Protonized Enneamolybdomonophosphate Anions

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In $Na_3H_6Mo_9PO_{34}(H_2O)_x$ the Mo, Na, P, and O positions have been determined from three dimensional X-ray diffraction data collected with a PAILRED diffractometer using Mo$K\alpha$-radiation. Chemical analysis indicated an x-value of around 12 – 13. However, none of these water molecules could be detected with certainty in the X-ray analysis. There are two formula units in the hexagonal unit cell and the cell dimensions of the crystal used are $a = 14.248$ Å and $c = 10.83$ Å. Different crystals seem to give slightly different cell dimensions. The space group is $P6_3$. It was found that the structure is built up of $H_6Mo_9PO_{34}^{3-}$ anions coupled together through O – Na – O bonds forming a three-dimensional network. Possible positions for the water molecules are discussed. Refinement by least squares methods using anisotropic vibrational parameters resulted in an R-value of 0.037, based on 1930 independent reflexions.

An equilibrium analysis in the aqueous system $H^+ - MoO_4^{2-} - HPO_4^{2-}$ has indicated that at excess of molybdate ions a series of protonized enneamolybdomonophosphates are formed and the complexes $(H^+)_{14}(MoO_4^{2-})_9(HPO_4^{2-})^{6-}$, $(H^+)_{15}(MoO_4^{2-})_9(HPO_4^{2-})^{5-}$, $(H^+)_{16}(MoO_4^{2-})_9(HPO_4^{2-})^{4-}$ and $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})^{3-}$ have been proposed.[1] By crystallisation of aqueous solutions with compositions lying between the complexes $(H^+)_{16}(MoO_4^{2-})_9(HPO_4^{2-})^{4-}$ and $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})^{3-}$ a crystalline phase of the formula $Na_3H_6Mo_9PO_{34}(H_2O)_x$ was obtained. In the present work the crystal structure of this compound will be presented and discussed especially with reference to $H_6Mo_9PO_{34}^{3-}$, a polyanion group which forms the buildning units in the structure. The mentioned anion corresponds to the complex $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})^{3-}$ found in the equilibrium analysis. Also the Na^+ coordination to the group is of particular interest.

EXPERIMENTAL

In a typical preparation of the crystals, $Na_2MoO_4.2H_2O$ and $NaH_2PO_4.2H_2O$ were dissolved in concentrated $HClO_4$ and then kept for crystallization at room temperature. The concentrations used were $[MoO_4^{2-}]_{tot} = 1.0$ M, $[HPO_4^{2-}]_{tot} = 0.11$ M and $[HClO_4]_{tot} = 1.78$ M. After a few days (sometimes weeks) of evaporation, yellowish crystals, grown as regular hexagonal prisms, were obtained. 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 capillary of Lindemann glass. The contents of Na, Mo, and P were determined by elemental analysis (carried out at the Department of Analytical Chemistry, University of Umeå). (Found weight-%: Na 4.3; P 1.8; Mo 49.8. Calc. for $Na_3H_6Mo_9PO_{34}(H_2O)_{12}$: Na 4.0; P 1.8; Mo 49.9). In some experiments we measured the loss of water in thermobalance analysis. The results found here were 12 – 13 H_2O per formula unit. From rotation photographs around [001] 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 hexagonal. The dimension of the c-axis was determined from rotation photographs and the a-axis was calculated from omega measurements on the diffractometer. The parameters of the crystals used in the collection of the intensity material had the values $a = 14.248$ Å and $c = 10.83$ Å. When the cell dimensions were calculated and refined from powder photographs the following parameters were obtained: $a = 14.182$ Å and $c = 10.758$ Å. The differences between the two determinations are too large to

arise from experimental errors; they are most probably due to variable water contents in the crystals. Systematic extinctions were found only for $00l$-reflexions with l odd. This is characteristic for the three space groups $P6_322$, $P6_3/m$, and $P6_3$. From the diffraction symmetry $P6_322$ could be rejected. Precession photographs were taken as a check on the space-group determination.

The density of the crystals was determined by flotation in a bromoform diiodomethane solution and the result was $d = 3.04 \pm 0.03$ g/cm^3 ($d_{calc} = 3.02$ with 12 H_2O; 3.05 with 13 H_2O). Three-dimensional intensity data were collected with a Philips PAILRED linear diffractometer using Mo$K\alpha$-radiation. The crystal was mounted along the c-axis. Reflexions with a relative statistical error of $\Delta I_o/I_o$ greater than 0.5 were omitted leaving a total of 5159 reflexions from the layers $hk0 - hk11$. The intensities were corrected for Lorentz and polarization effects and absorption correction was applied. In each level the reflexions h, k; $-k$, $(h+k)$ and $-(h+k)$, h were equivalent within experimental errors. For equivalent reflexions an arithmetic mean value was calculated which gave a set of 1930 independent reflexions. In connection with this calculation the quotient between the strongest and weakest reflexions in every triplet was computed. This test showed very good agreement between equivalent F_o-values. In about 90 % of the triplets the quotient varied from 0.9 to 1.1 and for the remaining triplets, which all included weak reflexions, the range was 0.8 – 1.2. The computer programs used were the same as those given in Ref. 2.

Crystal data

$Na_3H_6Mo_9PO_{34}(H_2O)_x$
Hexagonal, $P6_3$
$Z = 2$
$a = 14.248(1)$ Å
$c = 10.83(1)$ Å
$d_{calc} = 3.02$ ($x = 12$); 3.05 ($x = 13$) g/cm^3
$d_{exp} = 3.04 \pm 0.03$ g/cm^3
$V = 1903.9$ Å^3
$\mu = 30.2$ cm^{-1} (Mo$K\alpha$)

STRUCTURE DETERMINATION AND REFINEMENT

The structure determination was initiated assuming the space group $P6_3/m$ but this failed and the space group $P6_3$ was tried. In a Patterson synthesis the symmetry vectors should be found in Harker planes such as $(2x, 2y, \frac{1}{2})$ and $(2y, 2y-2x, \frac{1}{2})$. From the calculations of the highest of these peaks the three molybdenum atoms were located. A refinement at this stage gave an R-value of 0.17. Using the known Mo-atoms a three-dimensional Fourier synthesis was performed. This gave the positions of Na, P and the oxygens bound to P and Mo. The R-value decreased to 0.05 using isotropic temperature factors and to 0.04 when anisotropic temperature factors were used. A second Fourier synthesis using the known atoms gave no distinct water oxygen peaks neither did a difference Fourier map. The highest peaks in the latter were equivalent to an electron density of about 4e$^-$/Å^3. The reason for the failure to find the water oxygens is most likely that the water in the structure is not structural. The highest peaks in the difference Fourier map are probably only partly occupied positions. In the description and discussion of the structure the water content will be treated further.

The positional parameters and anisotropic temperature factors for the atoms were refined by full-matrix least squares methods and the final R-value was 0.037. $R = \sum||F_o| - |F_c||/\sum|F_o|$. The atomic scattering factors used for Mo^{3+} were those given by Cromer and Waber,[3] for P those given by Hanson, Herman, Lea and Skillman [4] and for Na^+ and O^- the values in International Tables.[5] Account was taken of the real part of the dispersion correction.[5] A weight-

Table 1. The fractional atomic coordinates and in parentheses their estimated standard deviations (referring to 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.

	X	Y	Z
Mo1	0.75741(6)	0.49246(6)	0.0001(1)
Mo2	0.71956(7)	0.59972(7)	0.3201(1)
Mo3	0.46374(6)	0.40204(7)	0.2643(1)
P	0.6667(0)	0.3333(0)	0.2745(5)
O(1)	0.8272(7)	0.5903(6)	−0.1090(8)
O(11′)	0.7909(6)	0.3771(5)	−0.0702(7)
OP(11′1″)	0.6667(0)	0.3333(0)	0.130 (1)
O(13)	0.8870(5)	0.5133(5)	0.1074(7)
O(12)	0.7303(5)	0.5607(5)	0.1206(7)
O1(2)	0.7742(7)	0.7330(6)	0.279 (1)
O2(2)	0.7051(8)	0.5979(8)	0.476 (1)
O1(23)	0.8522(5)	0.5884(6)	0.3191(9)
O2(23)	0.5693(6)	0.5491(6)	0.2717(9)
OP(23)	0.6298(6)	0.4123(6)	0.3182(9)
O1(3)	0.3516(7)	0.4137(8)	0.245 (1)
O2(3)	0.4636(7)	0.4274(7)	0.4660(9)
Na	0.167 (1)	0.339 (1)	0.172 (2)
Aq1	0.18	0.51	0.14
Aq2	0.03	0.25	0.01

Table 2. Final anisotropic thermal parameters ($\times 10^4$) and their estimated standard deviations ($\times 10^4$) in parentheses. The parameters are calculated according to the formula $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	19 (0)	17 (0)	23 (1)	18 (1)	2 (1)	4 (1)
Mo2	26 (0)	23 (0)	36 (1)	26 (1)	−2 (1)	−15 (1)
Mo3	22 (0)	26 (0)	28 (1)	29 (1)	4 (1)	−3 (1)
P	18 (1)	18 (1)	17 (4)	18 (1)	0 (0)	0 (0)
O(1)	40 (5)	24 (4)	39 (8)	26 (7)	18 (9)	23 (8)
O(11′)	24 (4)	30 (4)	14 (6)	32 (6)	1 (6)	0 (6)
OP(11′1″)	15 (4)	15 (4)	30(13)	15 (4)	0 (0)	0 (0)
O(13)	24 (4)	23 (4)	30 (7)	21 (6)	−3 (7)	5 (7)
O(12)	22 (4)	23 (4)	26 (6)	22 (6)	0 (7)	−7 (7)
O1(2)	40 (5)	31 (5)	71(10)	38 (8)	−5(11)	−10(11)
O2(2)	36 (5)	54 (7)	44(11)	39(10)	3(10)	−24(11)
O1(23)	23 (4)	30 (4)	44 (7)	29 (6)	−15 (8)	−25 (9)
O2(23)	28 (4)	25 (4)	48 (7)	32 (7)	−3(10)	−11 (9)
OP(23)	26 (4)	23 (4)	32 (7)	31 (6)	−1 (8)	−16 (8)
O1(3)	36 (5)	48 (6)	51(10)	63 (9)	10(10)	1(11)
O2(3)	46 (5)	40 (5)	34 (9)	44 (9)	21 (9)	−10 (9)
Na	166(13)	311(20)	184(19)	233(27)	−5(28)	−46(35)

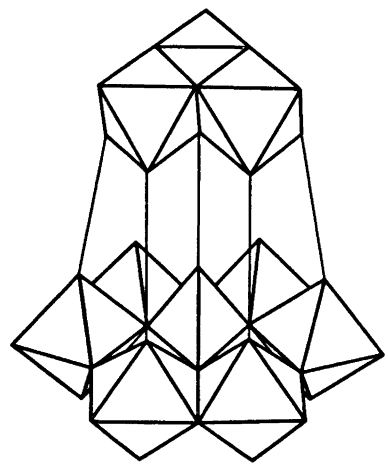
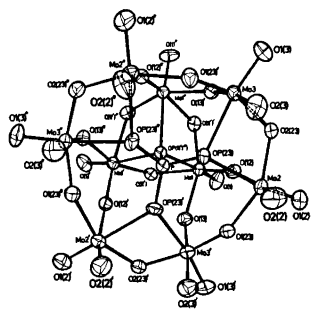


Fig. 1. The coupling of the nine MoO_6-octahedra and the PO_4-tetrahedron in the Mo_9PO_{34}-group. For clarity the figure is idealised.



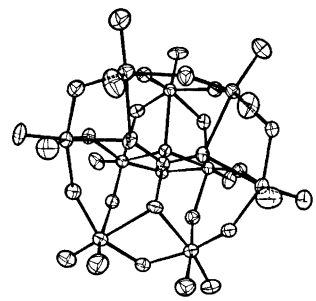


Fig. 2. Stereoscopic view of the Mo_9PO_{34}-group.

Table 3. Observed and calculated structure factors (× 10).

K	H		
L=	0		
1	2	1479	1847
1	3	105	13
1	4	1107	1310
1	5	1610	1538
1	6	527	512
1	7	121	87
1	8	239	159
1	9	407	375
1	10	1604	1559
1	11	493	460
1	12	716	726
1	13	165	147
1	14	743	739
1	15	146	83
1	16	408	394
2	16	127	132
2	15	257	274
2	14	200	196
2	13	670	665
2	12	96	109
2	11	100	43
2	10	1494	1557
2	9	160	147
2	8	538	434
2	7	437	486
2	6	2154	2146
2	5	2395	2279
2	4	170	20
2	3	314	590
2	2	122	400
2	1	861	800
2	0	278	89
3	0	442	384
3	1	2838	2777
3	2	159	165
3	3	1193	1018
3	4	930	897
3	5	2074	2115
3	6	3120	3084
3	7	125	42
3	8	257	296
3	9	236	285
3	10	1440	1413
3	12	499	479
3	13	243	255
3	14	907	875
4	14	415	421
4	13	669	667
4	12	296	310
4	11	254	268
4	10	580	565
4	8	733	708
4	7	98	48
4	6	1254	1302
4	5	486	564
4	4	1222	1385
4	3	621	721
4	1	2704	2492
4	0	918	521
5	0	277	102
5	1	465	442
5	2	997	970
5	3	274	301
5	4	175	252
5	5	502	524
5	6	153	161
5	7	446	416
5	8	120	91
5	9	148	155
5	10	391	379
5	11	1592	1606
5	12	509	512
5	13	677	703
6	13	412	416
6	12	262	270
6	11	633	639
6	10	573	573
6	9	137	148
6	8	161	195
6	7	1017	993
6	6	1546	1517
6	5	809	808
6	4	298	337
6	3	1314	1389
6	2	1550	1473
6	1	1668	1681
6	0	2089	2161
7	0	491	523
7	1	523	414
7	2	597	532
7	3	599	553
7	4	968	1024
7	5	1007	1031
7	6	452	437
7	7	91	31
7	8	325	343
7	9	239	250
7	10	456	448
7	11	557	574
7	12	611	632
8	11	134	132
8	10	179	188
8	9	470	490
8	8	717	717
8	7	463	459
8	6	195	202
8	5	791	842
8	4	1271	1253
8	3	587	610
8	2	514	534
8	1	888	905
8	0	1208	1124
9	0	1364	1376
9	1	925	923
9	2	205	132
9	3	210	193
9	4	695	688
9	5	929	944
9	6	712	679
9	8	788	799
9	9	369	375
9	10	471	493
10	9	362	376
10	7	764	782
10	6	233	217
10	5	106	78
10	4	823	836
10	3	525	493
10	2	321	350
10	1	569	549
10	0	112	37
11	0	611	612
11	1	130	88
11	2	1483	1518
11	3	861	829
11	4	438	441
11	5	754	773
11	6	452	430
11	7	512	517
11	8	554	533
12	7	567	574
12	6	265	272
12	5	351	352
12	4	1082	1084
12	3	113	124
12	2	181	174
12	1	500	523
12	0	352	347
13	0	499	493
13	1	343	329
13	2	112	99
13	3	314	301
13	4	347	315
13	5	107	87
14	5	473	482
14	4	382	373
14	3	396	401
14	2	133	110
14	1	295	306
14	0	437	391
15	0	859	863
15	1	258	253
15	2	685	687
15	3	241	258
16	2	346	351
16	1	679	689
16	0	108	86
17	0	397	415
L=	1		
1	2	1705	1886
1	3	1422	1205
1	4	1184	1189
1	5	844	786
1	6	324	274
1	7	537	499
1	8	967	975
1	9	516	488
1	10	323	272
1	11	700	674
1	12	332	367
1	13	588	594
1	14	967	958
1	15	475	473
2	16	326	321
2	15	354	345
2	14	620	626
2	12	547	537
2	11	301	277
2	10	1441	1449
2	9	908	888
2	8	902	896
2	7	772	828
2	6	2442	2502
2	5	290	203
2	4	621	539
2	3	918	792
2	2	426	481
2	1	616	339
2	0	1231	1133
3	0	1118	1209
3	1	3821	3767
3	2	1533	1561
3	3	230	206
3	4	1153	1063
3	5	2373	2282
3	6	208	201
3	7	939	896
3	8	408	421
3	9	1030	978
3	10	241	250
3	11	450	449
3	12	710	695
3	13	557	561
3	14	491	486
3	15	342	346
4	14	356	356
4	13	467	464
4	12	652	649
4	11	750	728
4	10	538	532
4	9	928	919
4	8	196	186
4	7	300	311
4	6	1629	1550
4	5	1293	1242
4	4	253	262
4	3	1909	1935
4	2	1032	1113
4	1	1301	1281
4	0	1985	2174
5	0	1011	1000
5	1	283	212
5	2	985	954
5	3	879	817
5	4	1023	1035
5	5	289	312
5	6	321	302
5	7	1070	1050
5	8	779	805
5	9	771	756
5	10	443	439
5	11	144	173
5	12	294	298
6	13	143	142
6	12	212	201
6	11	274	275
6	10	504	523
6	9	367	364
6	8	243	264
6	7	1428	1444
6	6	600	598
6	5	125	121
6	4	891	793
6	3	408	489
6	2	1202	1179
6	1	587	498
6	0	400	428
7	0	1242	1186
7	1	1170	1138
7	2	2549	2536
7	3	1148	1116
7	4	570	568
7	5	1054	1024
7	6	777	796
7	7	767	765
7	8	561	542
7	9	774	768
7	10	227	201
7	11	471	461
7	12	261	220
8	11	141	123
8	10	502	493
8	9	622	631
8	8	259	248
8	7	644	616
8	6	407	383
8	5	735	749
8	4	658	626
8	3	492	487
8	2	504	478
8	1	1535	1552
8	0	883	827
9	0	896	877
9	1	384	413
9	2	888	865
9	3	714	718
9	4	508	499
9	5	252	239
9	6	278	237
9	7	549	543
9	8	893	889
9	9	288	302
9	10	352	344
10	9	290	303
10	8	501	484
10	7	406	415
10	6	619	628
10	5	449	459
10	4	286	271
10	3	1253	1247
10	2	442	458
10	1	587	555
10	0	670	670
11	0	418	384
11	1	636	631
11	2	265	273
11	3	946	937
11	5	409	408
11	6	119	96
11	7	425	424
11	8	542	559
12	7	280	291
12	6	634	636
12	5	457	455
12	4	112	128
12	3	445	434
12	2	506	499
12	1	886	880
12	0	317	303
13	0	917	894
13	1	493	498
13	2	763	752
13	3	524	519
13	4	266	255
13	5	457	456
13	6	129	171
14	5	162	155
14	4	967	975
14	3	434	439
14	2	147	108
14	1	375	377
14	0	627	611
15	0	147	132
15	1	333	337
15	3	369	403
16	2	525	525
16	1	661	666
16	0	166	153
17	0	211	212
L=	2		
1	1	1687	1833
1	2	1381	1083
1	3	619	584
1	4	437	302
1	5	410	300
1	6	648	673
1	7	509	381
1	8	1005	1000
1	9	531	545
1	10	1789	1753
1	11	628	647
1	12	857	828
1	13	200	190
1	14	441	447
1	15	519	540
1	16	249	227
2	16	159	129
2	15	593	594
2	14	357	381
2	13	460	441
2	12	354	329
2	11	278	253
2	10	547	509
2	9	1346	1336
2	8	371	389
2	7	419	371
2	6	578	599
2	5	857	839
2	4	916	925
2	3	416	540
2	2	1264	1284
2	1	839	858
2	0	1574	1430
3	0	1047	994
3	1	816	649
3	2	1595	1573
3	3	1086	1202
3	4	435	468
3	5	605	547
3	6	787	725
3	7	461	438
3	8	1012	995
3	9	662	688
3	10	385	354
3	11	110	76
3	12	361	357
3	13	607	614
3	14	645	619
3	15	239	223
4	14	554	551
4	13	236	251
4	12	820	818
4	11	234	238
4	10	228	235
4	9	565	601
4	8	943	922
4	7	321	330
4	6	401	318
4	5	839	844
4	4	1450	1329
4	3	1060	1102
4	2	1383	1441
4	1	2353	2608
4	0	2490	2322
5	0	799	893
5	1	1478	1383
5	2	887	879
5	3	629	642
5	4	993	993
5	5	1591	1609
5	6	533	541
5	7	605	611
5	8	690	672
5	9	308	314
5	10	127	111
5	11	1192	1178
5	12	123	129
5	13	384	375
6	13	416	403
6	12	466	471
6	11	210	184
6	10	178	163
6	9	882	890
6	8	202	194
6	7	689	709
6	6	1943	1969
6	5	571	548
6	4	485	439
6	3	1031	982
6	2	766	723
6	1	415	356
6	0	1535	1437
7	0	938	908
7	1	1432	1469
7	2	1991	1991
7	3	425	434
7	4	550	515
7	5	181	179
7	6	1096	1100
7	7	228	202
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7	10	878	873
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7	12	155	171
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8	8	365	359
8	7	445	441
8	6	787	780
8	5	160	76
8	4	275	242
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8	0	1454	1435
9	0	389	324
9	1	545	493
9	2	696	706
9	3	366	387
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9	5	755	732
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9	7	326	319
9	8	402	371
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10	5	426	382
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10	1	907	896
10	0	502	514
11	0	403	369
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11	2	594	590
11	3	419	410
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11	7	116	84
11	8	214	207
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12	0	902	913
13	0	465	465
13	1	909	886
13	2	538	519
13	3	252	234
13	4	606	598
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14	5	343	352
14	4	497	511
14	3	236	239
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14	1	335	339
14	0	190	198
15	0	1092	1075
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15	3	533	536
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17	0	699	722
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1	8	1338	1324
1	9	194	173
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1	14	417	417
1	15	332	341
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2	16	238	245
2	15	358	381
2	14	671	691
2	12	932	928
2	11	540	556
2	10	627	637
2	9	617	640
2	8	665	642
2	7	685	674
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2	5	192	224
2	4	511	480
2	3	1027	1055
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7	5	615	631
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7	7	259	258
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7	9	211	206
7	10	280	280
7	11	164	165
7	12	420	430
8	10	414	405
8	9	485	474
8	8	415	403
8	7	559	561
8	6	852	848
8	5	1050	1054
8	4	775	791
8	3	1054	1027
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9	1	603	571
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9	3	103	93
9	4	631	648
9	5	206	206
9	6	525	532
9	7	542	550
9	8	812	806
9	9	178	173
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10	6	292	279
10	5	496	522
10	4	267	264
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10	2	286	287
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10	0	449	449
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11	1	559	558
11	2	174	178
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11	4	327	307
11	5	897	898
11	6	272	271
11	7	280	266
11	8	383	396
12	7	354	345
12	6	252	229
12	5	807	811
12	4	165	162
12	3	477	464
12	2	794	809
12	1	883	877
12	0	475	451
13	0	100	96
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13	2	326	342
13	3	490	503
13	4	414	437
13	5	485	484
14	4	716	721
14	3	213	189
14	2	531	551
14	1	491	470
14	0	639	635
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15	2	152	150
15	3	388	391
16	1	231	212
16	0	208	201
17	0	345	326
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1	3	485	444
1	4	847	827
1	5	1041	996
1	6	389	383
1	7	383	415
1	8	752	767
1	9	314	289
1	10	1104	1137
1	11	308	271
1	12	463	459
1	14	577	582
1	15	307	335
1	16	288	308
2	15	265	282
2	14	452	449
2	13	650	673
2	12	489	495
2	11	306	299
2	10	832	822
2	9	491	498
2	8	780	792
2	7	240	270
2	6	1264	1279
2	5	1812	1839
2	4	1423	1426
2	3	1402	1369
2	2	260	381
2	1	259	324
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3	0	303	269
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3	3	593	564
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3	8	475	491
3	9	583	611
3	10	1218	1216
3	11	292	300
3	12	227	236
3	14	415	410
3	15	130	104
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4	8	582	576
4	7	485	492
4	6	447	390
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4	1	1762	1712
4	0	1869	1833
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5	7	423	394
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5	12	412	411
5	13	578	603

Table 3. Continued.

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6	6	1034	1048
6	5	438	439
6	4	237	203
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6	2	797	796
6	1	1427	1462
6	0	1467	1462
7	0	892	956
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7	2	899	906
7	3	392	378
7	4	626	587
7	5	994	1055
7	6	803	791
7	7	278	288
7	8	814	819
7	9	206	179
7	10	528	529
7	11	435	424
8	11	142	132
8	10	614	625
8	9	382	403
8	8	739	747
8	7	190	188
8	6	414	402
8	5	717	730
8	4	1592	1612
8	3	509	503
8	2	701	711
8	1	609	620
8	0	703	687
9	0	764	766
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9	2	679	645
9	3	200	180
9	4	549	583
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9	6	360	351
9	7	185	193
9	8	681	658
9	9	506	506
9	10	355	352
10	9	472	472
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11	5	581	599
11	6	369	372
11	7	357	366
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12	7	566	584
12	6	215	229
12	5	118	105
12	4	780	787
12	3	118	117
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12	1	940	969
12	0	581	577
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13	4	293	301
13	5	326	323
14	4	265	254
14	3	174	181
14	2	225	238
14	1	422	432
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15	0	702	699
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15	2	956	981
15	3	376	397
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16	0	264	280
17	0	288	286
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1	7	578	618
1	8	446	422
1	9	369	379
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1	11	269	283
1	12	158	95
1	13	189	205
1	14	770	767
1	15	378	369
1	16	375	385
2	15	325	339
2	14	699	726
2	13	122	48
2	12	439	450
2	11	395	403
2	10	1174	1177
2	9	699	706
2	8	750	762
2	7	341	320
2	6	901	882
2	5	289	282
2	4	761	866
2	3	908	956
2	2	572	468
2	1	772	708
2	0	1181	1223
3	0	1201	1205
3	1	2778	2794
3	2	1107	1101
3	3	287	173
3	4	995	964
3	5	414	439
3	6	99	92
3	7	921	885
3	8	618	630
3	9	656	691
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3	11	205	208
3	12	537	557
3	13	408	404
3	14	355	353
3	15	333	335
4	13	304	315
4	12	427	439
4	11	516	504
4	10	686	678
4	9	696	705
4	8	121	131
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4	6	949	944
4	5	527	579
4	4	703	760
4	3	1625	1671
4	2	1044	964
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4	0	953	902
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5	2	1155	1248
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5	4	953	941
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5	12	231	233
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6	12	298	298
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6	7	971	987
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6	5	133	127
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6	3	532	545
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6	1	521	487
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7	6	600	621
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7	8	460	471
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8	9	722	736
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8	7	517	512
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8	5	579	558
8	4	519	540
8	3	398	383
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9	2	607	606
9	3	405	412
9	4	608	607
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9	6	507	514
9	7	267	261
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9	9	202	202
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10	8	256	262
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10	6	500	507
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11	2	175	165
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12	4	200	202
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12	2	448	442
12	1	951	965
12	0	687	704
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15	3	311	315
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1	15	228	268
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2	13	220	209
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2	11	184	188
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2	9	666	664
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2	7	330	318
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2	4	1079	1020
2	3	987	975
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3	8	1227	1249
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3	10	376	360
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3	12	509	485
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3	14	963	982
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4	14	179	178
4	13	414	423
4	12	618	636
4	11	368	370
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4	3	1507	1526
4	2	412	392
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5	0	916	925
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5	8	684	691
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5	10	237	230
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5	12	233	251
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6	12	128	114
6	11	195	204
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6	5	795	804
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2	4	750	766
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3	6	92	68
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3	8	555	544
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3	11	495	494
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3	13	575	574
3	14	325	325
4	14	215	227
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4	12	481	477
4	11	208	193
4	10	766	782
4	9	949	955
4	8	90	86
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4	6	104	90
4	5	958	947
4	4	539	510
4	3	1171	1151
4	2	105	145
4	1	1263	1262
4	0	646	662
5	0	833	808
5	1	511	513
5	2	1274	1246
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5	5	1179	1171
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5	8	615	604
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5	11	166	130
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7	7	271	264
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7	11	358	359
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8	5	771	774
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8	3	292	306
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8	1	723	706
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9	0	906	879
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9	2	411	416
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10	3	738	735
10	2	568	542
10	1	1431	1405
10	0	120	95
11	0	656	659
11	1	459	453
11	2	218	209
11	3	590	600
11	4	401	418
11	5	671	657
11	6	337	348
11	7	473	464
12	7	279	249
12	6	562	557
12	5	468	464
12	4	96	80
12	3	432	412
12	2	550	542
12	1	640	628
12	0	760	748
13	0	736	743
13	1	202	209
13	2	553	543
13	3	379	366
13	4	225	239
13	5	413	398
14	4	121	133
14	3	275	279
14	2	440	449
14	1	332	337
14	0	494	497
15	1	230	229
16	1	739	744
L=	8		
1	1	377	373
1	2	1310	1277
1	3	464	479
1	4	262	255
1	5	431	428
1	6	320	365
1	7	433	429
1	8	892	894
1	9	276	298
1	10	374	379
1	11	113	113
1	12	339	339
1	13	109	126
1	14	132	93
1	15	175	183
2	15	142	160
2	14	453	451
2	13	561	568
2	12	716	713
2	10	262	269
2	9	626	628
2	8	342	333
2	7	270	284
2	6	446	409
2	5	625	599
2	4	1469	1474
2	3	1094	1132
2	2	438	471
2	1	906	868
2	0	589	595
3	0	375	370
3	1	813	787
3	2	633	602
3	3	476	514
3	4	534	530
3	5	352	357
3	6	621	616
3	7	800	779
3	8	704	679
3	9	731	764
3	10	1104	1099
3	11	388	379
3	12	104	82
3	13	158	148
3	14	336	328
4	13	160	142
4	12	206	213
4	11	346	361
4	10	186	162
4	9	1214	1221
4	8	592	584
4	7	149	157
4	6	216	212
4	5	318	265
4	4	731	713
4	3	1209	1216
4	2	1403	1396
4	1	230	215
4	0	1523	1509
5	0	469	469
5	1	326	314
5	2	362	391
5	3	1062	1094
5	4	994	968
5	5	380	391
5	6	111	89
5	7	138	98
5	8	331	331
5	9	604	614
5	10	148	141
5	11	330	329
5	12	162	181
5	13	399	371
6	11	254	238
6	10	260	279
6	9	327	342
6	8	157	146
6	7	175	171
6	6	631	611
6	5	304	299
6	4	476	478
6	3	502	512
6	2	122	101
6	1	926	928
6	0	151	149
7	0	942	924
7	1	612	622
7	2	618	616
7	3	265	250
7	4	96	80
7	5	701	676
7	6	797	803
7	8	1063	1049
7	9	340	328
7	10	488	492
7	11	363	350
8	10	650	643
8	9	296	285
8	8	756	754
8	7	168	154
8	6	546	544
8	5	409	429
8	4	1265	1254
8	3	608	588
8	2	242	241
8	1	217	217
8	0	449	441
9	0	313	345
9	1	1181	1179
9	2	829	801
9	3	250	265
9	4	479	485
9	5	624	627
9	8	332	337
9	9	459	466
10	9	524	519
10	8	121	51
10	7	313	303
10	6	235	224
10	5	141	120
10	4	553	568
10	3	210	205
10	2	387	382
10	1	331	343
10	0	804	798
11	0	138	116
11	1	221	223
11	2	260	229
11	3	178	174
11	5	277	273
11	6	400	414
11	7	282	297
12	6	123	110
12	5	200	191
12	4	145	133
12	3	193	194
12	2	301	305
12	1	827	836
12	0	760	752
13	0	300	298
13	1	618	611
13	2	505	504
13	3	436	429
13	4	217	240
13	5	331	335
14	4	164	160
14	2	145	124
14	1	469	469
14	0	233	232
15	0	283	277
15	1	505	480
15	2	886	863
16	1	187	194
16	0	337	338
L=	9		
1	2	660	668
1	3	721	725
1	4	945	925
1	6	677	698
1	7	762	757
1	8	994	988
1	9	130	131
1	10	232	229
1	11	145	128
1	12	137	164
1	13	131	126
1	14	174	162
1	15	120	110
2	15	234	236
2	14	710	699
2	12	336	328
2	11	579	576
2	10	429	432
2	9	185	182

Table 3. Continued.

K	H		
L=	9		
2	8	383	360
2	7	238	234
2	6	308	315
2	5	83	54
2	4	536	533
2	3	845	813
2	1	365	355
2	0	602	638
3	0	1485	1500
3	1	898	885
3	2	292	283
3	3	283	286
3	4	666	656
3	5	621	633
3	6	117	114
3	7	818	806
3	8	789	793
3	9	658	659
3	11	455	447
3	12	325	319
3	13	713	697
3	14	258	261
4	14	269	266
4	13	596	610
4	12	335	316
4	11	237	222
4	10	302	305
4	9	440	439
4	8	299	294
4	7	969	972
4	6	534	536
4	5	610	596
4	4	470	469
4	3	446	424
4	2	221	208
4	1	617	617
4	0	92	81
5	0	625	607
5	1	153	151
5	2	627	639
5	3	523	538
5	4	581	571
5	5	1138	1167
5	6	247	238
5	7	625	636
5	8	306	312
5	9	180	193
5	10	171	166
5	11	129	82
5	12	198	222
5	13	211	218
6	12	289	282
6	11	412	416
6	10	642	649
6	9	658	641
6	8	263	263
6	7	465	477
6	6	357	343
6	5	119	101
6	4	570	562
6	3	197	197
6	2	444	438
6	1	556	571
6	0	1536	1580
7	0	394	354
7	1	507	495
7	2	148	124
7	3	537	528
7	4	592	573
7	5	452	441
7	6	322	305
7	7	301	300
7	8	536	533
7	9	324	330
7	10	435	414
7	11	116	138
8	10	418	412
8	9	316	316
8	8	305	321
8	7	120	120
8	6	615	613
8	5	566	551
8	4	522	526
8	3	138	148
8	2	375	372
8	1	622	622
8	0	629	603
9	0	1286	1315
9	1	274	261
9	2	345	339
9	3	131	136
9	4	577	563
9	5	138	108
9	6	648	654
9	8	122	151
9	9	214	214
10	7	298	303
10	6	311	313
10	5	303	309
10	4	262	272
10	3	171	158
10	2	121	100
10	1	840	840
10	0	478	481
11	0	262	275
11	1	478	494
11	2	220	219
11	3	181	172
11	4	405	404
11	5	973	974
11	6	284	291
11	7	193	197
12	6	301	300
12	5	649	652
12	4	123	125
12	3	290	279
12	2	461	470
12	1	958	964
12	0	680	658
13	0	263	270
13	1	124	118
13	2	318	325
13	3	289	283
13	4	221	224
13	5	381	379
14	4	170	148
14	3	187	198
14	2	484	505
14	1	131	138
14	0	141	124
15	0	137	128
15	1	440	432
15	2	145	172
16	0	157	156
L=	10		
1	1	440	494
1	2	1322	1361
1	3	179	146
1	4	81	87
1	5	286	261
1	6	179	166
1	7	314	305
1	8	998	999
1	9	470	477
1	10	450	449
1	11	197	199
1	12	219	212
1	13	182	185
1	14	148	173
1	15	202	191
2	15	133	154
2	14	144	175
2	13	306	308
2	12	488	496
2	10	239	235
2	9	546	547
2	8	167	185
2	6	90	95
2	5	283	303
2	4	924	938
2	3	797	765
2	2	564	583
2	1	382	429
2	0	1102	1125
3	0	341	345
3	1	305	316
3	2	554	599
3	3	268	258
3	4	262	257
3	5	379	364
3	6	668	652
3	7	627	634
3	8	979	987
3	9	295	304
3	10	508	517
3	11	246	240
3	12	373	358
3	13	512	491
3	14	708	703
4	13	270	276
4	12	562	563
4	11	196	206
4	10	115	83
4	9	647	670
4	8	544	540
4	7	106	100
4	6	316	322
4	5	888	886
4	4	802	785
4	3	1219	1251
4	2	668	667
4	1	595	601
4	0	899	897
5	0	489	484
5	1	745	749
5	2	218	217
5	3	776	782
5	4	376	369
5	5	517	515
5	6	221	208
5	7	265	261
5	8	482	483
5	9	288	294
5	10	223	226
5	11	117	74
6	12	134	79
6	10	189	182
6	9	507	496
6	8	237	215
6	6	352	344
6	5	328	346
6	4	399	401
6	3	402	407
6	2	199	199
6	1	505	499
7	0	241	226
7	0	498	507
7	1	272	257
7	2	653	657
7	3	138	150
7	4	195	194
7	5	278	284
7	6	613	600
7	7	128	96
7	8	626	623
7	9	564	561
7	10	522	510
7	11	318	335
8	10	387	384
8	9	276	275
8	8	321	327
8	7	133	122
8	6	728	736
8	5	215	212
8	4	533	548
8	3	367	358
8	2	281	293
8	1	598	591
8	0	1275	1251
9	0	257	277
9	1	412	405
9	2	501	495
9	3	154	142
9	4	309	312
9	5	876	883
9	6	127	98
9	7	110	96
9	8	109	145
9	9	216	249
10	7	121	145
10	6	478	463
10	5	273	260
10	4	507	515
10	3	195	204
10	2	536	542
10	1	273	274
10	0	434	446
11	1	519	503
11	2	594	590
11	4	181	187
11	5	130	119
11	6	569	564
12	6	288	280
12	5	385	395
12	4	344	348
12	3	190	194
12	2	247	234
12	1	438	433
12	0	458	462
13	0	523	548
13	1	363	363
13	2	584	582
13	3	249	263
13	4	178	171
13	5	285	307
14	3	113	102
14	2	128	121
14	1	448	443
14	0	151	175
15	0	325	321
15	1	207	221
15	3	252	262
16	0	240	246
L=	11		
1	2	657	658
1	3	457	461
1	4	1476	1495
1	5	294	273
1	6	611	602
1	7	246	234
1	8	211	206
1	9	284	284
1	10	120	127
1	11	429	434
1	12	226	226
1	13	236	234
1	14	292	290
1	15	227	181
2	14	149	152
2	13	137	117
2	12	406	410
2	11	116	77
2	10	553	550
2	9	335	314
2	8	231	227
2	7	209	224
2	6	633	635
2	5	269	292
2	4	353	371
2	3	508	516
2	2	435	405
2	1	361	358
2	0	482	491
3	0	129	128
3	1	660	599
3	2	250	254
3	3	125	111
3	4	355	353
3	5	559	583
3	6	102	74
3	7	369	379
3	8	177	161
3	9	687	678
3	11	115	113
3	12	541	535
3	13	174	167
3	14	204	200
4	13	120	85
4	12	286	301
4	11	157	150
4	10	574	581
4	9	771	772
4	8	134	132
4	7	414	404
4	6	296	295
4	5	685	709
4	4	451	466
4	3	934	962
4	2	364	365
4	1	799	786
4	0	124	142
5	0	563	582
5	1	209	197
5	2	681	698
5	3	218	222
5	4	330	335
5	5	768	764
5	6	137	138
5	7	147	153
5	8	559	552
5	9	338	333
5	12	126	135
6	12	120	147
6	9	440	428
6	8	252	234
6	7	271	280
6	6	341	338
6	5	133	119
6	4	508	492
6	3	316	301
6	2	165	173
6	1	232	221
6	0	951	952
7	0	545	553
7	1	616	615
7	2	421	431
7	3	147	140
7	4	713	709
7	5	871	877
7	6	303	309
7	7	270	274
7	8	250	239
7	9	621	619
7	10	287	264
7	11	347	336
8	10	154	170
8	9	614	628
8	8	252	270
8	7	278	258
8	6	129	90
8	5	432	437
8	4	434	421
8	3	362	352
8	2	514	538
8	1	690	703
8	0	429	414
9	0	145	138
9	1	338	340
9	2	473	461
9	3	383	391
9	4	150	159
9	5	132	126
9	6	373	380
9	7	115	128
9	8	318	334
9	9	117	62
10	8	162	172
10	7	247	232
10	6	313	309
10	5	134	107
10	3	332	352
10	2	288	301
10	1	915	918
11	0	509	517
11	1	304	298
11	2	125	112
11	3	346	353
11	4	154	162
11	5	288	295
11	6	245	269
11	7	384	385
12	6	552	535
12	5	164	183
12	4	167	175
12	3	355	366
12	2	243	242
12	1	254	219
12	0	556	550
13	0	596	597
13	2	508	517
13	3	338	328
13	4	144	128
14	3	347	345
14	1	289	290
14	0	247	263

ing scheme according to Cruickshank was applied:

$\omega = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ where the values of the constants were $a = 50$, $c = 0.0004$ and $d = 0.00009$.

Final atomic coordinates, vibrational parameters and corresponding standard deviations are given in Tables 1 and 2, and a comparison between the observed and calculated structure factors is reported in Table 3.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up of $H_6Mo_9PO_{34}^{3-}$-groups coordinated by sodium ions. Each Na^+-ion connects four adjacent groups by forming O–Na–O-bridges and in this way a three-dimensional network is formed.

The $H_6Mo_9PO_{34}^{3-}$-group. This group consists of a central PO_4 tetrahedron surrounded by nine MoO_6 octahedra. Three of the octahedra form a compact group in which each octahedron is linked to its neighbour on either side by a shared edge. The corner common to the three octahedra is then shared with the PO_4 tetrahedron. The structure of the compact group is shown in the upper part of Fig. 1.

The remaining six MoO_6 octahedra are then coupled together in a zigzag arrangement forming a ring. The ring may be considered as built up of three Mo_2O_{10}-groups linked together by sharing corners. The two MoO_6 octahedra in the Mo_2O_{10}-group share two oxygens in a common edge and one of these oxygens is shared with the PO_4 tetrahedron. The arrangement of the ring and the PO_4-group is illustrated in the lower part of Fig. 1. The ring is then linked to

Table 4. Distances (Å) and angles (degrees) within the $H_6Mo_9PO_{34}^{3-}$-group. The numbering of the atoms is in accordance with that shown in Table 1, with primes indicating atoms in symmetry related positions. The standard deviations given in parentheses refer to the last decimal place given.

Mo, P			
Mo1 – Mo1′	3.411(1)	P – Mo1	3.564(11)
Mo1 – Mo2	3.933(3)	P – Mo2	3.516 (2)
Mo1 – Mo3	3.690(3)	P – Mo3	3.486 (1)
Mo2 – Mo3	3.364(1)	Mo3 – Mo2 – Mo3′	117.23(4)
Mo2 – Mo3′	3.703(1)	Mo2 – Mo3 – Mo2′	117.04(4)
MoO_6-octahedra			
Mo1 – O(1)	1.713(9)	OP(11′1″) – Mo1 – O(13)	80.3(3)
Mo1 – O(11′)	2.080(7)	OP(11′1″) – Mo1 – O(12)	85.8(4)
Mo1 – O(11′)′	1.826(8)	OP(11′1″) – Mo1 – O(11′)	72.3(3)
Mo1 – O(12)	1.778(8)	OP(11′1″) – Mo1 – O(11′)′	76.4(3)
Mo1 – O(13)	2.075(8)	O(1) – Mo1 – O(13)	99.1(4)
Mo1 – OP(11′1″)	2.419(9)	O(1) – Mo1 – O(12)	104.9(4)
OP(11′1″) – O(13)	2.908(7)	O(1) – Mo1 – O(11′)	97.1(4)
OP(11′1″) – O(12)	2.894(7)	O(1) – Mo1 – O(11′)′	102.0(4)
OP(11′1″) – O(11′)	2.67 (1)	O(13) – Mo1 – O(12)	85.9(3)
O(1) – O(13)	2.89 (1)	O(12) – Mo1 – O(11′)′	101.2(3)
O(1) – O(12)	2.77 (1)	O(11′) – Mo1 – O(11′)′	87.0(4)
O(1) – O(11′)	2.85 (1)	O(11′) – Mo1 – O(13)	77.2(3)
O(1) – O(11′)′	2.75 (1)		
O(13) – O(12)	2.63 (1)		
O(12) – O(11′)′	2.79 (1)		
O(11′) – O(11′)′	2.70 (1)		
O(11′) – O(13)	2.59 (1)		
Mo2 – O1(2)	1.708(9)	O2(2) – Mo2 – O1(23)	97.2(5)
Mo2 – O2(2)	1.70 (1)	O2(2) – Mo2 – OP(23)	90.3(4)
Mo2 – O(12)	2.258(9)	O2(2) – Mo2 – O2(23)	98.8(5)
Mo2 – O1(23)	1.971(7)	O2(2) – Mo2 – O1(2)	104.9(5)
Mo2 – O2(23)	1.942(8)	O(12) – Mo2 – O1(23)	77.7(4)
Mo2 – OP(23)	2.312(7)	O(12) – Mo2 – OP(23)	76.8(3)
O2(2) – O1(23)	2.76 (1)	O(12) – Mo2 – O2(23)	81.5(3)
O2(2) – OP(23)	2.87 (1)	O(12) – Mo2 – O1(2)	88.4(5)
O2(2) – O2(23)	2.77 (1)	O1(23) – Mo2 – OP(23)	84.2(3)
O2(2) – O1(2)	2.70 (2)	OP(23) – Mo2 – O2(23)	72.9(3)
O(12) – O1(23)	2.66 (1)	O2(23) – Mo2 – O1(2)	97.8(4)
O(12) – OP(23)	2.84 (1)	O1(2) – Mo2 – O1(23)	100.1(4)
O(12) – O2(23)	2.75 (1)		
O(12) – O1(2)	2.79 (1)		
O1(23) – OP(23)	2.88 (1)		
OP(23) – O2(23)	2.55 (1)		
O2(23) – O1(2)	2.76 (1)		
O1(2) – O1(23)	2.83 (1)		
Mo3 – O1(3)	1.697(9)	O2(3) – Mo3 – O1(23)′	79.4(4)
Mo3 – O2(3)	2.21 (1)	O2(3) – Mo3 – OP(23)	80.4(3)
Mo3 – O(13)′	1.813(9)	O2(3) – Mo3 – O2(23)	81.2(4)
Mo3 – O1(23)′	1.825(8)	O2(3) – Mo3 – O1(3)	91.3(4)
Mo3 – O2(23)	1.886(7)	O(13)′ – Mo3 – O1(23)′	94.9(4)
Mo3 – OP(23)	2.375(7)	O(13)′ – Mo3 – OP(23)	87.7(3)
O2(3) – O1(23)′	2.60 (1)	O(13)′ – Mo3 – O2(23)	99.0(4)
O2(3) – OP(23)	2.96 (1)	O(13)′ – Mo3 – O1(3)	101.0(4)
O2(3) – O2(23)	2.68 (1)	O1(23)′ – Mo3 – OP(23)	80.8(3)
O2(3) – O1(3)	2.82 (1)	OP(23) – Mo3 – O2(23)	72.3(3)
O(13)′ – O1(23)′	2.68 (1)	O2(23) – Mo3 – O1(3)	99.9(4)
O(13)′ – OP(23)	2.93 (1)	O1(3) – Mo3 – O1(23)′	104.5(4)

Table 4. Continued.

O(13)′ – O2(23)	2.81 (1)		
O(13)′ – O1(3)	2.71 (1)		
O1(23)′ – OP(23)	2.75 (1)		
OP(23) – O2(23)	2.55 (1)		
O2(23) – O1(3)	2.74 (1)		
O1(3) – O1(23)′	2.79 (1)		
PO_4-tetrahedron			
P – OP(11′1″)	1.57 (2)	OP(11′1″) – P – OP(23)	108.0(6)
P – OP(23)	1.532(8)	OP(23) – P – OP(23)′	110.9(5)
OP(11′1″) – OP(23)	2.51 (1)		
OP(23) – OP(23)′	2.52 (1)		

the compact group by sharing of corners as outlined in the same figure. Fifteen of the oxygen atoms in the group are unshared, two per octahedron in the ring and one per octahedron in the compact group. The symmetry in the group is a three-fold rotation axis (parallel to the *c*-axis).

Distances and angles between the Mo-atoms are collected in Table 4. It can be seen that when the MoO_6 octahedra share edges the Mo – Mo distances are 3.41 Å (Mo1 – Mo1′) and 3.36 Å (Mo2 – Mo3).

When the octahedra share only a corner the distances increase to 3.70 Å (Mo2 – Mo3′), 3.69 Å (Mo1 – Mo3) and 3.93 Å (Mo1 – Mo2). All these Mo – Mo distances are quite normal [2] but the distance Mo1 – Mo2 = 3.93 Å is comparatively long. This is a result of the zigzag MoO_6 arrangement in the ring which in turn surely, is caused by the attached protons. However, the positions of these protons could not be determined in the present investigation.

The coordination of Na^+-ions around the $H_6Mo_9PO_{34}^{3-}$-groups. As mentioned above the $H_6Mo_9PO_{34}^{3-}$-group has fifteen unshared oxygens. To twelve of these Na^+-ions are coordinated. There is only one crystallographic sodium atom in the structure and this is attached to four Mo-oxygens, one in each of four different groups. In this way a three-dimensional network of $H_6Mo_9PO_{34}^{3-}$-groups connected by O – Na – O bridges is formed. In all there are twelve Na^+-ions around the group and since every ion is shared between four groups this implies that the charge of the group has been neutralized by the coordinated Na^+-ions.

The MoO_6-octahedra. Distances and angles are collected in Table 4. The MoO_6-octahedra are somewhat distorted from an ideal octahedron and the Mo – O distances can be divided into three groups according to the number of atoms that the oxygen atom is coordinated to:

(i) coordinated to one Mo atom, the distances are 1.71; 1.70; 1.71; 1.70; 2.21 (Å)

(ii) coordinated to two Mo atoms, the distances vary between 1.78 and 2.26 Å

(iii) coordinated to P and to two or three Mo atoms the distances vary between 2.31 and 2.42 Å.

The trend of increasing distances with increasing coordination numbers seems to be well documented. The same trend is found also in other structures.[2] An exception in the present study is the distance 2.21 Å occurring between Mo3 and O2(3). The explanation for this long distance must be that the oxygen is protonized.

The PO_4-tetrahedron. Distances and angles within the group are collected in Table 4. The distances P – O are 1.53 and 1.57 Å and the O – O distances are 2.51 and 2.52 Å. These distances and the angles O – P – O agree well with values found in other compounds containing phosphate groups and the group is almost regular.

The water molecules. The elemental analysis, calculation of formula weight from density and cell-volume as well as thermobalance analysis showed that the crystals contain 12 – 13 water molecules per formula unit. The positions of these water oxygens could, however, not be definitely determined in the structure analysis. One explanation for this could be that the water oxygen atoms are not structural. The positions of the oxygen atoms in relation to the Mo-atoms can also be so special that their contributions to the F_o-values are "drowned" in the contributions from the Mo-atoms. The small *R*-value (0.17), based on the Mo-atoms only,

shows how the contributions from these atoms dominate the intensity-material.

In earlier determinations of similar structures the Na^+-ions have always coordinated six oxygen atoms. The Na^+-ion in this structure coordinates four group-oxygens, therefore a reasonable assumption is that two water molecules should be found at a suitable distance from the sodium atom. Two of the highest peaks in the final difference Fourier map are also in such positions. (As these are general six-fold positions the two peaks correspond to six water molecules per formula unit). When these atoms were included in the refinement their temperature factors became very large and they were excluded in the final refinement. The positions of these presumed water oxygen atoms are, however, given in Table 1. It has not been possible to locate the remaining water molecules, perhaps they may be in the channels that can be found in the structure. In order to determine these remaining water oxygen positions, the intensity material must be completed with reflexions in a higher $\sin \theta/\lambda$ range perhaps also collected at lower temperatures. Work in this direction is in progress.

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