# A Large-angle X-Ray Scattering Study of Aqueous Pentamolybdodiphosphate and Heptamolybdate Solutions

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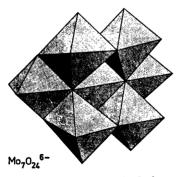
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Radial distribution curves have been calculated from X-ray scattering measurements on five solutions in each of which one of the complexes MoO<sub>4</sub><sup>2-</sup>, (H<sup>+</sup>)<sub>8</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>7</sub>, (H<sup>+</sup>)<sub>8</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>5</sub>(HPO<sub>4</sub><sup>2-</sup>)<sub>2</sub> or (H<sup>+</sup>)<sub>10</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>5</sub>(HPO<sub>4</sub><sup>2-</sup>)<sub>2</sub> should predominate according to equilibrium data. Comparison with calculated peak shapes for interatomic interactions within the complexes Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>, Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup> and H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>4-</sup>, which are known from crystal structure determinations, shows the identity of these complexes with those occurring in solution. No significant differences in the structures or in the interatomic distances seem to occur between the complexes in crystals and in solution. For the short Mo – Mo distances within the complexes changes of a magnitude of about 0.01 Å should have been observable in the distribution curves, if they occurred.

In recent emf-investigations by Pettersson 1-3 aqueous three component equilibria

$$pH^{+} + qMoO_{4}^{2-} + rHPO_{4}^{2-} \rightleftharpoons (H^{+})_{p}(MoO_{4}^{2-})_{q}(HPO_{4}^{2-})_{r}$$

were studied at 25 °C in 3.0 M Na(ClO<sub>4</sub>) medium. In the range  $1.5 < -\log [H^+] < 9$  and for  $B/C \le$ 2.5 (B is the total molybdenum concentration and C is the total phosphorus concentration) it was shown that the predominant ternary complexes formed are  $(H^+)_s(MoO_4^{2-})_s(HPO_4^{2-})_s$ ,  $(H^{+})_{9}(MoO_{4}^{2-})_{5}(HPO_{4}^{2-})_{2}$  and  $(H^{+})_{10}(MoO_{4}^{2-})_{5}$ -(HPO<sub>4</sub><sup>2-</sup>)<sub>2</sub>. By means of equilibrium analysis in aqueous solution one cannot distinguish between species containing different numbers of solvent molecules and the three pentamolybdodiphosphates may equally well be written as  $M_{0_5}P_2O_{23}$ ,  $HM_{0_5}P_2O_{23}$  and  $H_2M_{0_5}P_2O_{23}$ . Since discrete ions with such compositions are known from crystal structure determinations this shorter notation is to be preferred and will frequently be used in the following. Through slow evaporation of three different equilibrium solutions containing predominantly one or other of these pentamolybdodiphosphate complexes three crystalline phases could be ob-



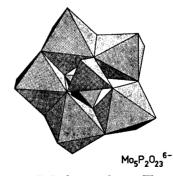


Fig. 1. A perspective view of the  $Mo_7O_{24}^{6-}$  and the  $Mo_5P_2O_{23}^{6-}$  complexes. The parameters used for the construction of the figures have been taken from the crystal structure determination of the compounds  $Na_6Mo_7O_{24}(H_2O)_{14}^{11}$  and  $Na_6Mo_5P_2O_{23}(H_2O)_{13}^{6-}$ .

tained with compositions corresponding to the formulas Na<sub>5</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>(H<sub>2</sub>O)<sub>13</sub> (phase I), Na<sub>5</sub>-HMo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>(H<sub>2</sub>O)<sub>8</sub>(phase II) and Na<sub>4</sub>H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>-O23(H2O)10 (phase III). Complete structure determinations have been carried out for I 4 and III.<sup>5</sup> For II a determination is in progress. It was found that phase I and phase III contain discrete units Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup> and H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>4-</sup>, respectively. These units are both built up from five MoOs-octahedra and two POs-tetrahedra as shown in Fig. 1. The hydrogens of the H<sub>2</sub>Mo<sub>5</sub>-P<sub>2</sub>O<sub>23</sub>4-group are probably attached to the apex oxygens of the PO4-tetrahedra thus forming a diprotonized pentamolybdodiphosphate anion. An interesting feature in these structures is the coordination of the sodium ions, which are bonded directly to the oxygens of the molybdenum octahedra.

Since the discrete polynuclear ions in the crystals have compositions equivalent to those derived from emf measurements it seems plausible to assume that the complexes in the crystals and in the solutions are identical. In order to investigate this further and more directly an X-ray scattering study of aqueous pentamolybdodiphosphate solutions was undertaken. For comparison two solutions containing no phosphate were included in the study. One alkaline solution, in which only MoO<sub>4</sub> ions and no polynuclear ions should be present, and one acidified solution, in which the predominant complex should be a heptamolybdate. The H<sup>+</sup>/MoO<sub>4</sub><sup>2-</sup> ratio (=Z) for the acidified solution was adjusted to be 1.14, corresponding to the composition (H+)<sub>8</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>7</sub>. Most investigations, for example the emf measurements by Sasaki and Sillén and the emf, Raman, and ultracentrifugation measurements by Aveston et al.,8 indicate that the predominant complex in a solution with Z=1.14 is a heptamolybdate (H+)<sub>8</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>7</sub>, although octamolybdates may also be present. Lindqvist has shown that from such solutions crystals with the composition (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>(H<sub>2</sub>O)<sub>4</sub> can be obtained, which contain discrete Mo,O246- complexes (Fig. 1). Identical complexes have been found in crystals of K<sub>8</sub>Mo<sub>7</sub>O<sub>24</sub>(H<sub>8</sub>O)<sub>4</sub>, 10 and Na<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>(H<sub>2</sub>O)<sub>14</sub>.<sup>11</sup> Accurate parameter values for the positions of the atoms within the discrete Mo<sub>7</sub>O<sub>24</sub> units are now known from threedimensional crystal structure determinations.11,12

## EXPERIMENTAL

Solutions investigated. Four molybdate-phosphate solutions were studied, one slightly alkaline solution, here denoted C, containing, according to equilibrium data, only mononuclear HPO<sub>4</sub><sup>2-</sup> and MoO<sub>4</sub><sup>2-</sup>-ions, and three with HClO<sub>4</sub> acidified solutions containing polyanions with compositions corresponding to the complexes (H+)<sub>6</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>5</sub>(HPO<sub>4</sub><sup>2-</sup>)<sub>2</sub>, (H+)<sub>6</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>5</sub>. (HPO<sub>4</sub><sup>4-</sup>)<sub>2</sub> and (H+)<sub>16</sub>(MoO<sub>4</sub><sup>2-</sup>)<sub>5</sub>(HPO<sub>4</sub><sup>2-</sup>)<sub>2</sub>, respectively. For these solutions the notations D, E, and F will be used. The compositions and concentrations of the solutions are given in Table 1. With the use of the equilibrium constants valid for a 3.0 M Na(ClO<sub>4</sub>) medium the distribution of complexes has been calculated as a function of  $-\log{[\mathrm{H}^+]}$  for B=1.60 M and C=0.64 M (B/C=2.5). The results, which are given in Fig. 2, show that it is possible to prepare solutions which are practically pure with respect to any one of Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup>, HMo<sub>5</sub>-P<sub>2</sub>O<sub>23</sub><sup>6-</sup>, and H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup>. The compositions chosen for the solutions investigated are marked with vertical lines. The compositions of the solutions containing no phosphate are given in Table 1. The alkaline solution is denoted by A and the acidified solution by B.

Table 1. Composition of solutions.

C

 $\mathbf{D}$ 

 $\mathbf{E}$ 

 $\mathbf{F}$ 

Solution

COII	entrati	on in n	101/1			
Mo	2.04	2.04	1.77	1.77		1.60
Cl	-	2.33		2.12	2.48	2.57
$\mathbf{P}$		_	0.71	0.71	0.71	
Na			<b>4.96</b>		<b>4.25</b>	
0		61.9				
H	101.6	91.1	101.2	91.7	89.8	90.2
Nun	aber of	atoms i	n the w	nit of v	olume	V
Mo	1	1	1	1	1	1
Cl	-	1.14		1.20	1.40	1.61
			0.40	0.40	0.40	0.40
$\mathbf{P}$	-					
	2.00	2.00	2.80	2.40	2.40	2.40
P	2.00	$\frac{2.00}{30.3}$	$\frac{2.80}{34.0}$	$\frac{2.40}{35.3}$	$\frac{2.40}{35.5}$	$\frac{2.40}{39.0}$
P Na O	2.00	$\frac{2.00}{30.3}$	2.80	$\frac{2.40}{35.3}$	2.40	$\frac{2.40}{39.0}$
P Na O	2.00 29.0 49.9	$\frac{2.00}{30.3}$	$\frac{2.80}{34.0}$	$\frac{2.40}{35.3}$	$\frac{2.40}{35.5}$	$\frac{2.40}{39.0}$
P Na O H	2.00 29.0 49.9	$\frac{2.00}{30.3}$	$\frac{2.80}{34.0}$	$\frac{2.40}{35.3}$	$\frac{2.40}{35.5}$	$\frac{2.40}{39.0}$
P Na O H	2.00 29.0 49.9 814	2.00 30.3 44.7	2.80 34.0 57.2	2.40 35.3 51.8	2.40 35.5 50.7	2.40 39.0 56.4

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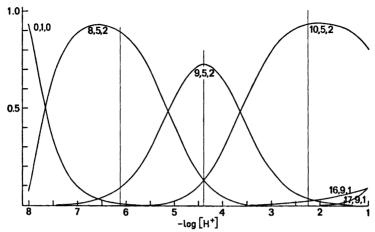


Fig. 2. Fraction of molybdenum bound in different complexes as a function of  $-\log [H^+]$  calculated for a 1.6 M molybdate solution ([HPO<sub>4</sub><sup>2-</sup>]=0.64 M) with a Mo/P ratio of 2.5 with the use of the stability constants given by Pettersson.<sup>1-3</sup> For simplicity the complexes are given in p,q,r notation, for instance 8,5,2 stands for  $(H^+)_8(MoO_4^{2-})_5(HPO_4^{2-})_2$ .

X-Ray measurements. The X-ray scattering from the free surface of the solution was measured with the use of a diffractometer described in previous papers. Because of strong fluorescence, MoK radiation could not be used and all the scattering curves were measured with AgK radiation ( $\lambda$ =0.5608 Å). A Philips X-ray generator, PW 1130, was used. Monochromatization was achieved by means of a focusing single crystal LiF monochromator placed between the sample and the scintillation counter. A pulse height discriminator was connected to the counter. The fraction of incoherent radiation passing through the monochromator was estimated in the way described in a previous paper. The scattering was measured from  $\theta \approx 1^{\circ}$  up

The scattering was measured from  $\theta \approx 1^\circ$  up to  $\theta \approx 70^\circ$ , where  $2\theta$  is the scattering angle. Slit openings of 1/12, 1/4, and  $1^\circ$  were used. From measurements in overlapping regions the scattering data were recalculated to a common slit width. The reproducibility was checked by repeated measurements at selected angles. Between 40 000 and 100 000 counts were taken at each angle, which corresponds to a statistical error of 0.5 % or better. Intervals of 0.25° were used except in the low angle region ( $\theta < \sim 5^\circ$ ), where measurements were taken at 0.1° intervals.

Treatment of intensity data. All calculations were carried out with an IBM360/75 computer using the KURVLR program.<sup>15</sup>

Corrections for absorption and multiple scattering were found to be negligible and were not applied. The correction for polarization was calculated by dividing with the factor  $(1+\cos^2 2\alpha\cos^2 2\theta)/(1+\cos^2 2\alpha)$ , where  $2\alpha$  is the scattering angle at the monochromator. For

each solution the intensities were normalized to a stoichiometric unit of volume corresponding to the volume containing one Mo atom (Table 1). The normalization was done by comparing observed intensities,  $I_{\rm corr}$  (s), corrected for polarization, with the sum of the independent coherent scattering and the incoherent scattering in the range 16 < s < 18, where  $s = 4\pi \sin \theta/\lambda$ . Reduced intensities, i(s), were calculated according to the expression:

$$\begin{split} i(s) = & KI_{\text{corr}}(s) - \sum_{\mathbf{i}} n_{\mathbf{i}} \{ [f_{\mathbf{i}}^{2}(s) + (\varDelta f_{\mathbf{i}}^{\prime\prime})^{2}] + \\ del(s)I_{\mathbf{i}}^{\text{inc}}(s) \} \end{split}$$

where the summation is taken over all atoms in the unit of volume. K is the normalization constant;  $n_i$  is the number of atoms "i" in the chosen unit of volume;  $f_i(s)$  is the scattering factor for the atom "i" corrected for the real part of the anomalous dispersion;  $\Delta f_i$ " is the imaginary part of the anomalous dispersion correction for atom "i";  $I_i^{\text{inc}}(s)$  is the incoherent scattering from atom "i"; del(s) is the fraction of incoherent radiation reaching the counter.

The scattering factors used were those given by Cromer and Waber <sup>16</sup> for Mo, Cl, P, Na, and O. For H the values given by Stewart et al.<sup>17</sup> were used. Anomalous dispersion corrections were taken from Cromer <sup>18</sup> Values for the incoherent radiation were taken from Cromer and Mann<sup>19</sup> for Mo, P, Cl, and Na, from Cromer <sup>20</sup> for O, and from Compton and Allison <sup>21</sup> for H. They were corrected for the Breit-Dirac factor.

Low-frequency additions to the i(s) curves, resulting in peaks in the radial distribution functions, D(r), below 1 Å, which were too

Table 2. Observed and reduced intensity values.

	, A I' i	B I 1	c I 1	D I i	B I 1	P I i	8	A 1 1	B 1 1	0	D i I i	r I 1	, I i
0.600 0.639 0.678 0.718	2605 -1895.8 2628 -1845.0 2626 -1814.5 2655 -1752.2	5205 764.8 4938 521.9 4445 54.8 3826 - 537.3	2706 -2202.7 2691 -2186.2 2787 -2056.9 2832 -1976.8	5269 51.0 4620 - 564.4 3938 -1210.6 3416 -1695.3	5836 692.4 5506 393.4 4672 - 407.9 4120 - 925.6	6966 1021.6 6329 409.6 5627 - 244.5 4958 - 863.2	9.482 9.570 9.658 9.747	322 - 13. 314 - 16. 308 - 18. 308 - 13.		.0 351 - .6 345 - .8 335 - .0 329 -	6.7 422 12.5 7.1 412 9.5 10.7 404 7.5 11.8 395 5.5	416 1 407 1 397 1 388	17.7 420 14.0 15.1 11.2 403 9.4 8.4 393 5.2
0.757 0.796 0.835 0.874	2654 -1718.8 2660 -1676.8 2644 -1655.2 2589 -1671.4 2626 -1595.0	3425 - 909.1 3004 -1300.2 2675 -1597.8 2403 -1837.0 2199 -2007.3	2816 -1955.1 2749 -1982.2 2803 -1888.7 2760 -1890.4	2988 -2084.4 2626 -2406.0 2411 -2579.3 2231 -2716.7	3607 -1402.3 3197 -1774.3 2826 -2105.5 2563 -2327.9	4408 -1362.4 3920 -1798.1 3607 -2058.2 3266 -2345.0	9.835 9.922 10.010 10.097 10.184	307 - 6. 300 - 9.	372 4 2 370 8 3 361 4 7 359 7	5 328 - 1 316 - 5 316 -	11.8 395 5.5 8.2 388 4.6 15.3 374 ~ 3.3 10.8 374 2.8 14.3 360 ~ 5.4 10.6 355 ~ 5.1	380 365 - 363 356 -	8.4 393 5.2 6.0 385 3.6 3.2 377 0.5 0.9 362 8.6 0.7 364 0.5 0.6 353 - 6.3
0.952 0.991 1.030 1.069	2617 -1563.5 2595 -1553.7 2584 -1512.7 2536 -1516.1	2031 -2139.8 1921 -2213.9 1866 -2231.8 1828 -2232.6	2782 -1826.5 2785 -1780.0 2764 -1755.5 2795 -1673.4 2873 -1556.3	2014 ~2845.3 1988 ~2825.7 1987 ~2779.9 1963 ~2756.7	2281 -2522.9 2176 -2583.1 2090 -2622.4 2061 -2605.0 2031 -2586.8	2871 -2627.6 2767 -2674.3 2652 -2731.1 2650 -2674.3	10.271 10.358 10.445 10.531	294 - 7. 290 - 7. 291 - 2. 284 - 6. 285 - 1.		.4 307 - .1 303 - .0 303 - .0 292 - .3 299 - .1 291 -	10.2 349 - 5.2 5.3 340 - 8.1 12.7 332 - 11.9 1.8 337 - 1.5	341 - 336 - 329 - 325 -	5.4 343 - 11.1 5.1 342 - 7.2 7.2 353 - 12.0 6.3 329 - 19.9
1.108 _1.147 1.186 1.226 1.265	2543 -1465.6 2572 -1392.2 2563 -1356.3 2585 -1289.0 2568 -1259.7	1814 -2206.0 1788 -2195.2 1855 -2088.3 1821 -2082.3 1811 -2051.8	2801 -1579.9 2734 -1598.1 2746 -1537.6	1995 -2676.2 2040 -2581.8 2107 -2465.5 2178 -2344.0 2225 -2246.9	2031 -2586.8 2060 -2508.1 2090 -2428.7 2160 -2308.9 2162 -2256.7	2631 -2633.5 2563 -2639.9 2603 -2538.6 2678 -2401.9 2737 -2280.1	10.517 10.703 10.789 10.875 10.960	260 - 3. 278 - 1. 273 - 2. 275 3. 269 0.	1 311 - 10 3 305 - 11 7 302 - 9 2 301 - 6 1 294 - 6	.3 291 - .2 291	6.1 322 - 11.1 1.3 322 - 7.3 2.1 320 - 3.6 0.5 316 - 3.6 4.1 315 - 0.1	319 - 314 - 314 - 306 - 305 -	7.9 8.2 323 - 7.9 3.9 321 - 4.7 6.8 316 - 5.4 3.6 319 1.5
1.283 1.304 1.343 1.382 1.421	2605 -1177.5 2619 -1117.9 2625 -1065.1 2578 -1065.7	1866 -1956.0 1929 -1852.6 2009 -1732.0 2084 -1615.6	2635 -1524.4 2674 -1362.2	2311 -2109.7 2415 -1955.7 2517 -1802.3 2602 -1666.5	2251 -2116.7 2329 -1988.3	2872 -2084.2 2995 -1899.5 3067 -1763.9 3282 -1487.0	11.045 11.130 11.215 11.300 11.384	269 0. 269 3. 266 4. 266 7. 259 4. 256 3. 252 3.	8 293 - 4 3 292 - 1 3 297 7	.1 286 .6 280 .5 279 .8 273 .1 269 .9 269	4.1 315 - 0.1 2.1 308 - 1.6 4.7 309 3.2 2.9 302 0.6 2.2 303 6.4 5.1 301 8.2	298	3.6 319 1.5 2.6 319 5.7 2.7 314 5.1 4.7 308 3.0 6.1 305 5.0 6.5 302 5.2 7.5 300 7.5
1.460 1.478 1.499 1.538	2578 -1065.7 2615 - 982.7 2675 - 876.5 2696 - 808.6 2726 - 732.8 2740 - 672.0	2201 -1457.7 2321 -1295.3 2405 -1169.9 2517 -1016.4	2751 -1161.3 2817 - 970.3	2711 -1505.3 2816 -1348.8 2928 -1186.0	2500 -1714.5 2730 -1433.1 2772 -1364.8	3321 -1384.7 3531 -1112.4 3613 - 967.8 3807 - 710.6	11.468 11.552 11.636 11.719	245 3	277 3	.9 270 .5 264	7.7 290 5.3 7.7 284 3.4 6.6 281 4.4	291 288 283 278	8.5 294 6.0 7.0 289 4.3 6.2 281 0.3
1.616 1.655 1.677 1.694	2846 - 520.5 2891 - 429.4	2921 - 507.1	2967 - 696.4	3442 - 490.5	3474 - 403.3	3991 - 463.7 4172 - 220.7 4305 - 24.8	11.802 11.885 11.968 12.051 12.133	238 6. 232 3. 228 2. 223 0.	0 259 1 5 259 4 8 257 6 8 253 5	.4 256 .4 251 .4 250 .4 244 .3 239 .7 235	7.5 271 2.6 3.8 270 4.6 2.3 254 - 7.6 1.4 254 - 3.3	264 - 256 - 253 - 247 -	0.1 269 - 3.9 4.4 262 - 7.4 3.9 259 - 6.6 7.0 260 - 1.8
1.733 1.772 1.811 1.869	2990 - 285.4 3085 - 145.4 3275 156.5	3421 98.6 3832 613.7	3229 - 513.8 3532 109.9	3884 79.0 4275 598.1	3862 1'14.2 4264 645.0	4551 282.7 4723 516.7 4804 660.1 4887 884.7	12.215 12.297 12.379 12.460	219 - 0. 213 - 3. 211 - 2.	3 238 - 1 0 238 1	.8 231 .9 227 .0 223 -	0.8 248 - 6.2 0.4 244 - 6.1 0.7 245 - 2.2 1.2 238 - 5.1	246 - 239 -	4.2 248 - 9.8 7.3 248 - 6.4 5.3 241 - 10.4 6.0 239 - 8.7
1.967 2.064 2.161	3412 405.0 3419 522.0 3176 389.2	3958 842.0 3816 800.4 3521 603.7 3141 320.8	3793 489.0 3805 620.0 3635 568.7	4524 972.4 4445 1018.1 4029 724.6	4434 941.0 4280 909.7 3876 625.9	4943 1046.0 4475 731.9 4004 411.1	12.541 12.622 12.703	206 - 4. 205 - 2. 202 - 2. 198 - 3. 197 - 1.	4 232 - 1 2 224 - 6 2 222 - 5 5 216 - 8	.1 216 - .1 213 - .0 207 -	2.1 236 - 4.0 1.7 233 - 4.1 5.1 229 - 4.2	227 -	7.7 257 - 7.2 6.7 252 - 8.8 4.1 255 - 2.2
2.259 2.356 2.453	2554 - 20.1	2836 110.5 2592 - 41.8	2879 45.7 2543 - 178.5	3567 383.0 3141 74.0 2820 - 133.9	3402 268.9 3017 - 1.9 2718 - 189.1	3563 117.0 3141 - 162.6 2857 - 309.5	12.783 12.863 12.943	191 - 4.	0 211 - 7 8 211 - 4	.4 205 - .1 204 -	2.2 223 - 3.5	220 -	231 - 3.4 3.9 226 - 5.4 1.5 226 - 2.3
2.550 2.647 2.744	2098 - 277.6 1981 - 301.2 1941 - 252.2	2353 - 190.1 2246 - 209.4 2127 - 243.2	2332 - 283.3 2224 - 289.1 2136 - 279.1	2561 - 282.6 2431 - 306.2 2351 - 283.9	2511 - 287.6 2355 - 338.9 2267 - 325.3	2644 - 391.0 2517 - 392.6 2430 - 358.5 2378 - 293.7	13.023 13.102 13.182	188 - 2. 184 - 3. 183 - 1. 178 - 4.	6 202 - 4	.5 196 - .2 194 - .7 190 -	4.4 219 - 1.6 3.8 216 - 2.6 4.8 213 - 1.4 2.1 212 0.1	212 -	2.9 220 - 1.3 0.6 218 - 0.9
2.841 2.938 3.035 3.132	1926 - 182.3 1924 - 103.3 1925 - 24.0 1917 42.6	2097 - 190.0 2050 - 157.5 1985 - 145,1 1938 - 116.3	2119 - 201.9 2110 - 121.8 2132 - 13.3 2114 52.2	2267 - 269.1 2250 - 209.7 2127 - 221.1 2043 - 216.4	2267 - 227.1 2166 - 234.7 2084 - 226.0 2024 - 198.4	2378 - 293.7 2276 - 285.1 2200 - 254.7 2122 - 231.1	13.260 13.359 13.418	178 - 4. 177 - 2. 175 - 2.	6 200 - 1 8 201 2	.6 191 - .1 189 - .3 186 - .5 183 -	1.7 207 - 1.9	212 - 209 - 213 207 207	0.2 218 1.4 6.4 215 1.5 3.0 217 5.9 5.5 211 2.7
3.229 3.326 3.422	1869 66.8 1808 75.7 1720 53.7	1814 - 168.0	2059 76.9 1987 82.2	1978 - 196.2	1913 - 224.9 1868 - 189.7	2009 - 246.1 1942 - 220.5	13.651 13.729	169 - 4.	1 198 4	.3 180 -	2.4 208 4.6 2.8 205 3.9 1.9 203 4.0 2.6 200 4.1	203	4.2 209 3.3
3.518 3.615	1557 12.8 1463 - 23.7	1676 - 117 A	1901 70.2 1792 31.1 1691 - 2.0 1599 - 30.4	1679 - 135.2 1876 - 63.4 1876 8.0 1851 50.8	1836 - 143.4 1843 - 62.4 1833 - 2.0 1818 50.3	1919 - 154.9 1893 - 98.0 1895 - 17.0 1875 - 37.5	13.806 13.883 13.959	168 - 1. 169 1. 160 - 4. 163 - 0.	9 188 1 4 187 1	.8 176 - .1 177 .6 174 - .4 171 -	0.4 199 5.1 0.6 195 3.1 2.0 193 3.1	200 198 194	5.3 206 5.1 6.2 204 5.5 3.9 202 5.2
3.712 3.808 3.905	1400 - 34.0	1579 - 20.3 1567 22.4	1512 - 57.4 1447 - 64.9	1851 50.8 1838 102.2 1785 110.3 1713 97.2	1796 92.8 1723 80.3 1666 80.5	1895 - 98.0 1895 - 17.0 1875 - 37.5 1838 - 71.5 1770 - 69.5 1729 - 92.0	14.036 14.112 14.188	163 - 0. 160 - 0. 159 - 0.		.5 169 -	1.5 191 4.1	190 186	3.9 202 5.2 4.7 199 5.0 4.3 195 3.2 2.1 192 1.3
4.001 4.097 4.193	1290 - 45.0 1264 - 25.9 1251 3.1 1227 19.4	1552 58.7 1546 102.8 1490 94.5 1451 101.6	1389 - 69.4 1361 - 46.7 1328 - 30.8 1298 - 15.4	1643 82.2 1565 57.3	1586 54.9 1532 52.9 1463 33.0	1644 66.0 1581 59.1 1507 37.2	14.263 14.339 14.414	160 - 0, 159 - 0, 157 - 0, 156 - 1, 153 0, 154 2, 152 2, 150 1, 149 1, 143 - 1,		.0 165 -	1.9 185 1.6 0.7 181 - 0.5 0.1 178 - 0.6 1.1 171 - 5.6	179 - 177 -	1.8 189 0.7 1.2 188 1.8 1.3 185 - 0.2 3.0 179 - 3.8 179 - 2.7
4.284 4.385 4.481	1210 41.0 1190 58.0	1420 113.3	1294 23.6	1429 18.4 1371 6.7	1400 17.7 1352 13.8	1457 36.7 1393 21.0	14.488	154 2. 152 2.	5 169 - 0	.6 164 .4 161 - .3 162 .1 159	0.2 172 - 3.4	170 -	179 - 2.7 3.2 177 - 2.6
4.577 4.672 4.768	1162 64.4 1120 56.2 1118 85.2 1094 91.1	1303 78.2 1240 53.6 1167 17.1	1249 59.5 1226 74.4 1199 82.2	1319 - 2.1 1276 - 4.6 1219 - 21.3	1252 - 2.5	1359 31.0 1300 14.1 1257 11.3 1202 - 5.2	14.637 14.711 14.784	150 1. 149 1. 145 - 1.	5 161 - 2	.9 159	0.5 168 - 0.6	166 -	3.2 177 - 2.6 3.1 178 - 1.1 2.3 174 - 3.2 2.7 174 - 2.3 0.4 174 - 0.5
4.863 4.959 5.054	1054 B0.1 1013 67.1	1103 - 12.2 1019 - 62.4 957 - 92.1 909 - 109.9	1168 85.8 1130 80.5 1092 72.9	1172 - 31.4 1137 - 30.5 1092 - 41.8	1109 - 34.0	1154 - 17.7	14.858 14.931 15.007	144 0.	3 155 - 5	.9 154 - .1 156 .0 153	2.4 162 - 3.1	166	0.0 172 - 1.4
5.149 5.244 5.539	970 50.3 922 27.5 875 4.5 828 - 19.0	887 - 102.8 887 - 74.8	1050 60.4 1004 43.3 967 32.9	1061 - 40.5 1043 - 27.1 1031 - 9.9	1044 - 33.0 1020 - 27.0 1018 0.5 1007 17.7	1078 - 27.4 1065 - 9.5 1053 7.2	15.076 15.148 15.220	158 - 1	9 151 - 3	.9 149 -	1.7 163 - 0.1 0.8 163 1.1 2.9 161 0.1	161	1.1 168 - 1.0 0.4 168 0.0
5.434 5.529 5.624	789 - 35.2 751 - 52.0	876 - 33.7	915 7.0 867 - 16.8 834 - 26.2	1033 20.2 1029 43.3 1027 66.5 1025 88.7	999 <b>36.</b> 1 993 55.3	1055 37.5 1044 53.1 1047 80.7	15.292 15.363 15.434	138 0. 134 - 3. 134 - 1.	.2 151 - ( .2 148 - 1	.7 148 .4 146 - .9 146 .4 146	0.1 161 1.1 0.5 156 - 2.6 0.4 155 - 1. 1,2 154 - 0.9	160 159 156 -	0.0 163 - 2.7
5.718 5.813 5.907	727 - 55.7 697 - 65.8 676 - 67.1 659 - 65.7	892 30.1 886 46.1 869 51.1 848 50.0	795 - 42.4 762 - 53.9 740 - 55.2	1025 88.7 997 84.4	994 80.9 981 91.3 1004 136.6	1047 80.7 1038 96.4 1011 92.3 958 61.8	15.505 15.575 15.645	134 - 1. 134 - 1. 134 0. 130 - 2. 132 0. 130 - 1. 129 - 1.	2 148 - 0 5 147 - 0 8 144 - 1	.6 141 -	0.2 154 - 0.4 1.7 154 1.6	154 -	0.4 161 - 2.7 1.2 161 - 1.8 1.7 158 - 3.3
6.002 6.096 6.190		837 58.7 790 30.1	715 - 60.6 701 - 54.7 686 - 51.8 675 - 45.5	930 62.0 886 38.3 834 6.1 791 - 17.8	913 66.6 864 37.8 807 0.5 766 - 21.2	925 50.5 891 27.4 819 - 15.0	15.715 15.785 15.854	130 - 2: 132 0: 130 - 1: 129 - 1:		.9 143 1.0 144 1.5 141	3.1 149 - 1.3 1.3 145 - 4.1	153	1.4 158 - 2.5 1.0 158 - 1.1 2.9 153 - 5.4 2.1 157 0.0
6.284 6.377 6.471	617 - 40.9	735 9.7	675 - 45.5 661 - 41.8 659 - 28.4	742 - 47.9 716 - 56.0	723 - 46.4 695 - 56.3	770 - 44.1 742 - 53.8 704 - 73.7	15.925 15.992 16.060	128 - 0. 127 - 0. 126 - 0. 126 0.	4 141 - 0 5 138 - 1 4 138 - 0	.1 139 - .4 138 - .4 138 .3 135 -	0.3 145 - 2.1	149	2.1 157 0.0 0.3 152 - 3.7 1.1 152 - 3.3
6.565 6.658 6.751	600 - 27.7 507 - 15.3	681 - 11.6 666 - 11.6	644 - 27.5 633 - 23.0 632 - 9.2 611 - 15.1	690 - 65.2 675 - 63.5 670 - 53.0	670 - 64.5 663 - 55.1 649 - 53.7 648 - 39.6	770 - 44.1 742 - 53.8 704 - 73.7 705 - 55.2 684 - 58.8 684 - 43.5 669 - 42.8	16.128 16.196 16.263	122 - 2. 124 - 0	.5 137 (	1.3 135 - 1.9 133 - 1.8 134 - 1.0 133	0.6 147 2.1 2.0 144 - 0. 0.3 144 0. 0.0 143 0.	145 -	0.5 153 - 0.6 1.0 152 - 1.0 0.3 151 - 0.5 0.5 150 - 0.8
6.845 6.938 7.030	590 - 8.9 585 - 0.3 571 - 0.6 567 8.6	653 - 9.8 624 - 25.8 608 - 27.5 593 - 30.4	615 1.8	679 - 28.0 669 - 24.1 662 - 16.2	648 - 24.8	676 - 21.3	16.330 16.397 16.464	123 0. 122 0. 121 - 0.	.1 133 (	1.2 133 1.7 131 -	0.3 142 0.4	144	1.0 149 - 1.1 0.5 148 - 1.2
7.125 7.216 7.308	552 5.9 547 13.2 536 13.5	579 - 31.6 569 - 30.0	590 4.1 577 3.8 567 5.4	645 - 19.4 650 - 0.8 633 - 5.0	634 - 10.2 616 - 15.2 613 - 4.9 599 - 7.0	647 - 20.9 640 - 13.3 635 - 4.4	16.530 16.596 16.661	120 - 0. 119 - 0. 118 - 0. 117 - 1.	5 132 8 132 6 131 0 131	.1 129 - .6 130 .8 129 - .6 128	1.2 141 1.0 0.3 139 - 0.0 0.1 137 - 0.0	142	1.2 149 1.1 0.8 146 - 0.9 0.1 149 2.5
7.401	536 13.5 521 9.8 515 14.4 509 19.9	560 - 16.4 560 - 5.0	567 5.4 564 14.9 544 6.8 534 7.3	617 - 8.1 603 - 9.9 594 - 6.9	599 - 7.0 591 - 2.6 573 - 9.2 567 - 3.1		16.726 16.791 16.856	117 - 1 117 - 0 116 - 0	.0 131 2 .4 127 0 .3 127	1.6 128 1.3 126 -	0.6 138 1.0 0.7 139 2. 0.3 136 0.0 0.9 132 - 2.	139	1.0 146 0.8 1.0 146 1.0 1.2 145 1.2
7.585 7.677 7.769			535 18.9 520 14.4 505 9.9	578 - 10.9 576 - 1.6	567 - 3.7 560 0.9 551 2.0	575 - 1.7	16.920 16.984 17.048	113 - 1 114 - 0	.9 125 - 0 .8 125 0	0.6 124 - 0.7 122 -	2.0 135 0.	138 136	1.2 145 1.2 1.4 145 2.1 2.8 143 1.1 0.6 141 0.0
7.952 8.043 8.134	470 19.3 458 16.5 447 14.6	545 19.2 538 21.4 527 19.3 518 19.0	498 13.5 496 20.3 482 15.7	565 9.9	549 10.9 545 17.6	561 7.2 557 14.0	17.111 17.174 17.237	111 - 2 111 - 0	.5 121 (	.4 120 - .5 120 -	2.1 133 0.4 1.7 134 1.4 1.3 131 0.4	133	0.9 142 2.1 1.2 142 2.6 0.8 142 3.3
8.154 8.225 8.516 8.407	488 18.5 475 15.2 470 19.3 458 16.5 447 14.6 442 17.8 428 12.3 419 10.4	505 14.4 488 6.3 474 - 0.3	470 12.8 458 10.1	556 21.4 547 22.5 523 7.8 512 6.4	537 19.4 520 11.3 508 9.4 489 - 0.3	547 14.6 5 535 12.9 5 517 5.4 7 505 2.8	17.299 17.361 17.423	111 0 110 0 109 0	0 121 (	1.7 119 - 1.5 118 - 1.2 118	0.7 132 1.1 1.5 130 0.1	132 130 -	0.4 136 - 0.9 1.2 137 0.9 1.6 136 0.6
8.498 8.588	410 8.9 399 5.5	470 4.0 453 - 5.9 457 - 13.9	443 11.1	503 6.1	483 1.9 466 - 6.8 454 - 10.4	489 - 4.1 3 473 - 10.3	17.484 17.545 17.606	109 0 109 1	9 118 - (	0.4 121 0.8 119 0.7 116	0.1 129 0. 3.0 127 - 0. 2.2 127 - 0. 0.6 126 - 0.	127 -	0.7 133 - 1.8
8.678 8.768 8.858	392 . 5.5 385 4.6 375 1.5 363 - 4.6	436 - 8.0	425 9.2 416 7.7 411 9.8	484 5.4 445 - 25.3 446 - 15.5 442 - 11.6	440 - 15.1 436 - 11.1 436 - 4.1	455 - 10.9 445 - 13.0	17.666	107 0 107 1	3 114 - 1	0.9 117 1.0 114	1.9 125 - 0.	124 -	2.1 132 - 0.7 1.8 131 - 1.3 2.3 131 0.0 2.0 130 - 0.4
8.948 9.037 9.127	357 - 4.7 352 - 4.0	410 - 13.2 406 - 10.5	411 9.8 396 1.3 384 - 3.5 384 2.4 368 - 6.3	442 - 11.6 443 - 3.1 444 5.9 439 8.5	436 - 4. 426 - 6. 432 6. 428 9.	446 4.1 8 443 8.9	17.786 17.845 17.904 17.962	106 1 105 1 106 2 105 2 103 1	.5 113 - 1 .8 111 -	0.5 114 1.7 115	0.8 122 - 1. 1.1 122 - 1. 3.2 121 - 1. 2.6 119 - 2.	123 -	1.9 127 - 2.1 1.4 127 - 1.9 2.7 126 - 2.3
9.216 9.305 9.394	342 - 8.7 335 - 9.7 332 - 7.8	398 - 5.0	368 - 6.3 366 - 3.0 358 - 5.3	439 8.5 441 17.1 427 10.5	428 9. 423 11. 422 17.	7 442 14.7 5 435 15.3 5 433 20.1	18.021	103 1	3 111 -	1.7 113	2.4 118 - 2.	120 -	2.7 125 - 2.4

short to correspond to interatomic distances, were removed by a Fourier transformation of that part of the D(r) curves, 15 account being taken of contributions of short interatomic distances extending into that region.

The electronic radial distribution functions,

$$D(r)$$
, were calculated from:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_0^{s_{\text{max}}} si(s) M(s) \sin(rs) ds$$

The modification function, M(s), was chosen to be:

$$\{f_{\text{Mo}}^{2}(0)/f_{\text{Mo}}^{2}(s)\} \exp(-0.01s^{2}).$$

Intramolecular contributions to the theoretical intensities were calculated from the expression:

$$\sum_{\substack{\mathbf{m} \ \mathbf{n} \\ \mathbf{m} \neq \mathbf{n}}} f_{\mathbf{m}} f_{\mathbf{n}} \frac{\sin (r_{\mathbf{m}\mathbf{n}}s)}{r_{\mathbf{m}\mathbf{n}}s} \exp (-b_{\mathbf{m}\mathbf{n}}s^2)$$

where  $r_{\rm mn}$  is the distance between the atoms n and m and  $b_{\rm mn}$  is a temperature factor. Corresponding peak shapes were obtained from these

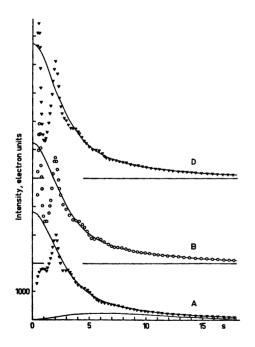


Fig. 3. Observed intensity values, I(s), compared with the independent coherent scattering (full-drawn curves) for the solutions A, B, and D. The lower full-drawn curve gives the estimated amount of incoherent radiation reaching the counter.

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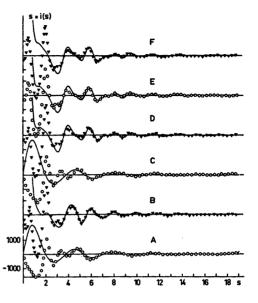


Fig. 4. A survey of the experimental si(s) values for the different solutions. Full-drawn lines represent theoretical curves calculated with the use of the parameters in Table 3.

intensities by a Fourier transformation analogous to that used for the experimental intensities.

#### ANALYSIS OF THE DATA

The observed intensities, I(s), after normalization to the chosen stoichiometric unit of volume, and correction for incoherent radiation are given in Table 2 and in Fig. 3. Table 2 also gives the reduced intensity values, i(s), corrected for spurious peaks below 1 Å in the radial distribution functions. A survey of values, si(s), for the different solutions is shown in Fig. 4.

For the acidified solutions B, D, E and F the radial distribution curves (Figs. 5 and 7) show several peaks, indicating intramolecular interactions, which are not present for the slightly alkaline solutions A and C. This is consistent with the occurrence of polynuclear complexes in the acidified solutions.

According to equilibrium data practically all molybdenum should occur as  $H_nMo_5P_2O_{23}^{(6-n)-}$  in solutions D (n=0), E (n=1), and F (n=2) (Fig. 2) and as  $Mo_7O_{24}^{6-}$  in solution B. With the use of the parameters obtained from the crystal structure determinations for the posi-

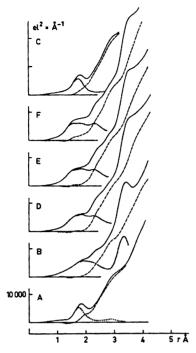


Fig. 5. Radial distribution curves, D(r). Dotted curves represent the sum of intramolecular contributions calculated from the parameters in Table 3. Broken curves represent the difference between the experimental D(r) function and the calculated intramolecular contributions.

tions of the atoms in the complexes  $\text{Mo}_7\text{O}_{24}^{6-11}$  and  $\text{Mo}_5\text{P}_2\text{O}_{23}^{6-4}$  the expected peak shapes for these complexes were calculated and are shown in Fig. 6. Comparison with the radial distribution functions, D(r), in Fig. 5, and,in particular, with the functions  $D(r) - 4\pi r^2\varrho_0$  in Fig. 7 shows similar peaks to be present for the acidified solutions. For the slightly alkaline solutions containing only molybdate ions (solution A) or molybdate and phosphate ions (solution C), a peak at 1.7<sub>5</sub> Å corresponds to the expected Mo - O distance. For comparison the calculated peak shape for a tetrahedral  $\text{MoO}_4^{2-}$  ion is shown in Fig. 6.

When the intramolecular interactions within the  $\text{Mo}_7\text{O}_{24}^{6-}$ , the  $\text{Mo}_5\text{P}_2\text{O}_{23}^{6-}$ , and the  $\text{ClO}_4^{-}$  groups for the acidified solutions, and the  $\text{MoO}_4^{2-}$  and the  $\text{PO}_4^{3-}$  groups for the alkaline solutions, are subtracted from the corresponding  $D(r) - 4\pi r^2\varrho_0$  functions, the difference curves, shown in Fig. 7, are obtained. These

curves, which are all very similar, represent residual interactions in the solutions. They show broad peaks at about 2.9 and 4.0 Å, which probably contain contributions from persistent parts of the water structure. The coordination of the sodium ions, which are present at approximately equal concentrations in all of the solutions, will also give contributions to this remaining structure, as will all intermolecular interactions. Beyond about 9 Å the curves indicate no significant deviations from the average,  $4\pi r^2 \varrho_0$ , function.

The similarity of the difference curves and the absence of sharp peaks and of deviations from a smooth background curve in the regions where sharp peaks have been subtracted, indicate that the complexes assumed are sufficient to explain all intramolecular interactions in the solutions.

For the calculations of the peak shapes temperature factors of 0.002 for Mo-Mo, 0.006 for Mo-O, and 0.01 for O-O interactions were used (Table 3). These values were estimated

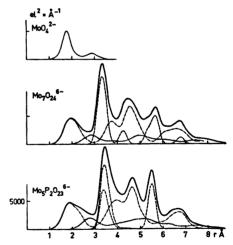


Fig. 6. Calculated peak shapes for the  $\mathrm{Mo_7O_{24}}^{\mathrm{c}-}$  and the  $\mathrm{Mo_5P_2O_{23}}^{\mathrm{c}-}$  complexes and for a tetrahedral  $\mathrm{MoO_4}^{\mathrm{2}-}$  group. The parameters used for the calculations are given in Table 3. For the  $\mathrm{Mo_7O_{24}}^{\mathrm{c}-}$  complexes the contributions from  $\mathrm{Mo}-\mathrm{Mo}$  (dashed lines),  $\mathrm{Mo}-\mathrm{O}$  (dashed-dotted lines), and  $\mathrm{O}-\mathrm{O}$  (dotted lines) interactions are separately drawn. The same is done for the  $\mathrm{Mo_5P_2O_{23}}^{\mathrm{c}-}$  complex but here the dashed-dotted line represents the sum of  $\mathrm{Mo}-\mathrm{O}$  and  $\mathrm{P}-\mathrm{O}$  interactions, and the two peaks at 3.3 Å represent  $\mathrm{Mo}-\mathrm{Mo}$  interactions (small peak) and the sum of  $\mathrm{Mo}-\mathrm{Mo}$  and  $\mathrm{Mo}-\mathrm{P}$  interactions (large peak).

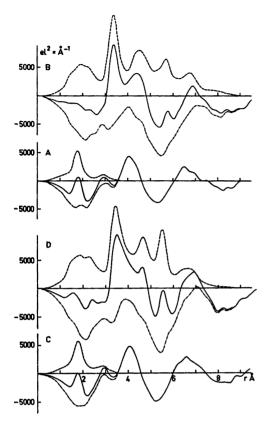


Fig. 7. Radial distribution functions for the solutions A, B, C, and D. Full-drawn lines represent the experimental  $D(r) - 4\pi r^2 \varrho_0$  functions. Dashed lines are the sum of calculated peaks for intramolecular interactions obtained with the parameters in Table 3. Dashed-dotted lines are the corresponding differences.

from a comparison between calculated and experimental i(s) values in the high-angle part of the intensity curves, where Mo-Mo interactions are the main contributors. A temperature factor of 0.002 for a Mo-Mo distance corresponds to an r.m.s. value for the variation of the distance of 0.06 Å. This indicates that the relative Mo-Mo (and Mo-P) distances in the Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> and the Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup> groups are closely similar in the solutions and in the crystals.

Slightly better agreement between observed and calculated intensities can be obtained by adjusting the temperature factors by means of a least squares procedure. However, since the number of parameters that can be included in such a refinement is limited, simplifying assump-

Table 3. Parameters used for the calculation of theoretical curves.

Molecule	Intramolec	Temperature				
	distances	(Å)	factor (Å2)			
MoO <sub>4</sub> 2-	Mo-O	1.75	0.002			
•	0 - 0	2.86	0.004			
Mo <sub>7</sub> O <sub>24</sub> 6-	Mo-Mo	a	0.002			
7 24	Mo-O	а	0.006			
	0 - 0	a	0.01			
Mo <sub>5</sub> P <sub>2</sub> O <sub>23</sub> 6-	$   \left. \begin{array}{l}     Mo - Mo \\     Mo - P \\     P - P   \end{array} \right\} $	b	0.002			
	$\left.\begin{array}{c} Mo-O \\ P-O \end{array}\right\}$	b	0.006			
	$\tilde{0} - \tilde{0}$	b	0.01			
ClO <sub>4</sub> -	Cl-O	1.43	0.002			
	0-0	2.34	0.002			
PO <sub>4</sub> 3-	P-0	1.54	0.002			
•	0 - 0	2.51	0.004			
$H_2O$	O-H	1.0	0.004			

 $^a$  Parameters taken from the crystal structure determination of  $\rm Na_6Mo_7O_{24}(H_2O)_{14}$  by Sjöbom and Hedman.  $^{11}$   $^b$  Parameters taken from the crystal structure determination of  $\rm Na_6Mo_5P_2O_{23}(H_2O)_{13}$  by Strandberg.  $^4$ 

tions must be made and, therefore, these rather extensive calculations did not seem justified. For the alkaline solutions an adjustment, by a least squares procedure, of the single Mo-O interaction present was, however, carried out. This led to a Mo-O distance of 1.78[1] Å, which is close to the value 1.77<sub>2</sub> Å found for the discrete  $MoO_4^{2-}$  ions in crystals of  $Na_2MoO_4$ - $(H_2O)_2$ .22

A comparison between the sum of the peak shapes for the assumed intramolecular interactions for each solution and the corresponding D(r) function at low r values is shown in Fig. 5. Below about 2 Å the D(r) curves are closely reproduced by the assumed interactions, which confirms that the average Mo-O coordination in the acidified solutions is the same as found in the crystals. A possible exception is solution F, where small deviations seem to occur.

A direct comparison between the radial distribution functions for the acidified solutions is more sensitive towards differences between the complexes in the crystals and in the solutions. The similar size and shapes and the approximately equal concentrations in the solutions of the Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> and the Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup>

complexes should result in closely similar intermolecular interactions. Thus, it may be expected that differences between the distribution curves for the acidified solutions will mainly reflect differences between the intramolecular interactions within the complexes. The resulting difference curves, obtained by subtracting the  $D(r) - 4\pi r^2 \varrho_0$  function for solution D from those of the other acidified solutions, are shown in Fig. 8. For this calculation the stoichiometric unit of volume for solution B, containing  $\text{Mo}_7 O_{24}^{4-}$  complexes, was increased to 947 Å<sup>3</sup> in order to give the same average scattering power,  $\varrho_0$ , as solution D (Table 1).

The difference between solution B, containing Mo<sub>7</sub>O<sub>24</sub> complexes, and solution D, containing Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub> complexes, is compared in Fig. 8 with the difference between the peak shapes calculated for the assumed intramolecular interactions in these solutions. The close correlation between the two curves confirms that no significant differences occur between the structures of the complexes in the crystals and in the solutions. For comparison, differences are also

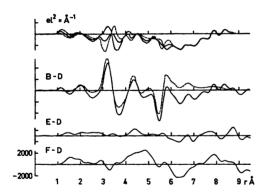


Fig. 8. Differences curves between the radial distribution functions for the solutions and between calculated peak shapes for the assumed intramolecular interactions. The full-drawn curves marked B-D, E-D, and F-D represent the functions obtained by subtracting the  $D(r)-4\pi r^2\varrho_0$  function for solution D from those of solutions B, E, and F, respectively. The dashed curve, B-D, gives the difference between the calculated intramolecular interactions for solutions B and D obtained with the use of the parameters in Table 3. The upper full-drawn curve is the calculated difference between the two curves, B-D. The dashed and the dotted curves are corresponding differences obtained after shifting the calculated peak shape curves +0.05 or -0.05 Å relative to each other.

given which are calculated after shifting one of the peak shape curves +0.05 or -0.05 Å relative to the other. The resulting curves, shown in Fig. 8, indicate that if differences in Mo-Mo distances occur between crystals and solutions they are probably less than about 0.01 A, at least for the short Mo-Mo distances. Even for the Mo-O distances, which do not give rise to peaks as sharp as those of the Mo-Mo interactions (Fig. 6), there are no indications of significant differences. This is seen by comparing those parts of the curves in which the Mo-O interactions make their largest contributions (Figs. 6, 7, and 8). Interactions involving only oxygen atoms are too diffuse to allow any conclusions as to a possible difference (Fig. 6).

The predominant complex in solution E is  $\mathrm{HMo_5P_2O_{23}^{5-}}$  (Fig. 2). The difference between the  $D(r)-4\pi r^2\varrho_0$  function for this solution and for solution D, containing the  $\mathrm{Mo_5P_2O_{23}^{6-}}$  complexes, is shown in Fig. 8. No significant peaks are present and, apparently, the addition of a proton to the  $\mathrm{Mo_5P_2O_{23}^{6-}}$  complex does not change its basic structure.

In solution F the predominant complex should have the composition H2Mo5P2O234- according to emf measurements.1-3 The discrete complex H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>4-</sup> has been found in crystals and the structure determination 5 has shown it to be built up in the same way as the Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>6complex with the two protons probably associated with the two phosphate oxygens not shared with molybdenum atoms (Fig. 1). The corresponding difference curve, however, indicates larger deviations than those found for solution E (Fig. 8), and these deviations are not attributable to the small structural differences between the complexes H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub>4- and Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup>, as found from the crystal structure determinations.

#### DISCUSSION OF THE RESULTS

The close correlation between the observed radial distribution curves and the calculated intramolecular interactions, shown in Figs. 7 and 8, strongly supports the identification of the polymolybdates in the solutions, with the Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>6-</sup> and the Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> units found in crystals. However, since the distribution curves give only one-dimensional representations of the

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three-dimensional complexes they are insensitive towards minor differences in structures and this could make the uniqueness of the interpretation uncertain. By repeating the calculations, the results of which are summarized in Figs. 7 and 8, after making small changes in the assumed structures of the complexes, an estimate of the "degree of significance" in the conclusions can be obtained. Adding or removing a Mo atom without changing other atomic parameters in the structures leads to significant deviations between observed and calculated distribution curves. The nuclearity of the predominant complexes, therefore, is uniquely determined by the diffraction measurements.

The effect of small differences in the average distances between the complexes in solution and the corresponding complexes in crystals is illustrated in Fig. 8. The difference curves are particularly sensitive towards small differences in the short Mo-Mo distances. The agreement between the observed distribution curves and the calculated curves indicates that such differences do not occur or, at least, cannot be of a magnitude larger than about 0.01 Å. Apparently the Mo frame work in the complexes is unchanged when the complex is transferred from a crystal to a solution. The oxygen positions also seem to be unaffected, but the distribution curves are less sensitive towards changes in distances involving oxygen atoms, if they do not lead to large changes in the average Mo - O distances.

In crystals of the pentamolybdodiphosphates 4,5 and in the heptamolybdate 11 the sodium ions are closely associated with the polymolybdate ions. This association may also occur in solution, but because of the low atomic number of Na and the many interactions involved when a sodium atom is added to the complex, the effects on the distribution curves will be too small and too diffuse to allow any conclusions to be made regarding this.

# CONCLUSIONS

In an apparently unique way, the solution X-ray scattering measurements lead to an identification of the discrete  $\mathrm{Mo_5P_2O_{23}}^{6-}$  and  $\mathrm{Mo_7O_{24}}^{6-}$  units found in crystal structures,  $^{4,5,10,11,23}$  with polymolybdate species in solution, which have been identified by equi-

librium studies.<sup>1-3,7</sup> The scattering data indicate that no significant change occurs in the structures of these complexes when they are transferred from a crystal to the dissolved state.

The homonuclearity of the protonized pentamolybdodiphosphate species is supported by the present measurements. Only in the most acidified of the solutions, where H<sub>2</sub>Mo<sub>5</sub>P<sub>2</sub>O<sub>23</sub><sup>4</sup> should be the predominant complex, are peaks present in the distributions curves, which might indicate an incipient association of the complexes into larger groups.

In molybdate-phosphate solutions with Mo/ P > 2.5 other types of complexes seem to form. The occurrence of a series of complexes with Mo/P = 9 has been suggested on the basis of emf measurements and is supported by crystal structure determinations of Na<sub>3</sub>H<sub>6</sub>Mo<sub>9</sub>PO<sub>34</sub>(H<sub>2</sub>O)<sub>12</sub><sup>24</sup> and Na<sub>6</sub>Mo<sub>18</sub>P<sub>2</sub>O<sub>62</sub>(H<sub>2</sub>O)<sub>24</sub>, <sup>25</sup> which contain discrete polynuclear complexes. X-Ray scattering measurements are now being made to identify these complexes in the solutions. In the binary H<sup>+</sup>-MoO<sub>4</sub><sup>2-</sup> system the solubilities of the molybdate complexes at the larger H+/MoO<sub>4</sub>2ratios are considerably increased when sodium ions are replaced by lithium ions in the solutions. This makes it possible to study the molybdate complexes in these solutions by X-ray scattering measurements over a large range of acidities. Such measurements are now being done in order to establish if an equilibrium between hepta- and octamolybdates occurs in the solutions.

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