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

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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_4^{2-}, $(H^+)_8(MoO_4^{2-})_7$, $(H^+)_8(MoO_4^{2-})_5(HPO_4^{2-})_2$, $(H^+)_9(MoO_4^{2-})_5(HPO_4^{2-})_2$ or $(H^+)_{10}(MoO_4^{2-})_5(HPO_4^{2-})_2$ should predominate according to equilibrium data. Comparison with calculated peak shapes for interatomic interactions within the complexes $Mo_7O_{24}^{6-}$, $Mo_5P_2O_{23}^{6-}$ and $H_2Mo_5P_2O_{23}^{4-}$, 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

$$pH^+ + qMoO_4^{2-} + rHPO_4^{2-} \rightleftharpoons$$
$$(H^+)_p(MoO_4^{2-})_q(HPO_4^{2-})_r$$
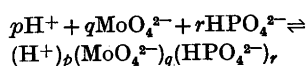
were studied at 25 °C in 3.0 M Na(ClO_4) medium. In the range $1.5 < -\log [H^+] < 9$ and for $B/C \leq 2.5$ (B is the total molybdenum concentration and C is the total phosphorus concentration) it was shown that the predominant ternary complexes formed are $(H^+)_8(MoO_4^{2-})_5(HPO_4^{2-})_2$, $(H^+)_9(MoO_4^{2-})_5(HPO_4^{2-})_2$ and $(H^+)_{10}(MoO_4^{2-})_5-(HPO_4^{2-})_2$. 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 $Mo_5P_2O_{23}^{6-}$, $HMo_5P_2O_{23}^{5-}$ and $H_2Mo_5P_2O_{23}^{4-}$. 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-
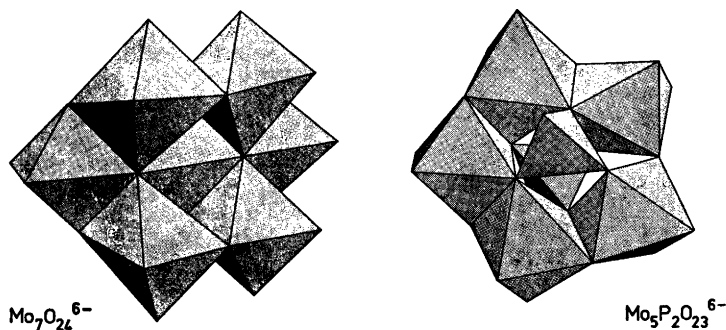

Fig. 1. A perspective view of the $Mo_7O_{24}^{6-}$ and the $Mo_5P_2O_{23}^{6-}$ complexes. The parameters used for the construction of the figures have been taken from the crystal structure determination of the compounds $Na_6Mo_7O_{24}(H_2O)_{14}$[11] and $Na_6Mo_5P_2O_{23}(H_2O)_{13}$.[4]

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tained with compositions corresponding to the formulas $Na_6Mo_5P_2O_{23}(H_2O)_{13}$ (phase I), Na_5-$HMo_5P_2O_{23}(H_2O)_8$(phase II) and $Na_4H_2Mo_5P_2$-$O_{23}(H_2O)_{10}$ (phase III). Complete structure determinations have been carried out for I[4] and III.[5] For II a determination is in progress. It was found that phase I and phase III contain discrete units $Mo_5P_2O_{23}{}^{6-}$ and $H_2Mo_5P_2O_{23}{}^{4-}$, respectively. These units are both built up from five MoO_6-octahedra and two PO_4-tetrahedra as shown in Fig. 1. The hydrogens of the H_2Mo_5-$P_2O_{23}{}^{4-}$-group are probably attached to the apex oxygens of the PO_4-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 $MoO_4{}^{2-}$ ions and no polynuclear ions should be present, and one acidified solution, in which the predominant complex should be a heptamolybdate. The $H^+/MoO_4{}^{2-}$ ratio $(=Z)$ for the acidified solution was adjusted to be 1.14, corresponding to the composition $(H^+)_8(MoO_4{}^{2-})_7$. Most investigations,[6] for example the emf measurements by Sasaki and Sillén[7] 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 $(H^+)_8(MoO_4{}^{2-})_7$, although octamolybdates may also be present. Lindqvist[9] has shown that from such solutions crystals with the composition $(NH_4)_6Mo_7O_{24}(H_2O)_4$ can be obtained, which contain discrete $Mo_7O_{24}{}^{6-}$ complexes (Fig. 1). Identical complexes have been found in crystals of $K_6Mo_7O_{24}(H_2O)_4$,[10] and $Na_6Mo_7O_{24}(H_2O)_{14}$.[11] Accurate parameter values for the positions of the atoms within the discrete $Mo_7O_{24}{}^{6-}$ units are now known from three-dimensional 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 $HPO_4{}^{2-}$ and $MoO_4{}^{2-}$-ions, and three with $HClO_4$ acidified solutions containing polyanions with compositions corresponding to the complexes $(H^+)_8(MoO_4{}^{2-})_5(HPO_4{}^{2-})_2$, $(H^+)_9(MoO_4{}^{2-})_5$-$(HPO_4{}^{2-})_2$ and $(H^+)_{10}(MoO_4{}^{2-})_5(HPO_4{}^{2-})_2$, 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 $Na(ClO_4)$ medium the distribution of complexes has been calculated as a function of $-\log[H^+]$ 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 $Mo_5P_2O_{23}{}^{6-}$, HMo_5-$P_2O_{23}{}^{5-}$, and $H_2Mo_5P_2O_{23}{}^{4-}$. 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.

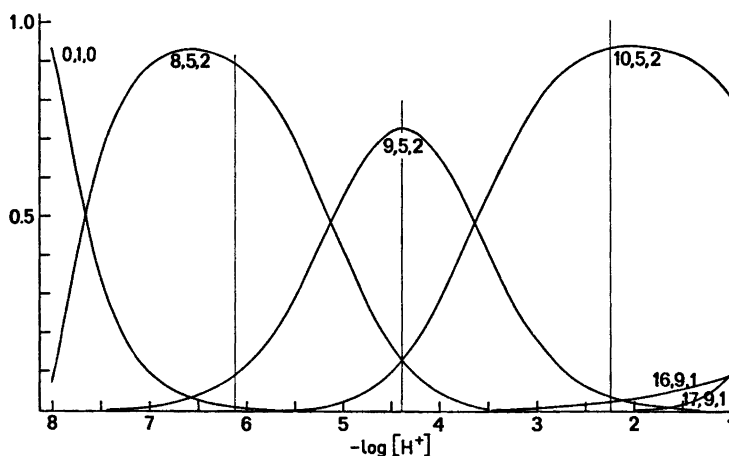|	Solution					
	A	B	C	D	E	F
Concentration in mol/l						
Mo	2.04	2.04	1.77	1.77	1.77	1.60
Cl	–	2.33	–	2.12	2.48	2.57
P	–	–	0.71	0.71	0.71	0.64
Na	4.07	4.08	4.96	4.25	4.25	3.84
O	59.0	61.9	60.1	62.5	62.8	62.4
H	101.6	91.1	101.2	91.7	89.8	90.2
Number of atoms in the unit of volume V						
Mo	1	1	1	1	1	1
Cl	–	1.14	–	1.20	1.40	1.61
P	–	–	0.40	0.40	0.40	0.40
Na	2.00	2.00	2.80	2.40	2.40	2.40
O	29.0	30.3	34.0	35.3	35.5	39.0
H	49.9	44.7	57.2	51.8	50.7	56.4
V Å³	814	814	938	938	938	1038
ϱ_0 el²/Å³	145.5	167.9	176.3	195.3	198.6	212.1

Fig. 2. Fraction of molybdenum bound in different complexes as a function of $-\log [H^+]$ calculated for a 1.6 M molybdate solution ($[HPO_4{}^{2-}] = 0.64$ M) with a Mo/P ratio of 2.5 with the use of the stability constants given by Pettersson.[1-3] 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.[13] 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.[14]

The scattering was measured from $\theta \approx 1°$ up to $\theta \approx 70°$, where 2θ is the scattering angle. Slit openings of 1/12, 1/4, and 1° 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 ($\theta < \sim 5°$), 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.[15]

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 2α is the scattering angle at the monochromator.[15] 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_{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:

$$i(s) = KI_{corr}(s) - \sum_i n_i\{[f_i^2(s) + (\Delta f_i'')^2] +$$

$$del(s)I_i{}^{inc}(s)\}$$

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"; $I_i{}^{inc}(s)$ 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 [16] for Mo, Cl, P, Na, and O. For H the values given by Stewart *et al.*[17] were used. Anomalous dispersion corrections were taken from Cromer.[18] Values for the incoherent radiation were taken from Cromer and Mann[19] for Mo, P, Cl, and Na, from Cromer [20] for O, and from Compton and Allison [21] 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.

The table contains columns grouped under headings A, B, C, D, E, F (repeated in two halves of the page), with each group having sub-columns *s*, *I* and *i* (observed and reduced intensity values). Due to the extreme density of numerical data, representative structure is shown below.

s	A I	A i	B I	B i	C I	C i	D I	D i	E I	E i	F I	F i
0.600	2605	-1895.8	5205	764.8	2706	-2202.7	5269	51.0	5836	692.4	6966	1021.6
0.639	2528	-1845.0	4938	521.9	2691	-2186.2	4620	-564.4	5506	393.4	6329	409.6
0.678	2626	-1814.5	4445	54.8	2787	-2056.9	3938	-1210.6	4672	-407.9	5627	-244.5

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:

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

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

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

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

$$\sum_m \sum_n f_m f_n \frac{\sin (r_{mn}s)}{r_{mn}s} \exp (-b_{mn}s^2)$$
$$m \neq n$$

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

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 $H_n Mo_5 P_2 O_{23}^{(6-n)-}$ in solutions D $(n=0)$, E $(n=1)$, and F $(n=2)$ (Fig. 2) and as $Mo_7 O_{24}^{6-}$ in solution B. With the use of the parameters obtained from the crystal structure determinations for the posi-
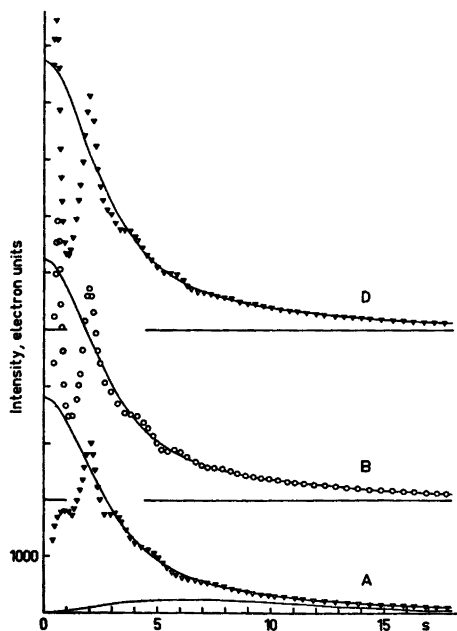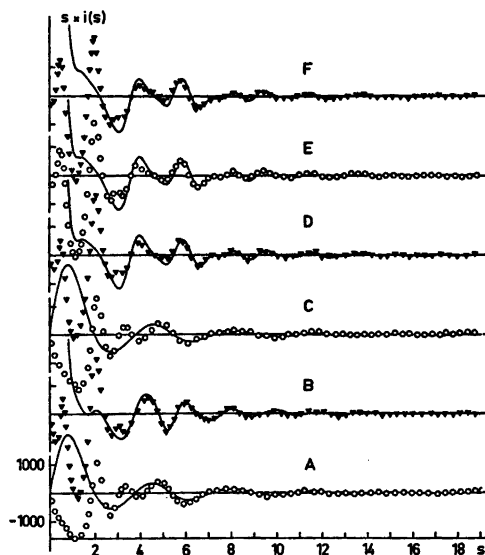

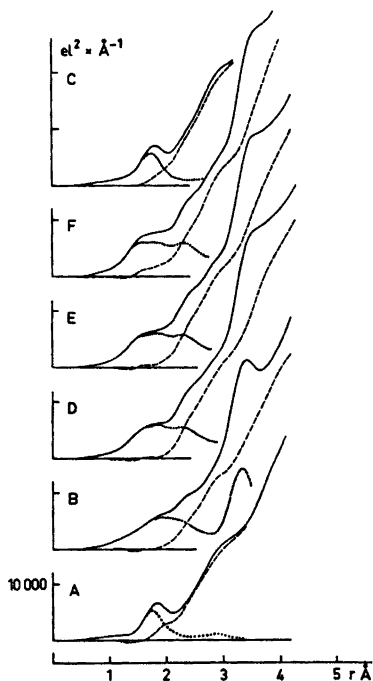Fig. 3. Observed intensity values, $I(s)$, compared with the independent coherent scattering (full-drawn curves) for the solutions A, B, and D. The lower full-drawn curve gives the estimated amount of incoherent radiation reaching the counter.

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 inter-molecular 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
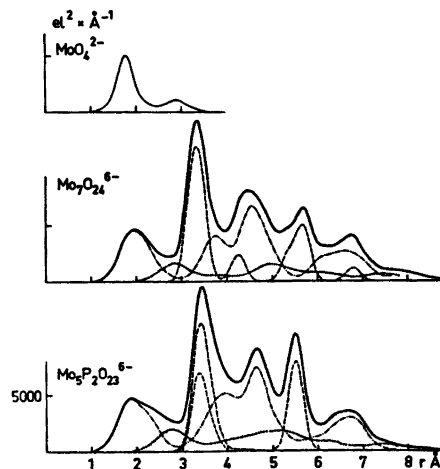

Fig. 5. Radial distribution curves, $D(r)$. Dotted curves represent the sum of intramolecular contributions calculated from the parameters in Table 3. Broken curves represent the difference between the experimental $D(r)$ function and the calculated intramolecular contributions.

tions of the atoms in the complexes $Mo_7O_{24}{}^{6-}$ [11] and $Mo_5P_2O_{23}{}^{6-}$ [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_5 Å corresponds to the expected Mo − O distance. For comparison the calculated peak shape for a tetrahedral $MoO_4{}^{2-}$ ion is shown in Fig. 6.

When the intramolecular interactions within the $Mo_7O_{24}{}^{6-}$, the $Mo_5P_2O_{23}{}^{6-}$, and the $ClO_4{}^{-}$ groups for the acidified solutions, and the $MoO_4{}^{2-}$ and the $PO_4{}^{3-}$ 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

Fig. 6. Calculated peak shapes for the $Mo_7O_{24}{}^{6-}$ and the $Mo_5P_2O_{23}{}^{6-}$ complexes and for a tetrahedral $MoO_4{}^{2-}$ group. The parameters used for the calculations are given in Table 3. For the $Mo_7O_{24}{}^{6-}$ complexes the contributions from Mo − Mo (dashed lines), Mo − O (dashed-dotted lines), and O − O (dotted lines) interactions are separately drawn. The same is done for the $Mo_5P_2O_{23}{}^{6-}$ complex but here the dashed-dotted line represents the sum of Mo − O and P − O interactions, and the two peaks at 3.3 Å represent Mo − Mo interactions (small peak) and the sum of Mo − Mo and Mo − P interactions (large peak).
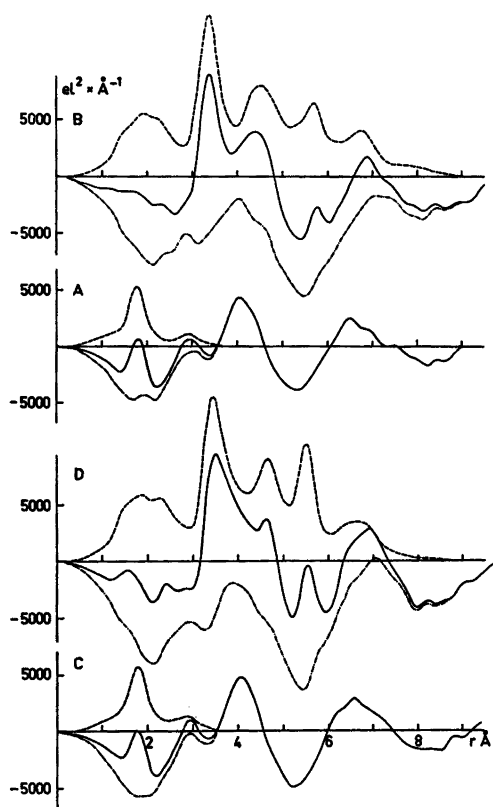
Fig. 7. Radial distribution functions for the solutions A, B, C, and D. Full-drawn lines represent the experimental $D(r) - 4\pi r^2 \varrho_0$ functions. Dashed lines are the sum of calculated peaks for intramolecular interactions obtained with the parameters in Table 3. Dashed-dotted lines are the corresponding differences.

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

Molecule	Intramolecular distances	(Å)	Temperature factor (Å²)
$MoO_4{}^{2-}$	Mo – O	1.75	0.002
	O – O	2.86	0.004
$Mo_7O_{24}{}^{6-}$	Mo – Mo	*a*	0.002
	Mo – O	*a*	0.006
	O – O	*a*	0.01
$Mo_5P_2O_{23}{}^{6-}$	Mo – Mo ⎫		
	Mo – P ⎬	*b*	0.002
	P – P ⎭		
	Mo – O ⎫	*b*	0.006
	P – O ⎬		
	O – O	*b*	0.01
$ClO_4{}^-$	Cl – O	1.43	0.002
	O – O	2.34	0.002
$PO_4{}^{3-}$	P – O	1.54	0.002
	O – O	2.51	0.004
H_2O	O – H	1.0	0.004

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

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 $Mo_7O_{24}{}^{6-}$ and the $Mo_5P_2O_{23}{}^{6-}$ 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-

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_2 Å found for the discrete $MoO_4{}^{2-}$ ions in crystals of $Na_2MoO_4 \cdot (H_2O)_2$.[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 $Mo_7O_{24}{}^{6-}$ and the $Mo_5P_2O_{23}{}^{6-}$

complexes should result in closely similar inter-molecular 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 $Mo_7O_{24}{}^{6-}$ complexes, was increased to 947 ų in order to give the same average scattering power, ϱ_0, as solution D (Table 1).

The difference between solution B, containing $Mo_7O_{24}{}^{6-}$ complexes, and solution D, containing $Mo_5P_2O_{23}{}^{6-}$ 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
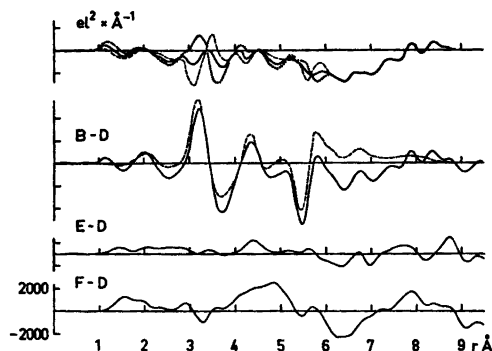

Fig. 8. Differences curves between the radial distribution functions for the solutions and between calculated peak shapes for the assumed intramolecular interactions. The full-drawn curves marked B−D, E−D, and F−D represent the functions obtained by subtracting the $D(r) - 4\pi r^2 \varrho_0$ function 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 Å, 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 $HMo_5P_2O_{23}{}^{5-}$ (Fig. 2). The difference between the $D(r) - 4\pi r^2 \varrho_0$ function for this solution and for solution D, containing the $Mo_5P_2O_{23}{}^{6-}$ complexes, is shown in Fig. 8. No significant peaks are present and, apparently, the addition of a proton to the $Mo_5P_2O_{23}{}^{6-}$ complex does not change its basic structure.

In solution F the predominant complex should have the composition $H_2Mo_5P_2O_{23}{}^{4-}$ according to emf measurements.[1−3] The discrete complex $H_2Mo_5P_2O_{23}{}^{4-}$ has been found in crystals and the structure determination [5] has shown it to be built up in the same way as the $Mo_5P_2O_{23}{}^{6-}$ complex 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 $H_2Mo_5P_2O_{23}{}^{4-}$ and $Mo_5P_2O_{23}{}^{6-}$, 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 $Mo_5P_2O_{23}{}^{6-}$ and the $Mo_7O_{24}{}^{6-}$ units found in crystals. However, since the distribution curves give only one-dimensional representations of the

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 $Mo_5P_2O_{23}{}^{6-}$ and $Mo_7O_{24}{}^{6-}$ units found in crystal structures,[4,5,10,11,23] with polymolybdate species in solution, which have been identified by equi-

librium studies.[1-3,7] 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 $H_2Mo_5P_2O_{23}{}^{4-}$ 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 $Na_3H_6Mo_9PO_{34}(H_2O)_{12}{}^{24}$ and $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$,[25] which contain discrete polynuclear complexes. X-Ray scattering measurements are now being made to identify these complexes in the solutions. In the binary $H^+-MoO_4{}^{2-}$ system the solubilities of the molybdate complexes at the larger $H^+/MoO_4{}^{2-}$ ratios 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.

REFERENCES

1. Pettersson, L. *Acta Chem. Scand.* 25 (1971) 1959.
2. Pettersson, L., Andersson, I., Lyhamn, L. and Ingri, N. *Trans. Roy. Inst. Technol. Stockholm 1972* No. 256.
3. Pettersson, L. *Chem. Scr.* 7 (1975) 145.
4. Strandberg, R. *Acta Chem. Scand.* 27 (1973) 1004.
5. Hedman, B. *Acta Chem. Scand.* 27 (1973) 3335.

6. Sillén, L. G. and Martell, A. E. (compilers). *Stability Constants, Chem. Soc. Spec. Publ. No. 17* (1964); *Suppl. No. 1, Spec. Publ. No. 25* (1971).
7. Sasaki, Y. and Sillén, L. G. *Acta Chem. Scand. 18* (1964) 1014; *Ark. Kemi 29* (1968) 253.
8. Aveston, J., Anacker, E. W. and Johnson, J. S. *Inorg. Chem. 3* (1964) 735.
9. Lindqvist, I. *Ark. Kemi 2* (1950) 325.
10. Gatehouse, B. M. and Leverett, P. *Chem. Commun. 15* (1968) 901.
11. Sjöbom, K. and Hedman, B. *Acta Chem. Scand. 27* (1973) 3673.
12. Dunitz, J. D. and Ibers, J. A. *Perspectives in Structural Chemistry*, Vol IV, Wiley, New York 1971, p. 36.
13. Johansson, G. *Acta Chem. Scand. 25* (1971) 2787; *20* (1966) 553.
14. Pocev, S. and Johansson, G. *Acta Chem. Scand. 27* (1973) 2146.
15. Johansson, G. and Sandström, M. *Chem. Scr. 4* (1973) 195.
16. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
17. Stewart, R. F., Davidson, E. K. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
18. Cromer, D. T. *Acta Crystallogr. 18* (1965) 17.
19. Cromer, D. T. and Mann, J. B. *J. Chem. Phys. 47* (1967) 1892.
20. Cromer, D. T. *J. Chem. Phys. 50* (1969) 4857.
21. Compton, A. H. and Allison, S. K. *X-Rays in Theory and Experiment*, van Nostrand, New York 1935.
22. Yamamura, K., Kobayashi, A. and Sasaki, Y. *Private communications*.
23. Evans, H. T., Jr. *J. Amer. Chem. Soc. 90* (1968) 3275.
24. Strandberg, R. *Acta Chem. Scand. A 28* (1974) 217.
25. Strandberg, R. *Acta Chem. Scand. To be published*.

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