A Large-angle X-Ray Scattering Study of

9-Molybdomonophosphate Complexes in Aqueous Solution

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Radial distribution curves have been calculated from X-ray scattering measurements on two solutions which according to equilibrium data contain complexes of the compositions $(H^+)_{15}(MoO_4^{2-})_9$-(HPO_4^{2-}) and $(H^+)_{16}(MoO_4^{2-})_9(HPO_4^{2-})$. Comparison with calculated peak shapes for intramolecular interactions within the complex $Mo_9PO_{31}(OH_2)_3^{3-}$, which is known from a crystal structure determination, shows the complexes in solution to have the same basic structure. Small differences in the interatomic distances are, however, found, which can be ascribed to slightly changed positions of the Mo atoms.

The aqueous three component equilibria $pH^+ + qMoO_4^{2-} + rHPO_4^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q$-$(HPO_4^{2-})_r$ have been extensively studied mainly by means of emf methods at 25 °C and in 3.0 M $Na(ClO_4)$ medium.[1–4] The existence of two series of complexes has been established. For $B/C \leq 2.5$ (with B the total molybdenum concentration and C the total phosphorus concentration in the solution) the predominant ternary complexes formed are $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$ with $p=8$, 9 and 10. For $B/C \geq 9$ and $-\log [H^+] < 5$ the predominant complexes are $(H^+)_p(MoO_4^{2-})_9$-(HPO_4^{2-}) with $p=14$, 15, 16 and 17. For simplicity these complexes will in the following often be referred to by their (p,q,r) values.

By slow evaporation of equilibrium solutions, crystalline phases with compositions corresponding to those of all the three proposed pentamolybdodiphosphates and one of the four 9-molybdomonophosphates have been obtained. Structure determinations have shown the crystals to contain discrete polyanions $Mo_5P_2O_{23}^{6-}$,[5,6]

$HMo_5P_2O_{23}^{5-}$,[7] $H_2Mo_5P_2O_{23}^{4-}$,[8] (corresponding to the (8,5,2) (9,5,2) and (10,5,2) complexes, respectively) and $Mo_9PO_{31}(OH_2)_3^{3-}$,[9,10] (corresponding to the (17,9,1) complex). Since the number of water molecules in a complex cannot be deduced from the emf data, $(H^+)_8(MoO_4^{2-})_5$-$(HPO_4^{2-})_2$ is equivalent to $Mo_5P_2O_{23}^{6-}$, $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})$ to $Mo_9PO_{31}(OH_2)_3^{3-}$ etc.

X-Ray diffraction measurements on solutions of the pentamolybdodiphosphates were reported in a previous paper,[11] in which a comparison was made between the structure of the pentamolybdodiphosphates in solution and the structure of the discrete $Mo_5P_2O_{23}$ groups found in crystals. In the present paper a similar investigation of the 9-molybdomonophosphate complexes is reported.

EXPERIMENTAL

Solutions investigated. In order to get significant effects in the diffraction curves high concentrations of the complexes in the solutions are necessary. For $B/C=9$, the ratio at which an optimal amount of 9-molybdomonophosphate complexes is formed, solutions with concentrations larger than about 1.6 M in molybdate cannot be prepared. By means of the stability constants given by Pettersson,[3] the fraction of molybdenum bound in the different complexes has been calculated for a molybdophosphate solution as a function of $-\log [H^+]$ for $B=1.60$ M and $C=0.178$ M ($B/C=9$). The distribution of complexes is shown in Fig. 1. Provided that the stability constants are valid at this high concentration, it should, therefore, be possible to prepare solutions, which are practically pure in either the (15,9,1) or the (16,9,1) complex, *i.e.* in $(H^+)_p(MoO_4^{2-})_9(HPO_4^{2-})$ with $p=15$ or 16.
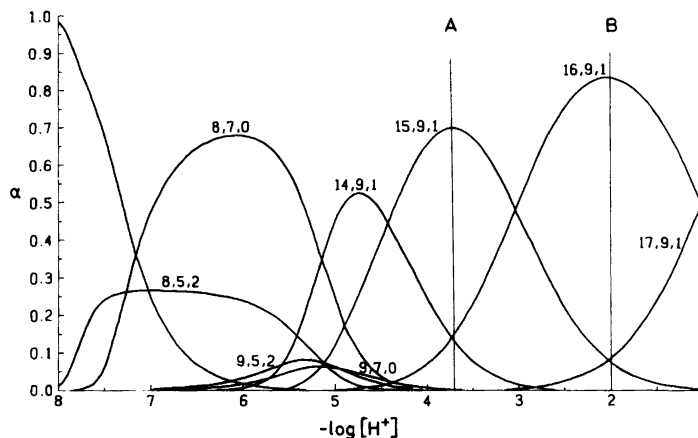
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Fig. 1. The fraction of molybdenum, α, bound in different complexes in a 1.6 M molybdate solution with an Mo(VI)/P(V) ratio of 9.0, as a function of log[H$^+$]. The stability constants given by Pettersson[3] have been used for the calculation.

Solutions with compositions given by A and B in Fig. 1 and in Table 1 were chosen for the diffraction measurements. For the analysis of the X-ray data three reference solutions, C, D, and E, were used, the compositions of which are given in Table 1. These solutions should contain all molybdenum bound as $Mo_5P_2O_{23}^{6-}$, $Mo_7O_{24}^{6-}$ and MoO_4^{2-}, respectively.[11]

X-Ray measurements. The scattering measurements and the data treatment were carried out as described in previous papers.[11-14] AgKα-radiation

was used. The measured intensities were normalized to a stoichiometric unit of volume containing one molybdenum atom. For one of the solutions the normalized intensity values, $I(s)$, the independent coherent scattering $\sum_i f_i^2$, with the summation carried out over all atoms in a stoichiometric unit, and the incoherent scattering reaching the counter are shown in Fig. 2 as a function of $s = 4\pi\lambda^{-1} \sin\theta$, ($\lambda = 0.5608$ Å). The scattering factors, f_i, were taken from the same sources as in the previous work.[11]

The corresponding reduced intensity values

Table 1. Composition of solutions.

|	A (15,9,1)	B (16,9,1)	C (8,5,2)	D (8,7,0)	E (0,1,0)
Concentrations in mol/l					
Mo	1.600	1.600	1.770	2.040	2.035
P	0.178	0.178	0.710	–	–
Na	3.378	3.378	4.250	4.080	4.070
Cl	2.489	2.678	2.120	2.330	–
O	61.6	61.7	62.5	61.9	59.0
H	91.9	90.8	91.7	91.1	101.6
Number of atoms in the unit of volume, V					
Mo	1	1	1	1	1
P	0.111	0.111	0.401	–	–
Na	2.111	2.111	2.401	2.000	2.000
Cl	1.556	1.674	1.198	1.142	–
O	38.5	38.6	35.3	30.3	29.0
H	57.4	56.7	51.8	44.7	49.9
$V/\text{Å}^3$	1038	1038	938.2	814.0	816.0
$\rho_0/\text{el}^2\text{Å}^{-3}$	202.8	204.4	196.2	168.9	146.4
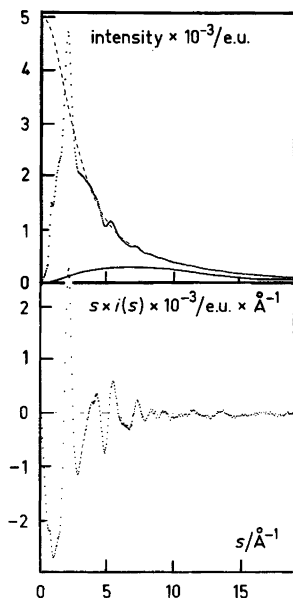
Fig. 2. The normalized intensity values (dots), the independent coherent scattering (dashed line) and the incoherent scattering, estimated to reach the counter (solid line), as a function of $s = 4\pi\lambda^{-1} \sin \theta$, for the solution B (upper part) and the reduced intensity values, given as $si(s)$, for the same solution (lower part).
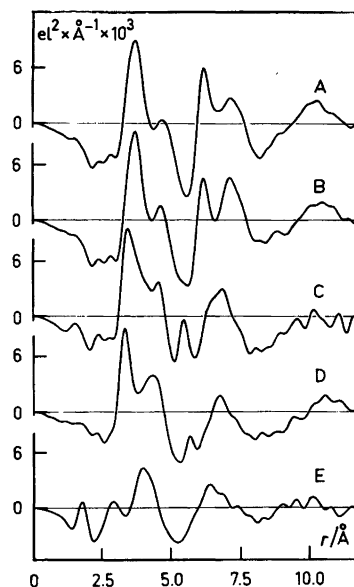
Fig. 3. The $D(r) - 4\pi r^2 \rho_0$ functions for the solutions A and B and for the reference solutions C, D, and E, the compositions of which are given in Table 1.

$i(s) = I(s) - \sum_i f_i^2$, multiplied by s, are shown in the same figure. The radial distribution functions, $D(r)$, were calculated as

$$4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{max}} s \, i(s) \, M(s) \sin (rs) \, ds.$$

The modification function, $M(s)$, was chosen to be $\{f_{Mo}^2(0)/f_{Mo}^2(s)\} \exp (-0.01s^2)$. The functions $D(r) - 4\pi r^2 \rho_0$ are shown in Fig. 3.

ANALYSIS OF THE DATA

The representation of the scattering data, that seems best suited for the analysis, is the distribution function $D(r) - 4\pi r^2 \rho_0$ given in Fig. 3. The pronounced peaks obtained for the solutions A and B are indicative of the occurrence of polynuclear complexes. This is particularly apparent when comparing with the corresponding function for the alkaline molybdate solution (E in Fig. 3) in which only mononuclear tetrahedral MoO_4^{2-} ions should be present.

Approximate shape functions for the polymolybdates in the solutions A and B were derived by the following procedure, which makes use of the scattering data from the reference solutions C, D and E, for which the structures of the complexes are known.[11]

Theoretical $i(s)$ values can be calculated by summing over all pair interactions. Assuming the solutions to contain discrete complexes: $(H^+)_p (MoO_4^{2-})_q (HPO_4^{2-})_r$, ClO_4^-, Na^+, and H_2O, the summation can be separated into intra- and intermolecular interactions:

$$i(s) = \sum_j n_j \{i_{intra}(s) + i_{inter}(s)\}$$

where n_j is the number of molecules "j" in the stoichiometric unit of volume, V. A simple approximation for the intermolecular interactions is to assume each complex to occupy a spherical hole of radius R_j in a uniform scattering density. The following expressions will then hold for each complex:[14]

Table 2. Parameter values used in the calculations of the shape functions.

Complex	Intramolecular distances, Å	Temperature coefficients			Intermolecular interactions	
		Mo − Mo	Mo − O	O − O	R	B
MoO_4^{2-}	Mo − O 1.79	−	0.003	0.0002	3.0	0.02
ClO_4^{-}	Cl − O 1.43	−	0.002	0.002	2.8	0.02
H_2O	−				1.8	0.02
$Mo_5P_2O_{23}$	see Ref. 5	0.004	0.002	0	5.0	0.02
Mo_7O_{24}	see Ref. 18	0.002	0.004	0.006	5.5	0.02
Mo_9PO_{34}	see Ref. 9	0.006	0.006	0.006	6.5	0.02
$Mo_{18}P_2O_{62}$	see Ref. 15	0.006	0.006	0.006	8.5	0.02

$$i_{intra}(s) = \sum_{u \neq v} \Sigma f_u f_v \sin sr_{uv}/(sr_{uv}) \exp(-b_{uv}s^2)$$

$$i_{inter}(s) \approx i_{sphere}(s) =$$

$$- (4\pi R_j^3)/(3V)3[\sin sR_j - sR_j \cos sR_j]/(sR_j)^3 \times$$

$$\exp(-B_js^2)\sum_{u=1}^{m}f_u \sin(sr_u)/(sr_u)\sum_{n=1}^{n_{stoich}} n_if_i$$

where the last two summations are over the number of atoms in the complex (m) and the number of atoms (n_{stoich}) in the stoichiometric unit of volume, respectively. Distances within a molecule are represented by r_{uv} and b_{uv} and B_j are temperature factors.

The total expression for $i(s)$ can now be written as

$$i(s) = \sum_j n_j\{i_{intra}(s) + i_{sphere}(s)\} + i_{corr}$$

where i_{corr} represents contributions from remaining structure in the solution not taken into account by the idealized model.

A Fourier transformation of each separate term in the expression for $i(s)$ gives the corresponding contribution to the distribution function:

$$D(r) - 4\pi r^2\rho_0 = \sum_j n_j\{P_j(intra) + P_j(sphere)\} + P_{corr}$$

From the experimental distribution curves and the known structures of the complexes the P_{corr} terms can easily be derived for the reference solutions C, D and E. If the values obtained are used as approximations for the corresponding terms for the solutions A and B the peak shapes for the molybdate complexes in these solutions can be derived.

The parameter values used in the calculations are given in Table 2. The resulting shape functions as derived from the C, D, and E reference solutions, respectively, are shown in Fig. 4. The differences between them are minor, in particular between the shape functions derived with the use of the two reference solutions C and D, which both contain polynuclear complexes. This may be taken as a confirmation that differences between the P_{corr} terms do not seriously affect the derived shape functions.

Information from crystal structure determinations. From (16,9,1) solutions (B in Table 1) two types of
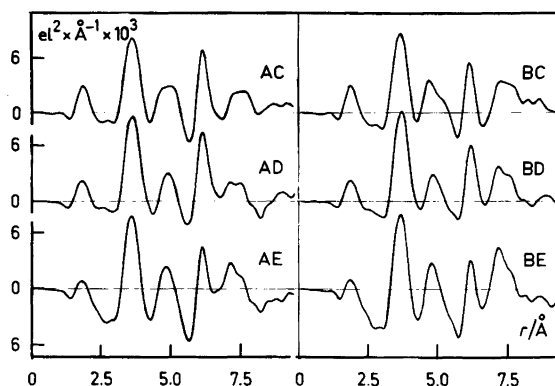

Fig. 4. The shape functions for the polymolybdate complexes in the solutions A and B derived with the use of the reference solutions C, D, and E, respectively.
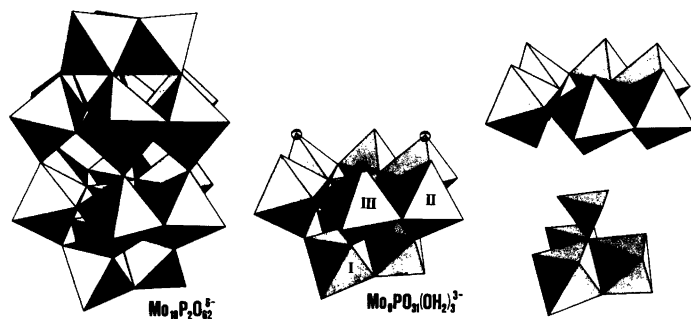
Fig. 5. The structures of the $Mo_9PO_{31}(OH_2)_3^{3-}$ and the $Mo_{18}P_2O_{62}^{6-}$ complexes as found in the crystal structure determinations of $Na_3H_6Mo_9PO_{34}(H_2O)_{12-13}$ and $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$ by Strandberg.[9,15] The water molecules bonded to the MoIII atoms in $Mo_9PO_{31}(OH_2)_3^{3-}$ are marked by circles. In the right-hand side of the figure the Mo_9PO_{34} group is separated into two parts: The ring of six MoO_6 octahedra and the compact group of three edge-sharing octahedra with the attached PO_4 tetrahedron.

crystals with the compositions $Na_3H_6Mo_9PO_{34}$-$(H_2O)_{12-13}$ and $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$ can be obtained. Crystal structure determinations carried out by Strandberg show both of them to contain discrete polyanions with the formulae Mo_9PO_{31}-$(OH_2)_3^{3-}$,[9] and $Mo_{18}P_2O_{62}^{6-}$,[15] respectively. Their structures are illustrated in Fig. 5.

Apart from the number of protons, the Mo_9PO_{34} group has a composition which is equivalent to that derived from emf measurements ($Mo_9PO_{34}^{9-}$ + $6H^+ + 6H_2O = (H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})$). Its structure is related to the well-known Keggin model for $PW_{12}O_{40}^{3-}$,[16] from which it can be derived by removing three of the twelve MoO_6 octahedra. The $Mo_{18}P_2O_{62}$ group is closely related to the structure of the $P_2W_{18}O_{62}$ group determined by Dawson,[17] although the molybdenum atoms within the two six-fold rings are zigzagged. The group may be considered as being built up by a condensation of two $Mo_9PO_{31}(OH_2)_3^{3-}$ groups.

The parameters from the crystal structure determination were used to calculate the expected contribution from an Mo_9PO_{34} complex to the radial distribution curve. The resulting "molecular peak shape" normalized to the same molybdenum concentration and the same stoichiometric unit of volume as the experimental data, is compared in Fig. 6 with the shape function derived for the solutions A and B. The same has been done for the $Mo_{18}P_2O_{62}$ complex and for a fraction of the Mo_9PO_{34} group Mo_6PO_{28}, *i.e.* the ring of six MoO_6 octahedra with the attached PO_4 tetrahedron. These units are illustrated in Fig. 5.

Since the same characteristic unit of six edge and

corner sharing MoO_6 octahedra occurs in all the three complexes used for the comparison, many of the characteristic features in their shape functions are similar. The same features appear also in the shape functions derived from the scattering data. It is obvious, however, that the number of interactions — as judged by the peak sizes — in the experimental curves are in best agreement with those calculated for the Mo_9PO_{34} unit.

Structural differences between the Mo_9PO_{34} group in solution and in crystals. Although the shape
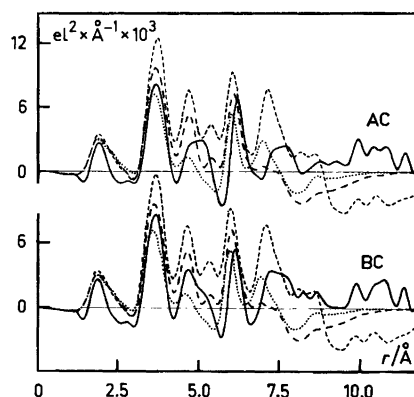

Fig. 6. Comparison between the derived shape functions for the polymolybdate complexes in the solutions A and B (solid lines) and the sum of the peak shapes calculated from the crystal structure parameters for the complexes $Mo_{18}P_2O_{62}$ (short dashes), Mo_9PO_{34} (long dashes), and Mo_6PO_{28} (dots). The parameter values used are summarized in Table 2.

function derived from the experimental distribution curves is consistent with the calculated shape function for the Mo_9PO_{34} group, deviations occur primarily in the region around 5 to 6 Å. The two peaks at 4.7 and 5.4 Å in the calculated function correspond to a single broad peak in the experimental curve. This is independent of the reference solution used for the derivation of the shape function (Fig. 4) and, therefore, probably reflects a difference in structure between the complex in the crystalline state and in solution.

In Fig. 7 the separate contributions from the different types of intramolecular interactions to the shape function of the Mo_9PO_{34} complex are given. The O−O interactions, although the largest in number, result in a rather smooth curve, which does not significantly contribute to the characteristic features of the total curve. The Mo−O interactions, which are also large in number, give more pronounced contributions to the curve, but the main features are caused by the well-defined Mo−Mo (and Mo−P) interactions. Minor changes in the
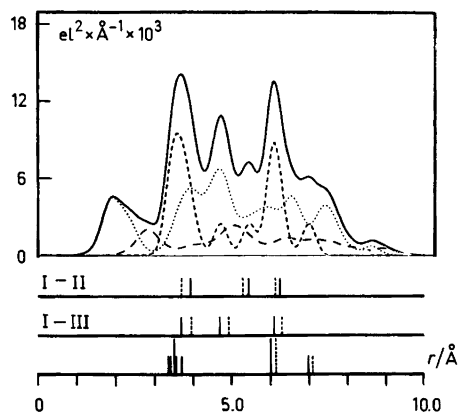

Fig. 7. The shape function for the Mo_9PO_{34} complex (solid line) as calculated from the crystal structure parameters (Table 2). Separately shown are the contributions to the shape function from O−O interactions (long dashes), Mo(P)−O interactions (dots), and Mo(P)−Mo(P) interactions (short dashes). The distances between the Mo atoms (MoI−MoII and MoI−MoIII on the two upper lines and remaining distances on the lower line) are marked by vertical lines having heights proportional to the frequency of the distances. Full lines are calculated from the crystal structure parameters. Dashed lines are calculated for the modified structure giving the best agreement with the distribution curves.

structure leading to changed Mo−Mo distances should, therefore, show up clearly in the distribution curves, while corresponding changes in the Mo−O distances would probably to a large extent average out causing only minor changes. The search for a structural interpretation of the differences between the observed and the calculated distribution curves was, therefore, limited to the Mo positions, assuming the Mo−O, P−O, and O−O interactions to be unchanged.

The Mo−Mo distances calculated with the use of the crystal structure parameters[9] are marked in Fig. 7. Three crystallographically independent Mo atoms occur within the Mo_9PO_{34} group: MoI in the compact group of three octahedra sharing edges, MoII and MoIII in the ring of six octahedra sharing corners and edges (Fig. 5). The MoIII atoms are closer to MoI than are the MoII atoms. In relation to the best plane through the Mo atoms in the ring of six MoO_6 octahedra, which is parallel to a plane through the three MoI atoms, MoIII is situated 0.3 Å below while Mo II is 0.3 Å above this plane. The three water molecules, incorporated into the complex in the crystals, are bonded to the MoIII atoms, which leads to a long distance, 2.21 Å, from MoIII to its apex oxygen, compared to only 1.70 Å for the corresponding MoII−O distance.

The two separated peaks at 4.7 and 5.4 Å observed in the shape function calculated from the crystal structure parameters result from the different MoIII−MoI and MoII−MoI distances. Con-
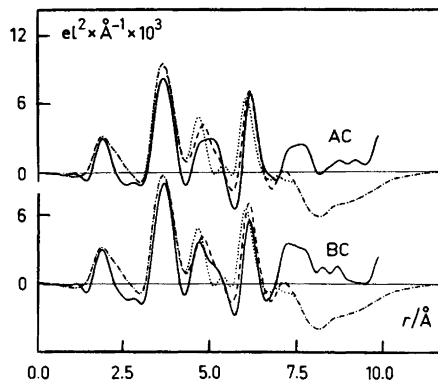

Fig. 8. Comparison of the derived shape functions (solid lines) for the polymolybdate complexes in solutions A and B with calculated functions for a Mo_9PO_{34} complex. The dotted lines are obtained with the crystal structure parameters, and the dashed lines with the modified parameter values.

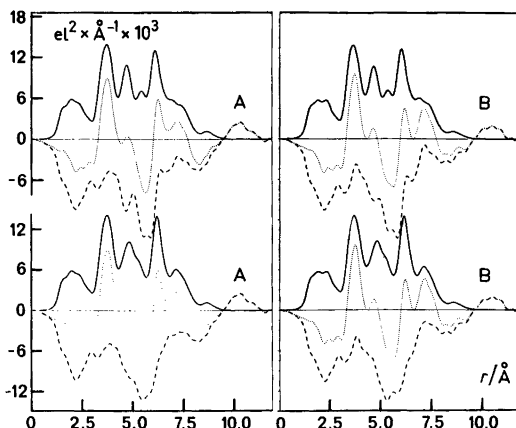*Fig. 9.* Comparison between the $(D(r) - 4\pi r^2 \rho_0)$ functions (dotted lines) for the solutions A and B and the shape function for an Mo_9PO_{34} complex (solid lines) calculated from the crystal structure parameters (upper part) and from the modified parameter values (lower part). Dashed lines are corresponding differences.

ceivably, therefore, since these peaks are not separated in the shape function derived for the complexes in solution, the corresponding distances in solution are more equal, possibly as a result of a change in the number of protons attached to the oxygen atoms of MoIII and MoII. A markedly improved agreement between observed and calculated shape functions is obtained by making the MoI – MoIII and MoI – MoII distances more equal and by slightly enlarging the six-ring. From systematic variations of the Mo positions a "best" set of parameter values was obtained, which corresponded to almost equal MoIII – MoI and MoII – MoI distances, with all the MoII and MoIII atoms positioned in a plane parallel to the plane through the MoI atoms. The resulting shape function is shown in Fig. 8. The relation between the Mo – Mo distances obtained with this set of parameter values and the Mo – Mo distances in the crystal structure is shown in Fig. 7.

The parameter values giving the best agreement between observed and calculated shape functions (Fig. 8) also lead to the smoothest background curves when the corresponding peak shapes are subtracted from the $D(r) - 4\pi r^2 \rho_0$ functions (Fig. 9).

For solution B the results indicate that the same conclusions are valid as those derived for A. There are, however, indications that in B part of the molybdenum may occur as larger complexes, probably as $Mo_{18}P_2O_{62}$, since the peak at 7.2 Å is relatively more pronounced than for solution A.

The additional intramolecular interactions of $Mo_{18}P_2P_{62}$ compared to those of Mo_9PO_{34} are, however, rather evenly distributed over the shape function and, therefore, do not lead to any characteristic differences between the two complexes, (Fig. 6), apart from the long distances for $r > 6$ Å. This makes the distribution curves less useful for a differentiation between them.

DISCUSSION OF THE RESULTS

The scattering data confirm that the (15,9,1) complex, *i.e.* $(H^+)_{15}(MoO_4^{2-})_9(HPO_4^{2-})$, used by Pettersson for the interpretation of emf data on molybdophosphate solutions (Fig. 1), has the same basic structure as the discrete polyanions Mo_9PO_{31}-$(OH_2)_3^{3-}$, found in crystals of $Na_3H_6Mo_9PO_{34}$-$(H_2O)_{12-13}$.[9] In a slightly more acid solution, which according to emf data should contain the (16,9,1) complex (Fig. 1), part of the molybdate seems to be bonded in larger complexes, probably dimers of $Mo_9PO_{31}(OH_2)_3^{3-}$ which have the formula $Mo_{18}P_2O_{62}^{6-}$ and are found as discrete polyanions in crystals of $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$.[15]

These conclusions are supported by Raman measurements.[4] Raman spectra of solution A and of $Na_3H_6Mo_9PO_{34}(H_2O)_{12-13}$ are similar. In the Raman spectrum of solution B, however, a new strong peak appears, which is also present in Raman spectra from crystals of $Na_6Mo_{18}P_2O_{62}$-$(H_2O)_{24}$.

The slight difference between the structure of the Mo_9PO_{34} complexes in solution and in crystals as indicated by the radial distribution curves can be ascribed to slightly changed positions of the Mo atoms in the ring of six octahedra, which forms part of the Mo_9PO_{34} structure (Fig. 5). The structural change may be caused by a change in the positions of the protons attached to the group.

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