On the Identification of Molybdophosphate Complexes in Aqueous Solution

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Aqueous solutions containing sodium phosphate and sodium molybdate ([P] = 0.01—0.07 mol l^{-1}, [Mo] : [P] = 1.25—15) were acidified with concentrated HCl and the formation of molybdophosphate anions was followed by ^{31}P n.m.r. spectroscopy with a view to establishing this technique as an easily applicable method for the identification of molybdophosphate species in solution. For comparative purposes and to aid the interpretation of the n.m.r. spectra, Raman spectroscopy and differential pulse polarography were also applied. Of the eight n.m.r. resonances observed, two had already been reported: they stem from $[PMo_{12}O_{40}]^{3-}$ and $[P_2Mo_{18}O_{62}]^{6-}$. Lines corresponding to $[P_2Mo_5O_{23}]^{6-}$, $[PMo_9O_{31}(OH)_3]^{6-}$, and $[PMo_{11}O_{39}]^{7-}$ were also identified. A controversy concerning the relative importance of the last two species has been resolved. Three lines could not be unequivocally assigned: one may correspond to $[PMo_{10}O_{34}]^{3-}$, one to $[PMo_6O_{25}]^{9-}$, while for the third there are no further data on which to base a suggestion. It is shown that various reports concerning molybdophosphate solutions are inconsistent with the pertinent ^{31}P n.m.r. spectroscopic data.

Molybdate-containing impregnation solutions used to prepare hydrodesulphuration catalysts, (Co)Mo–Al_2O_3, often also contain phosphoric acid. In the context of the precise role of this acid we became interested in easily applicable methods to identify molybdophosphate complexes in solution. Apparently, none was available.

The most important early contribution to the study of acidified phosphate–molybdate solutions is that by Souchay.[1,2] More recently, much attention has been devoted to the subject by Ingri's group at the University of Umeå.[3–12] Unfortunately, the two groups are not in agreement as to what species exist(s) in solution. Taking into account other recent literature,[13] the following points can be established. (*i*) The existence of $[P_2Mo_5O_{23}]^{6-}$, $[P_2Mo_{18}O_{62}]^{6-}$, and $[PMo_{12}O_{40}]^{3-}$ has been demonstrated beyond doubt. (*ii*) The relative importance of $[PMo_{11}O_{39}]^{7-}$ and $[PMo_9O_{31}(OH)_3]^{6-}$ is controversial. The latter species is greatly favoured by the Umeå group, but is not mentioned by most other workers. Indeed, one and the same Raman spectrum has been ascribed to the former[14] and to the latter[7]! On the other hand, under certain conditions $[PMo_9O_{31}(OH)_3]^{6-}$ can be made to crystallize[9,15] and so this species is likely to exist in solution as well. (*iii*) There is no universal agreement on the stoicheiometry of $[PMo_{11}O_{39}]^{7-}$, Murata and Ikeda,[16] *e.g.*, preferring the formula $[PMo_{11}O_{37}]^{3-}$. (*iv*) Rather ill defined species are $[PMo_{10}O_{34}]^{3-}$, mentioned in a study of the decomposition kinetics of $[PMo_{12}O_{40}]^{3-}$,[17] and $[P_2Mo_2O_{13}]^{4-}$ mentioned by Souchay and Faucherre.[1]

It appears, then, that although a wide variety of experimental techniques has been applied, *viz.* Raman and u.v. spectroscopy, large-angle *X*-ray scattering, potentiometry, formation and decomposition kinetics, cyclic voltammetry, and a.c. polarography,[18] and crystallization followed by elemental analysis and (sometimes) structure determination, none has been established as a reliable means to identify molybdophosphate species in solution. What is surprising is that the one method that could be expected to provide such means, *viz.* ^{31}P n.m.r. spectroscopy, has not been widely applied: spectra are known only for $[PMo_{12}O_{40}]^{3-}$ and $[P_2Mo_{18}O_{62}]^{6-}$.[19–22] The object of the present study was to ascertain the ability of this technique to elucidate heteropolyanion formation in acidified phosphate–molybdate solutions. For comparison and to aid in the interpretation of the n.m.r. data, we also employed Raman spectra and differential pulse polarography (d.p.p.), both methods being easy to apply and yielding results that should also be sensitive to relatively small changes in molybdophosphate structure. When this study had also been completed, a paper from the Umeå group appeared,[23] in which some preliminary results of a similar n.m.r. study were reported, mainly pertaining to $[P_2Mo_5O_{23}]^{6-}$.

Experimental

The salts $Na_2[MoO_4]\cdot 2H_2O$ (Merck p.A.) and $Na_3PO_4\cdot 12H_2O$ (UCB pur) were dissolved in demineralized water and the resulting solutions acidified with concentrated HCl. Phosphate concentrations were between 0.01 and 0.07 mol l^{-1} and the phosphate:molybdate molar ratio was varied from 1:1.25 to 1:15.

Raman spectra of the acidified solutions were obtained with a Spex Ramalog RSS-1 and a Spex Triplemate spectrometer (excitation with the 488-nm line of an argon-ion laser). The ^{31}P n.m.r. spectra were recorded on a Bruker WM 250 instrument (101.3 MHz), chemical shifts being negative to higher field and referenced to external 85% H_3PO_4. Differential pulse polarograms were measured using a conventional three-electrode cell, a PAR model 174A polarographic analyzer, and a Wenking model VSG 72 voltage scan generator (for a brief description of the technique see ref. 24). A saturated calomel electrode (s.c.e.) served as reference electrode, and a gold button as measuring electrode.

Results and Discussion

First we will discuss the ^{31}P n.m.r. results and show how the main signals observed can be attributed to the various molybdophosphate anions, then the Raman and d.p.p. results. It will become apparent that although ^{31}P n.m.r. is much the best of the three techniques for dealing with mixtures of heteropolyanions, Raman and d.p.p. can nevertheless be used to fortify some of the n.m.r. assignments proposed. Lastly, we will make use of the results obtained in a discussion of the inconsistencies noted in the Introduction and of some related questions.

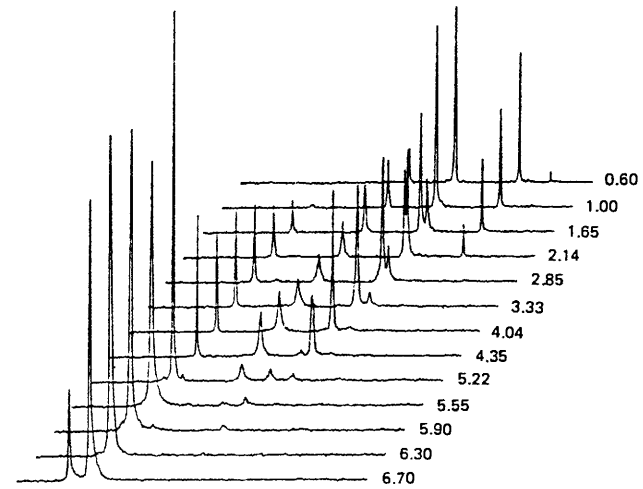

Figure 1. ^{31}P N.m.r. spectra of Na_2MoO_4–Na_3PO_4 solutions. [P] = 0.06, [Mo] = 0.54 mol l^{-1}. The signal at δ 2.8 p.p.m. (pH 6.70) is due to free phosphate

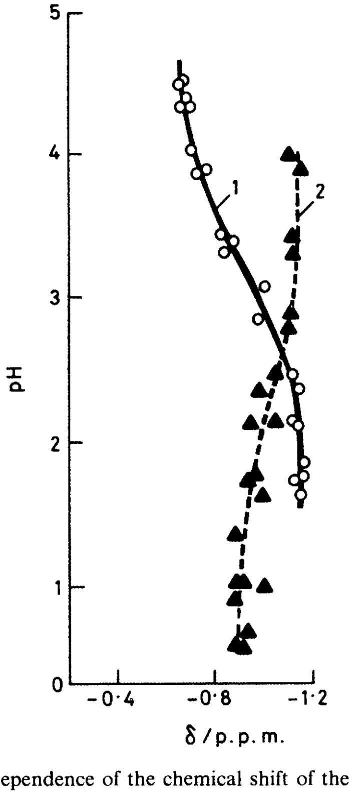

Figure 2. pH Dependence of the chemical shift of the two resonances occurring around δ −1 p.p.m. Signals 1 are due to $[PMo_{11}O_{39}]^{7-}$, signals 2 to $[PMo_9O_{31}(OH)_3]^{6-}$ (see text)

^{31}P *N.M.R. Spectroscopy.*—A series of ^{31}P n.m.r. spectra for acidified phosphate–molybdate solutions, [P]:[Mo] = 1:9 and [P] = 0.06 mol l^{-1}, is shown in Figure 1. As expected, the structure is quite rich, and we have only to find out which signal corresponds to which species.

The conditions under which $[PMo_{12}O_{40}]^{3-}$ and $[P_2Mo_{18}O_{62}]^{6-}$ exist in solution are well known,[1,2,10,18,19,21] and from the spectra of the pertinent solutions we attribute δ = −3.2 p.p.m. to the former and δ = −2.4 p.p.m. to the latter, values

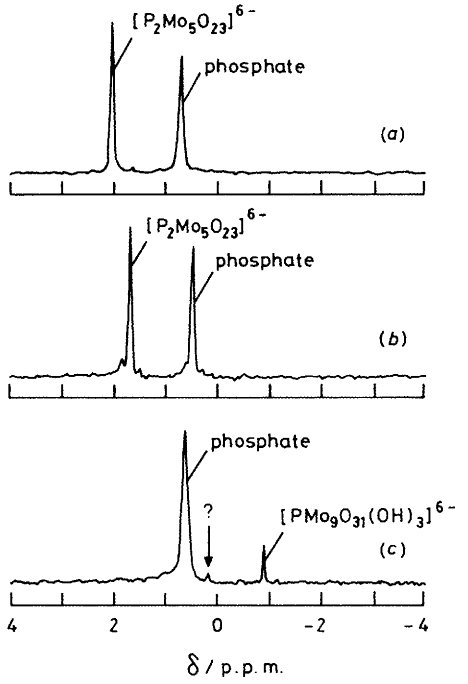

Figure 3. ^{31}P N.m.r. spectra of Na_2MoO_4–Na_3PO_4 solutions; [P] = 0.04, [Mo] = 0.05 mol l^{-1}. (*a*) pH 2.03, (*b*) as in (*a*) but saturated with NaCl, (*c*) pH 0.66

consistent with those reported in the literature.[19–22] The next molybdophosphate species whose formation is well attested is $[P_2Mo_5O_{23}]^{6-}$.[2,4,5,16] It is the first complex to form upon acidification. Its chemical shift is pH dependent (*cf.* Figure 1): at pH about 7, δ = +2.3 p.p.m., shifting to a constant value of + 2.0 p.p.m. at pH ⩽ 5.* This shift is probably due to protonation.[4,5] The assignment agrees with one published by Petterson *et al.*[23] We now consider the pair of lines at around δ = −1 p.p.m. Their position is also sensitive to pH, as shown in Figure 2. If we assume that only two molybdophosphate species correspond to the two signals, the results clearly show that the lines cross at a pH value of about 2.5: *e.g.* in Figure 1 it is evident that the decreasing signal crosses the growing one between pH 2.85 and 2.14. We assign the resonance labelled 1 in Figure 2 to $[PMo_{11}O_{39}]^{7-}$ and that labelled 2 to $[PMo_9O_{31}(OH)_3]^{6-}$. The arguments in favour of this assignment are: (*i*) the solutions from which salts of $[PMo_{11}O_{39}]^{7-}$ can be precipitated,[16] and from which the sodium salt of $[PMo_9O_{31}(OH)_3]^{6-}$ can be crystallized,[9] do indeed contain the respective heteropolyanions almost exclusively; (*ii*) it is in solutions containing $[PMo_9O_{31}(OH)_3]^{6-}$ that $[P_2Mo_{18}O_{62}]^{6-}$ forms, through dimerization, *cf.* Figure 1; (*iii*) species 1 is more prominent at higher than at lower Mo:P ratios, while the opposite is true for species 2, showing that the former has a higher Mo:P ratio.

The line centred at δ = 0.52 p.p.m. at higher pH values and which approaches 0.1 p.p.m. as the pH decreases (Figure 1) is not due to free phosphate ions, although their chemical shifts are quite close. Solutions can be prepared whose n.m.r. spectra contain both a resonance due to free phosphate and the resonance under discussion (*cf.* Figure 3). It is difficult to determine the composition of the molybdophosphate which gives rise to the latter signal, since we do not know the amount

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* The chemical shift is also somewhat sensitive to ionic strength, *cf.* Figure 3.

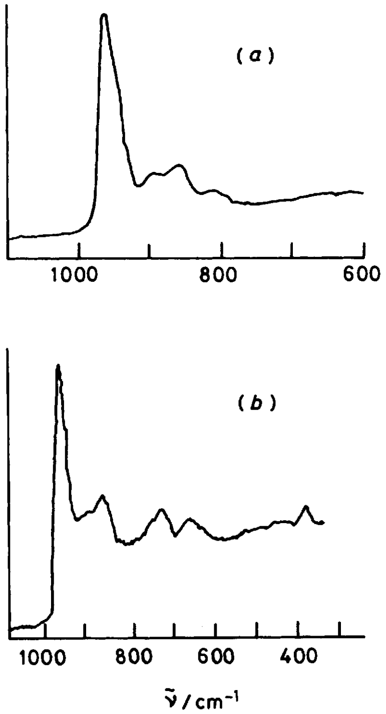

Figure 4. Solution Raman spectra of solutions of (*a*) $[PMo_{11}O_{39}]^{7-}$ and (*b*) $[PMo_9O_{31}(OH)_3]^{6-}$. Solutions: (*a*), [P] = 0.06, [Mo] = 0.72 mol l^{-1}; pH 3.40; (*b*), [P] = 0.015, [Mo] = 0.09 mol l^{-1}; pH 1.00 {85% $[PMo_9O_{31}(OH)_3]^{6-}$, 15% 'PMo_6'}

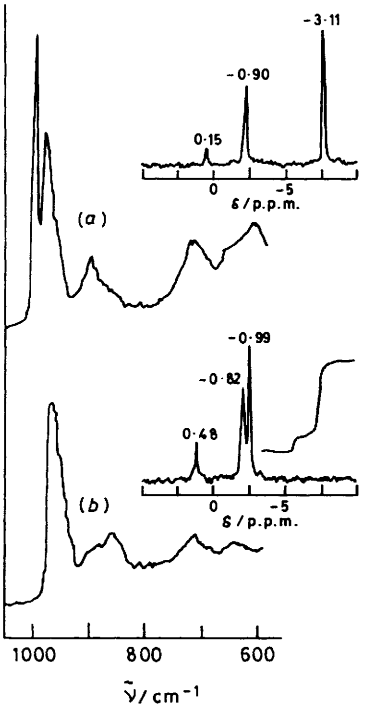

Figure 5. Raman and (inset) ^{31}P n.m.r. spectra of solutions containing $[PMo_9O_{31}(OH)_3]^{6-}$. Solutions: (*a*), [P] = 0.06, [Mo] = 0.72 mol l^{-1}; pH 0.2; (*b*), [P] = 0.01, [Mo] = 0.12 mol l^{-1}; pH 2.38

of free molybdate in solution, if any. {Efforts to precipitate it from solution failed; salts of either $[PMo_{11}O_{39}]^{7-}$ or $[PMo_9O_{31}(OH)_3]^{6-}$ separated out.} However, assuming that there is no free molybdate, we derive for the Mo:P ratio of the complex (from n.m.r. line intensities; solutions do contain free phosphate) values of $\geqslant 6$. We therefore tentatively conclude that it is a PMo_6 species, see below.

A small resonance occurs at $\delta = -0.1$ to -0.4 p.p.m. between pH 6 and 4 (Figure 1). We will come back to it when discussing the d.p.p. experiments. There is still another unexplained signal at -1.7 p.p.m., which occurs in solutions of pH $\leqslant 1.0$ and [P]:[Mo] $\leqslant 1:12$. No further data on the species responsible for this line could be collected.

Raman Spectroscopy.—The Raman spectra obtained for solutions of $[PMo_{12}O_{40}]^{3-}$ and of $[P_2Mo_5O_{23}]^{6-}$ are similar to those reported in the literature (996vs, 975m, 895m, and 605m;[25,26] and 935vs and 890m cm^{-1} [7,16] respectively).

It is impossible to prepare solutions which contain $[PMo_{11}O_{39}]^{7-}$ as the only Raman-active species. Figure 4(*a*) shows the best we can do: virtually all phosphate and 11/12 of the molybdate present are incorporated in this species. Nothing better can be gained from solutions with [P]:[Mo] = 1:11, *i.e.* either the formation of this species is not complete, or, at lower pH, $[PMo_9O_{31}(OH)_3]^{6-}$ is formed. So we will take the Raman spectrum in Figure 4(*a*) as characteristic of $[PMo_{11}O_{39}]^{7-}$.

It is also impossible to prepare solutions in which all the molybdenum is tied up in $[PMo_9O_{31}(OH)_3]^{6-}$. The Raman spectrum of one of the more suitable solutions is presented in Figure 4(*b*). It is rather similar to that of $[PMo_{11}O_{39}]^{7-}$, the main difference being that the former has a band at 715 cm^{-1} and a smaller one at 650 cm^{-1}, while the latter has not. Accordingly, we have tried to ascertain whether the band at 715 cm^{-1} can be used as a diagnostic for $[PMo_9O_{31}(OH)_3]^{6-}$. Raman spectra of solutions in which a reasonable proportion of the molybdenum is in this form all feature an absorption at 715 cm^{-1}. Two examples are shown in Figure 5. However, two problems remain: (*i*) since we are dealing with a band which is not very strong, it is difficult to detect in cases where the concentration of $[PMo_9O_{31}(OH)_3]^{6-}$ is low; (*ii*) the spectrum of $[P_2Mo_{18}O_{62}]^{6-}$ has a very intense band[7,21] at 720 cm^{-1}, which makes it difficult to determine the proportion of $[PMo_9O_{31}(OH)_3]^{6-}$ and $[P_2Mo_{18}O_{62}]^{6-}$ present in a given solution. These problems are exemplified in Figure 6, where we have collected Raman spectra of some solutions whose ^{31}P n.m.r. spectra are shown in Figure 1. The n.m.r. results show clearly the presence, albeit in relatively small amounts, of $[PMo_9O_{31}(OH)_3]^{6-}$ in solutions of pH 3.33 and 2.85, while only for the latter solution is a faint band at 715 cm^{-1} visible in the Raman spectrum. {This implies that Raman spectroscopy provides little support for our contention that the n.m.r. lines of $[PMo_{11}O_{39}]^{7-}$ and $[PMo_9O_{31}(OH)_3]^{6-}$ cross: when the signal due to the latter is upfield from that due to the former it is always small. However, evidence for this crossing has been gained through d.p.p., see below.} At pH 1.0, on the other hand, a very strong absorption at 715 cm^{-1} is observed (this solution is not stable under laser irradiation), mainly due to $[P_2Mo_{18}O_{62}]^{6-}$, the presence of which is evident from the n.m.r. data.

One could suppose, as Lyhamn and Petterson[7] have done, that the band at 715 cm^{-1} is not characteristic of $[PMo_9O_{31}(OH)_3]^{6-}$ at all, but that under laser irradiation of solutions containing this anion $[P_2Mo_{18}O_{62}]^{6-}$ is formed, which would then give rise to the observed band. We do not accept this supposition, since, whereas solutions containing $[P_2Mo_{18}O_{62}]^{6-}$ are rather susceptible to reduction (greening of the initially yellow solution), solutions containing only $[PMo_9O_{31}(OH)_3]^{6-}$ such as those shown in Figure 5 appear to be stable.

As to the Raman spectrum of the proposed PMo_6 species, we note the following: solutions can be made, whose ^{31}P n.m.r.

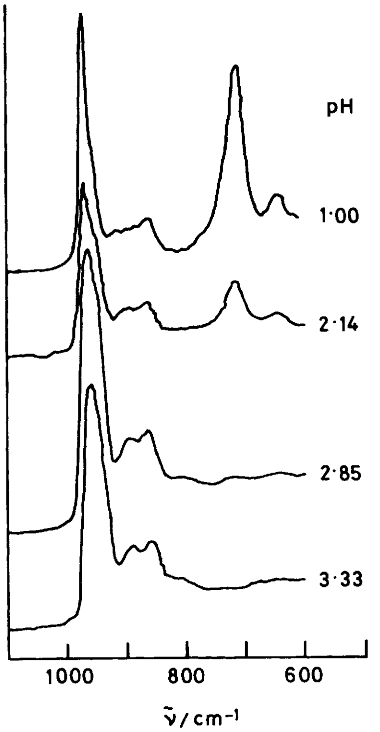

Figure 6. Raman spectra of some solutions whose ^{31}P n.m.r. spectra are shown in Figure 1

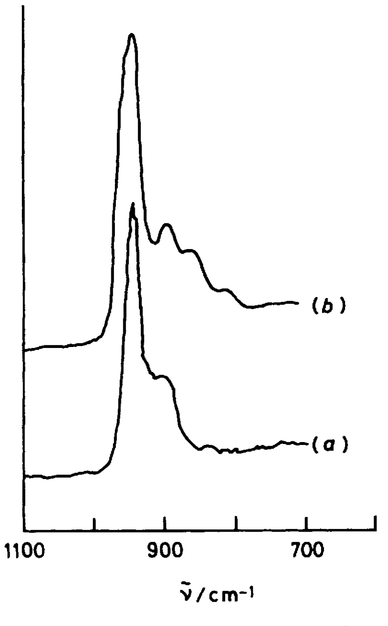

Figure 7. Solution Raman spectra of (*a*) $[Mo_7O_{24}]^{6-}$, and (*b*) PMo_6–$[PMo_{11}O_{39}]^{7-}$ (1:1) ([P] = 0.01, [Mo] = 0.12 mol l^{-1}; pH 4.3)

spectra show only the presence of $[PMo_{11}O_{39}]^{7-}$ and PMo_6, *e.g.* [P]:[Mo] = 1:12, pH = 4.3, and $[PMo_6]$:$[PMo_{11}]$ *ca.* 1:1. The Raman spectrum of this solution looks like a superposition of that of $[PMo_{11}O_{39}]^{7-}$ and that of heptamolybdate [*cf.* Figures 4(*a*) and 7], which implies that the Raman spectrum of the PMo_6 species is similar to that of heptamolybdate.

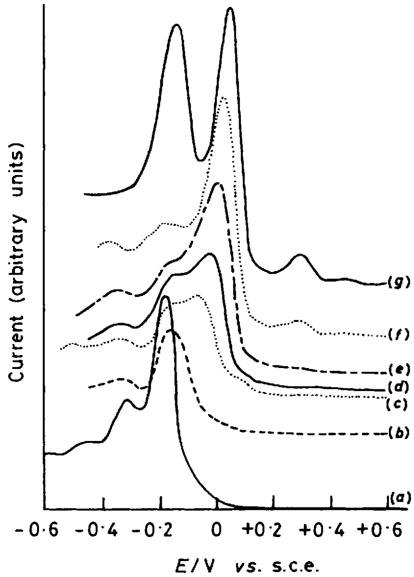

Figure 8. D.p. polarograms of Na_2MoO_4–Na_3PO_4 solutions; [P] = 0.03, [Mo] = 0.30 mol l^{-1}. pH 4.0 (*a*), 3.3 (*b*), 2.5 (*c*), 2.4 (*d*), 2.1 (*e*), 1.8 (*f*), and 1.5 (*g*). Polarogram (*a*) is typical of $[PMo_{11}O_{39}]^{7-}$ and (*g*) of $[PMo_9O_{31}(OH)_3]^{6-}$

Differential Pulse Polarography (*d.p.p.*).—It is not possible to reduce $[P_2Mo_5O_{23}]^{6-}$ under our conditions (lower limit of potential about −0.7 V *vs.* s.c.e.). This is in agreement with a rule, proposed by Pope,[27] to the effect that complexes in which each molybdenum atom has two *cis* unshared oxygens $\{[P_2Mo_5O_{23}]^{6-}$ is such a complex[4]$\}$ are irreducible. The species which we propose to be PMo_6 ($\delta \sim +0.5$ p.p.m.) is also irreducible, as can be deduced from *e.g.* the fact that solutions containing only $[PMo_{11}O_{39}]^{7-}$ or the latter and PMo_6 show exactly the same reduction pattern. Thus, in this complex each molybdenum should also have two *cis* unshared oxygens. A possible structure could therefore be one derived from the Anderson structure of heptamolybdate (*cf.* ref. 13, pp. 22,26) by replacing the central octahedron by one PO_4 tetrahedron, giving (in the absence of protonation) the formula $[PMo_6O_{25}]^{9-}$.*

To our knowledge, polarograms of $[PMo_{11}O_{39}]^{7-}$ and $[PMo_9O_{31}(OH)_3]^{6-}$ have not been published before. That for the former [Figure 8(*a*)] is easy to obtain, since $[P_2Mo_5O_{23}]^{6-}$, PMo_6, and heptamolybdate are all irreducible and so do not interfere with the measurement. Apparently, $[PMo_{11}O_{39}]^{7-}$ is much more difficult to reduce than $[PMo_{12}O_{40}]^{3-}$ [18] (see below). Solutions in which $[PMo_9O_{31}(OH)_3]^{6-}$ is the only reducible species are difficult to prepare, however, because at the low pH needed for its formation (*cf.* Figures 1 and 2) any free molybdate will also be reducible. However, if our assignment for PMo_6 is correct, it is possible to obtain such a solution and its d.p. polarogram is presented in Figure 8(*g*).

D.p. polarograms of solutions which contain both $[PMo_{11}O_{39}]^{7-}$ and $[PMo_9O_{31}(OH)_3]^{6-}$ are also presented in Figure 8 (*b*)—(*f*). It is seen that: (*i*) $[PMo_9O_{31}(OH)_3]^{6-}$ is somewhat easier to reduce than $[PMo_{11}O_{39}]^{7-}$; (*ii*) the first reduction

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* One referee suggested that the unknown species was PMo_7. Since the accuracy of our estimate of the [P]:[Mo] ratio in the complex is certainly not better than 10% (see above) this could in fact be the case. The structure would then probably be the one suggested by this referee: it is derived from the Anderson structure by removing the central octahedron and placing a MoO_4 tetrahedron above the ring, and a PO_4 tetrahedron below the ring.

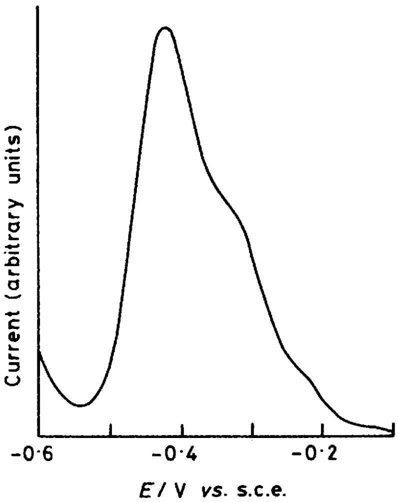

Figure 9. D.p. polarogram of a solution with [P] = 0.06, [Mo] = 0.72 mol l^{-1}, and pH 5.40

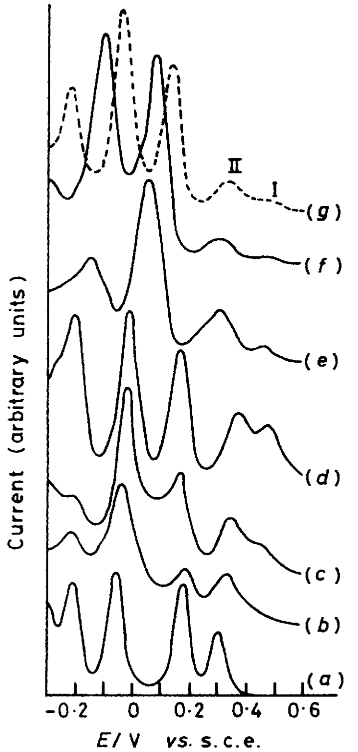

Figure 10. D.p. polarograms of (*a*) 0.01 mol l^{-1} $[PMo_{12}O_{40}]^{3-}$ in dioxane-water (1:1), (*b*) 0.1 mol l^{-1} $[PMo_{12}O_{40}]^{3-}$ in water {about 5% decomposition to $[PMo_9O_{31}(OH)_3]^{6-}$}, (*c*) as in (*b*) + NaCl {about 20% decomposition to $[PMo_9O_{31}(OH)_3]^{6-}$}, (*d*) [P] = 0.06, [Mo] = 0.72 mol l^{-1}, pH 0.3 {60% $[PMo_{12}O_{40}]^{3-}$ and 40% $[PMo_9O_{31}(OH)_3]^{6-}$}, (*e*) as in (*d*), but pH 1.25 {$[PMo_{12}O_{40}]^{3-}$–$[PMo_9O_{31}(OH)_3]^{6-}$ (*ca.* 1:1, most abundant solution species is $[PMo_{11}O_{39}]^{7-}$}, (*f*) [P] = 0.06, [Mo] = 0.54 mol l^{-1}, pH 1.25, and (*g*) as in (*f*), but pH 0.60. The last two solutions contain $[PMo_9O_{31}(OH)_3]^{6-}$ and $[P_2Mo_{18}O_{62}]^{6-}$ (*cf.* Figure 1), d.p.p. for $[PMo_9O_{31}(OH)_3]^{6-}$ see Figure 8(*g*)

peak of $[PMo_9O_{31}(OH)_3]^{6-}$ depends on the pH of the solution; (*iii*) the second reduction peak develops only at pH 1.6 (we have no explanation for this); and, most importantly for the present purposes, (*iv*) the polarogram at pH 3.3 neatly fits into this sequence. Since for this last solution the n.m.r. signal for $[PMo_9O_{31}(OH)_3]^{6-}$ is still upfield with respect to that of $[PMo_{11}O_{39}]^{7-}$, our assumption that this signal is indeed due to the former would seem to be correct.

Although the relative concentration is always low, the reducibility of the species corresponding to the ^{31}P n.m.r. signal at about −0.2 p.p.m. can be determined because it tends to form at a slightly higher pH than does $[PMo_{11}O_{39}]^{7-}$, so that no other reducible species are there to interfere. The pertinent d.p. polarogram is shown in Figure 9. This species has a reducibility similar to that of $[PMo_9O_{31}(OH)_3]^{6-}$ and $[PMo_{11}O_{39}]^{7-}$. This, together with the fact that it does not exist in solutions with [P]:[Mo] > 1:9, leads us tentatively to identify the complex as $[PMo_{10}O_{34}]^{3-}$ D.p. polarograms of solutions containing $[PMo_{11}O_{39}]^{7-}$, $[PMo_{10}O_{34}]^{3-}$, and PMo_6 are superpositions of those pertaining to the first two complexes, the relative intensities being similar to those derived from the n.m.r. spectra.

D.p. polarograms of highly acidic solutions, which contain $[PMo_{12}O_{40}]^{3-}$, $[PMo_9O_{31}(OH)_3]^{6-}$, and $[P_2Mo_{18}O_{62}]^{6-}$ as the major species, look more alike than one would have expected from the literature[13,18,28,29] (which pertains, however, to mixed solvents, normally 50% organic, used to suppress the hydrolytic instability of the molybdophosphates[13,30]). Some results are collated in Figure 10. It is observed that: (*i*) the presence of peak I is correlated with the presence of $[PMo_9O_{31}(OH)_3]^{6-}$; (*ii*) the relative intensity of peaks I and II with respect to the peaks at lower potentials increases with increased ratio of $[PMo_{12}O_{40}]^{3-}$ to $[PMo_9O_{31}(OH)_3]^{6-}$; and (*iii*) the reduction patterns for $[PMo_9O_{31}(OH)_3]^{6-}$ and of its mixtures with $[P_2Mo_{18}O_{62}]^{6-}$ are virtually indistinguishable. It appears, then, that ^{31}P n.m.r. spectroscopy is much more powerful in ascertaining the number of species in solution than either d.p.p. or Raman spectroscopy.

Applications.—With the major ^{31}P n.m.r. signals more or less identified, we can proceed to address the questions mentioned in the Introduction and related ones. Upon acidification of a sodium phosphate–sodium molybdate solution the following molybdophosphate species form successively (*cf.* Figure 1): $[P_2Mo_5O_{23}]^{6-}$, $[PMo_{10}O_{34}]^{3-}$ (?), $[PMo_{11}O_{39}]^{7-}$, PMo_6 (?), $[PMo_9O_{31}(OH)_3]^{6-}$, and $[PMo_{12}O_{40}]^{3-}$ {$[P_2Mo_{18}O_{62}]^{6-}$ only forms when the concentration of $[PMo_9O_{31}(OH)_3]^{6-}$ is high enough}. This sequence is independent of the [P]:[Mo] ratio (disregarding minor species), although, of course, at higher ratios, $[PMo_9O_{31}(OH)_3]^{6-}$ follows $[PMo_{11}O_{39}]^{7-}$ after a smaller pH interval, $[P_2Mo_5O_{23}]^{6-}$ persists till lower pH values, and formation of $[PMo_{12}O_{40}]^{3-}$ is delayed. Curiously, this sequence is neither in agreement with Souchay's scheme[1,2] (later echoed by Murata and Ikeda[16]), in which $[PMo_9O_{31}(OH)_3]^{6-}$ does not feature at all, nor with Lyhamn's,[8] in which $[PMo_{11}O_{39}]^{7-}$ is accorded only a very minor role. However, the n.m.r. data would seem to be quite clear on this point.* Note (*i*) that pure $[PMo_{12}O_{40}]^{3-}$ solutions can be prepared only when there is an excess of molybdate ([P]:[Mo] < 15), and (*ii*) that the first decomposition product of this species is $[PMo_9O_{31}(OH)_3]^{6-}$ and not $[PMo_{11}O_{39}]^{7-}$ as is usually thought.

Murata and Ikeda[16] have proposed that the formation of the various molybdophosphates can be correlated with the appearance of certain molybdenum polyanions in the acidified solutions. As far as $[P_2Mo_5O_{23}]^{6-}$ and heptamolybdate are concerned, we agree with the proposition that the formation of heptamolybdate triggers the formation of $[P_2Mo_5O_{23}]^{6-}$; until all phosphate has reacted the solution contains only

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* As is evident from their latest publication,[23] referred to in the Introduction, the Umeå group are in the process of revising their scheme.

$[P_2Mo_5O_{23}]^{2-}$ and monomolybdate. The other correlations are less acceptable, since the formation of $[PMo_9O_{31}(OH)_3]^{6-}$ and several minor species has not been taken into account.

On the basis of u.v. absorption spectra, Kircher and Crouch[31] report that quite high concentrations of $[PMo_{11}O_{39}]^{7-}$ exist in solutions of pH <1. Also, they assume that $[PMo_9O_{31}(OH)_3]^{6-}$ occurs only in its dimeric form, $[P_2Mo_{18}O_{62}]^{6-}$. Neither of these conclusions is consistent with the ^{31}P n.m.r. spectra: such solutions contain mainly $[PMo_{12}O_{40}]^{3-}$ and/or $[PMo_9O_{31}(OH)_3]^{6-}$, only a fraction of which dimerizes, and some unidentified minor species (PMo_6? and a species with $\delta = -1.7$ p.p.m.). However, Kircher and Crouch's finding that cyclic voltammetry of these solutions is not very enlightening agrees with our experience.

What would appear to be the correct Raman spectra of $[PMo_{11}O_{39}]^{7-}$ and $[PMo_9O_{31}(OH)_3]^{6-}$ are shown in Figure 4 [*cf.* Introduction, item (*ii*)]. Lyhamn and Petterson have published four Raman spectra (Figure R4 of ref. 7) which they ascribe to $[PMo_9O_{31}(OH)_3]^{6-}$ in different stages of protonation. However, the two spectra at higher pH do not contain a band at 715 cm^{-1}, and so, in our view, correspond instead to $[PMo_{11}O_{39}]^{7-}$. This conclusion is corroborated by the fact that salts of $[PMo_9O_{31}(OH)_3]^{6-}$ crystallize only at low pH.[7] The Raman spectrum which Kasprzak *et al.*[14] ascribe to $[PMo_{11}O_{39}]^{7-}$ does contain a band at 715 cm^{-1} and so some $[PMo_9O_{31}(OH)_3]^{6-}$ must also be present in the solution used.

As to the correct composition of PMo_{11} [Introduction, item (*iii*)] we favour $[PMo_{11}O_{39}]^{7-}$ in view of the rather large difference between the chemical shifts observed at low and at high pH (−1.15 *vs.* −0.6 p.p.m.), which is probably connected with extensive protonation. This would imply that the compound Murata and Ikeda[16] obtained from a [P]:[Mo] = 1:12 solution at pH 2.1 is not, as they report, $[NEt_4]_3[PMo_{11}O_{37}]$, but rather $[NEt_4]_3[H_4PMo_{11}O_{39}]$, the elemental analysis of which is even closer to the one determined experimentally.

Of the two species mentioned in the Introduction, item (*iv*), $[PMo_{10}O_{34}]^{3-}$ does perhaps exist in acidified solutions, but no sign of $[P_2Mo_2O_{13}]^{4-}$ could be detected.

It has been reported that $[PMo_{12}O_{40}]^{3-}$ is not stable towards H_2O_2, but decomposes into phosphate and peroxomolybdate anions.[32] We have found, however, that adding H_2O_2 to a 10^{-1} mol l^{-1} solution of $H_3PMo_{12}O_{40}$ leads, in the first instance, to the formation of $[PMo_9O_{31}(OH)_3]^{6-}$ and peroxomolybdate. What happens at high concentrations of H_2O_2 is obscure, the ^{31}P n.m.r. spectrum showing many lines of unknown provenance.

Massart *et al.*[19] have argued that there should be a correlation between the frequencies of the P–O vibrations and the chemical shift, since both reflect the electron density at the phosphorus atom. Attributing the highest-frequency band to the ν_1 vibration of the PO_4 tetrahedron[26,33] (but see ref. 25), we see from the Table that such a correlation indeed exists for the present series of molybdophosphates.

Table. Frequency of the most intense Raman band and the ^{31}P n.m.r. chemical shifts of some molybdophosphate complexes

Complex	δ/p.p.m.	Raman band (cm^{-1})	Remarks
$[PMo_{12}O_{40}]^{3-}$	−3.2	995	
	−2.9	987	50% dioxane
$[P_2Mo_{18}O_{62}]^{6-}$	−2.4	980	
$[PMo_9O_{31}(OH)_3]^{6-}$	−0.85	967	pH 1.0
$[PMo_{11}O_{39}]^{7-}$	−1.05	970	pH 2.5
	−0.79	963	pH 3.4
$[P_2Mo_5O_{23}]^{6-}$	+2.0	935	
$[PMo_6O_{25}]^{9-}$ (?)	+0.5	950	

Recently, some solid-state ^{31}P n.m.r. data for heteropolyanions have been reported.[34] In $H_3PMo_{12}O_{40}$ an impurity was detected having $\delta = -1.5$ p.p.m. and tentatively identified as $[PMo_{11}O_{39}]^{7-}$. On the basis of the present results, it could equally well have been $[PMo_9O_{31}(OH)_3]^{6-}$. If the $H_3PMo_{12}O_{40}$ had been prepared under strongly acidic conditions, as seems likely, the latter is more probable.

Conclusions

We have not entirely succeeded in realizing our aim, *i.e.* to establish an easily applicable method for the identification of molybdophosphate species in solution, ^{31}P n.m.r. spectra of acidified phosphate–molybdate solutions showing the presence of more species than hoped for.

Of the ^{31}P n.m.r. resonances observed, two had already been reported in the literature {−3.2 p.p.m., $[PMo_{12}O_{40}]^{3-}$, −2.4 p.p.m., $[P_2Mo_{18}O_{62}]^{6-}$} and three others could be assigned making use of literature information on acidified molybdate–phosphate solutions: +2 p.p.m., $[P_2Mo_5O_{23}]^{6-}$ (*cf.* ref. 23); −0.6 (high pH) to −1.14 p.p.m. (low pH), $[PMo_{11}O_{39}]^{7-}$; and −1.1 (medium pH) to 0.9 p.p.m. (low pH), $[PMo_9O_{31}(OH)_3]^{6-}$. Of the three remaining signals, two could be tentatively assigned, +0.5 (high pH) to +0.17 p.p.m. (low pH), PMo_6, and *ca.* −0.3 p.p.m., $[PMo_{10}O_{34}]^{3-}$, while one, at −1.7 p.p.m., is of entirely unknown provenance.

Of all the techniques tested so far, only ^{31}P n.m.r. spectroscopy gives a reliable indication of the number of molybdophosphate species in solution. Therefore, any conclusion regarding the composition of molybdophosphate solutions reached *via* another method should be checked against n.m.r. data.

The confusion in the literature as to the relative importance of $[PMo_9O_{31}(OH)_3]^{6-}$ and $[PMo_{11}O_{39}]^{7-}$ is understandable, since their properties are indeed very similar. They can be distinguished, however, *cf.* Figure 2 (n.m.r.), 4 (Raman), and 8 (d.p.p.).

The ion $[P_2Mo_5O_{23}]^{6-}$ is irreducible, in accordance with Pope's rule. There is a parallelism between the frequency of the P–O vibrations and the chemical shift for the present series of heteropolyanions.

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