

SYNTHESIS AND PROPERTIES OF SIMPLE AND COMPLEX POLYMETAPHOSPHATE GLASSES OF ALKALI METALS

R. C. MEHROTRA*

*Chemical Laboratories, University of Rajasthan,
Jaipur-302004, India*

ABSTRACT

Synthesis of a large number of simple and complex polymetaphosphate glasses of alkali metals with the general formulae $(M_x M'_{(1-x)} PO_3)_n$ and $(M_x M''_{1-x/2} PO_3)_n$ has been described, where M and M' = Li, Na, K, Rb or Cs; M'' = Be, Mg, Ca, Sr, Ba, Zn, Cd, Pb, Cu or Ni; and $x = 1, \frac{2}{3}, \frac{1}{2}$ or $\frac{1}{3}$. The preparations have been carried out by heating alkali dihydrogen phosphate, metal oxide (or carbonate) and diammonium hydrogen phosphate together in the desired stoichiometric ratios at 700°, 800° or 900°, followed by chilling the clear melts obtained. Some of these complex derivatives have also been prepared by treating metal salt solutions with alkali polymetaphosphate followed by precipitation with alcohol.

A detailed study has been made of the following properties of these derivatives: molecular weights (M_w and M_n), viscosity, conductivity, i.r. and n.m.r. spectra. All the derivatives have been shown to behave as long chain metaphosphates and their polymeric character has been further supported by chromatographic and metachromatic studies.

INTRODUCTION

The chemistry of polymetaphosphates of alkali metals has been receiving considerable attention in recent years, because of the growing interest in the field of inorganic polymers and polyelectrolytes. Several reviews¹⁻⁸, dealing with various facets of their chemistry, have appeared during the last two decades.

Sodium polymetaphosphate known as Graham's salt was prepared⁹ as early as 1834 by heating sodium dihydrogen phosphate to a high temperature, followed by chilling the melt suddenly. Considered erroneously as sodium 'hexametaphosphate' for over 100 years, its highly polymeric character was revealed by studies involving ultracentrifugation by Lamm and Malmgren¹⁰, dialysis by Karbe and Jander¹¹, end group titration by Samuelson¹², viscosity measurements by Malmgren and co-workers^{13, 14}, light scattering by Strauss and co-workers¹⁵, conductometry by Davies and Monk¹⁶, electrolytic transference measurements by Schindewolf¹⁷, chromatography by Westman and Scott¹⁸ and by Ebel¹⁹, fractional precipitation by Van Wazer²⁰ and x-ray diffraction by Brady²¹.

*Present address: Vice-Chancellor, University of Delhi, Delhi-7, India.

The highly polymeric character of Graham's salt has thus been established and the end group titrations have shown it to have the composition, $\text{Na}_{n+2}\text{P}_n\text{O}_{3n+1}$ or $[(\text{NaPO}_3)_n\text{Na}_2\text{O}]$. When n is large (say, 10^2 to 10^6), the composition approximates to the formula, $(\text{NaPO}_3)_n$. These long chain polyphosphates have, therefore, been termed polymetaphosphates. Apart from these and other short chain oligopolyphosphates, cyclic tri- and tetra-metaphosphates have been characterized. A detailed phase diagram for the system, $\text{NaH}_2\text{PO}_4\text{-NaPO}_3$ has been established²² as a result of the detailed investigations of Boulle²³ and several other workers²⁴⁻²⁶. Following many doubtful claims, evidence has been more recently adduced²⁷⁻²⁸ for the existence of rings up to octametaphosphates. Hexametaphosphates of lithium and sodium were actually synthesized by Griffith and Buxton²⁹ in 1965.

Although much less complete, similar studies have been made for potassium^{24, 30-32} (sometimes called potassium Kurrol salt), rubidium³³ caesium³³, lithium^{24, 34, 35} and ammonium^{36, 37} polymetaphosphates and concerted efforts are being made to throw light on their special structural features by various physicochemical techniques.

COMPLEXATION REACTIONS OF SODIUM POLYMETAPHOSPHATES

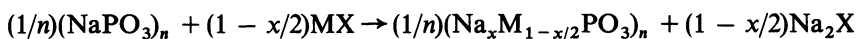
A renewed interest was created in the chemistry of Graham's salt in 1934, when Hall³⁸ drew pointed attention to its capacity to sequester calcium ions. This led to its use as water-softener (Calgon) and to a number of complexation studies³⁹⁻⁴⁷. Thilo⁴⁸ has pointed out a close similarity between the above complexation reactions with polyvalent cations in solution and ion-exchange phenomena.

Early observations by Tammann⁴⁹ about incomplete (30-40 per cent) dissociation of sodium polymetaphosphate have been confirmed in more recent studies⁵⁰; the degree of dissociation α for 0.01 M solutions (on empirical formula) of alkali polyphosphates has been found to increase from 0.34 for Li^+ to 0.4 for Cs^+ . These workers have from conductivity and electrostatic data shown the order of 'specific site-bonding' of ions on polyphosphate chains to be $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Ca}^{2+} > (\text{CH}_3)_4\text{N}^+$. With increasing chain length, the value of α first decreases rapidly and then more slowly to a limiting value of about 0.33 at the chain length of approximately 100. Van Wazer and Campanella⁵¹ made a potentiometric and polarographic study of complex ion formation of calcium and barium ions with sodium polymetaphosphate. Irani and Cullis⁵² found that the pK value of calcium ions in polyphosphate solutions, of ionic strength, say 1, changed from 5.78 to 5.80 when the degree of polymerization of $(\text{NaPO}_3)_n$ was changed from 6 to 60. Evidence about the exchangeability of cations on polyphosphate chains has been adduced by Ohashi and co-workers⁵³ and by Ripan and Stanislav⁵⁴.

SYNTHESIS OF COMPLEX SODIUM POLYMETAPHOSPHATE GLASSES BY FUSION

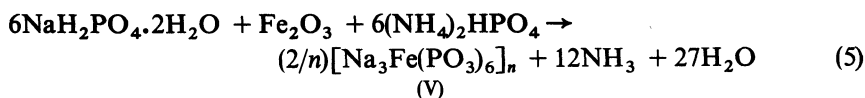
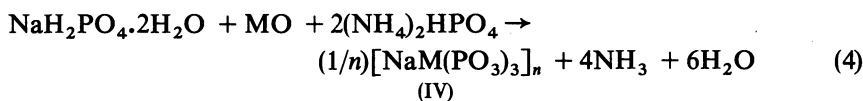
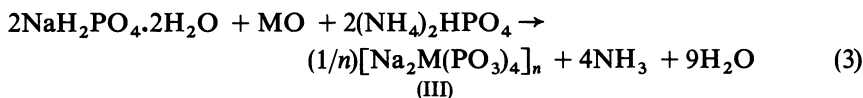
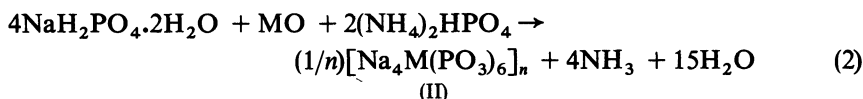
From a detailed study of the measurements of solubility of insoluble salts like CaCO_3 , CaC_2O_4 , SrSO_4 , BaSO_4 and PbSO_4 in solutions of sodium polymetaphosphate and from the increments in the conductivity of the latter

on dissolution of these salts, Mehrotra⁴⁶ (1946–48) concluded that equilibria of the following type exist in such systems :



As confirmed by later detailed studies of several authors, for example, in the case of calcium salts, the value of x was found to be approximately two thirds in dilute solutions. Strontium and barium behaved almost similarly, but in the case of lead sulphate higher dissolution indicated the formation of derivatives with empirical formulae up to $(\text{Na}_{1/3}\text{Pb}_{1/3}\text{PO}_3)_n$.

Interpretation of these data was based on the assumption that the degree of ionization of sodium ions from $(\text{NaPO}_3)_n$ and say, $(\text{Na}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$ was almost similar and hence the conductivities of their equivalent solutions would have almost equal values. In order to check this, Mehrotra and Gupta^{55–59} attempted the synthesis of a series of complex polymetaphosphate glasses with the general formula $(\text{Na}_x\text{M}_{1-x/a}\text{PO}_3)_n$, where $x = \frac{2}{3}, \frac{1}{2}$ or $\frac{1}{3}$ and $\text{M} = \text{Li}, \text{K}, \text{Ca}, \text{Ba}, \text{Zn}, \text{Cu}, \text{Pb}$ and Fe(III) . These glasses were prepared by fusing the reactants together for one hour at a temperature of 700 or 800°C in the stoichiometric ratios indicated by equations (1)–(5). For comparison, sodium metaphosphate itself was prepared under similar conditions :



The simple sodium metaphosphate (I) as well as mixed metaphosphates of type II were obtained in the form of clear melts with Ca, Ba, Zn, Cu or Pb, which were chilled between stainless steel plates to give transparent glasses.

Attempts to prepare complex derivatives of type III led to clear melts in each of the above cases ; soluble complexes were, however, obtained only with Ca, Zn and Pb. The rate of dissolution of even the above soluble varieties is slower compared to that of derivatives of type II.

Preparation of complex derivatives of type IV was attempted several times in the case of calcium, even by the use of higher temperature and longer (even five) hours of heating but clear melts could not be obtained. Similarly, a clear melt could not be obtained in reaction (5) in any stoichiometric ratio.

BONDING IN SIMPLE AND COMPLEX POLYMETAPHOSPHATE GLASSES

Mehrotra⁴⁶ (1948) had tried to explain the partial ionizability⁴⁹ of sodium ions from sodium metaphosphate on the basis of inductive and field effects due to which sodium atoms on alternate metaphosphate units should show a greater tendency towards ionization. It was further suggested that the bonding of the remaining sodium atoms would tend to be further stabilized by six-membered chelate ring formation and resonance effects :

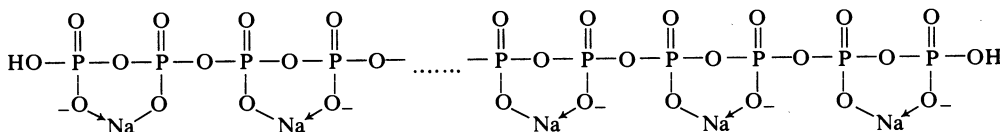


Figure 1. Structure of sodium polymetaphosphate anions, $[\text{Na}(\text{PO}_3)_2]_n^-$.

In spite of their strongly electropositive character, atoms of alkali metals have been shown to depict covalent bonding⁶⁰ in β -diketone⁶¹, polyetherate⁶² and alkoxide⁶³ derivatives, due to similar effects.

In the case of sodium polyphosphates, the concept of partial ionization was further supported by electrolytic transference measurements^{64, 65} and by sodium ion activity measurements with cation exchange membranes⁶⁶.

The sequestration of bivalent ions M^{2+} (e.g. Ca^{2+} , Ba^{2+} , Zn^{2+} , Pb^{2+}) was also explained by Mehrotra⁴⁶ to arise from chelate bonding of the following type :

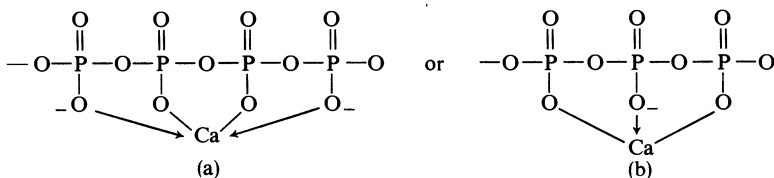


Figure 2. Structures of calcium polymetaphosphate anions, $[\text{Ca}(\text{PO}_3)_4]_n^{2n-}$ and $[\text{Ca}(\text{PO}_3)_3]_n^{n-}$.

The above simple structures were supported to some extent by the findings of Van Wazer and Campanella⁵¹ that the coordination numbers of alkali and alkaline earth metals in polyphosphate complexes are two and four respectively. On the basis of coordination number four for calcium, the former structure appeared to be more probable for the calcium complex. On preparation of actual models, structure 2(a), however, appears to be rather strained and therefore, the alternative possibility of bivalent atoms attaining higher coordination numbers by forming dianionic chains from structures

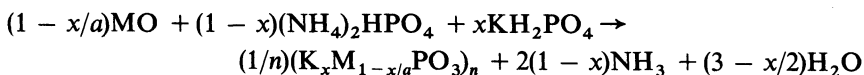
of the type 2(b) also cannot be ruled out and in fact, appears to be more probable.

The above conclusion is in accordance with the structural features of various long chain phosphates, a detailed review of which has been published recently⁸.

SYNTHESIS OF COMPLEX POTASSIUM POLYMETAPHOSPHATE GLASSES BY FUSION

Although potassium Kurrol salt is a long chain polyphosphate like Graham's salt, yet it differs from the latter in being insoluble in water and in showing a different structure in the solid state⁶⁷. Andress and Fischer⁶⁸ showed by x-ray studies that the anion of the compound consists of a long polymeric chain of $(\text{PO}_3)_n^{n-}$ units. Following the work of Corbridge⁶⁹, Jost⁷⁰ has shown that the crystals of $(\text{KPO}_3)_n$ are monoclinic. He has assigned to it the space group $P_{21/a}$ with the lattice constants as $a = 14.02 \text{ \AA}$; $b = 4.54 \text{ \AA}$; $c = 10.28 \text{ \AA}$ and $\alpha = 111.5^\circ$. The phosphate chain is that of a screw type with four PO_4 tetrahedra per period; each potassium appears to be surrounded by seven or eight oxygen atoms. According to Jost, the swelling in water or salt solutions and ion exchange properties of $(\text{KPO}_3)_n$ can be attributed to relatively weak forces between 201 planes.

As the insolubility of potassium Kurrol salt could be ascribed to the special lattice characteristics of the salt, it was predicted that the complex derivatives of the type $(\text{K}_x\text{M}_{1-x/a}\text{PO}_3)_n$ should behave differently and might be expected even to be soluble in water. This conjecture has been confirmed⁷¹⁻⁷³ by the synthesis of complex potassium polymetaphosphate glasses of mono- and bi-valent metals according to the general reaction:



where M = Li, Na, Be, Mg, Ca, Ba, Zn, Cd, Cu, Ni or Pb; $x = \frac{2}{3}, \frac{1}{2}$ and $\frac{1}{3}$; and a = valency of metal M.

The reactions have been followed thermogravimetrically and by differential thermal analysis. All these derivatives were prepared by heating the required reaction mixture at 800° and the product obtained in each case was a clear (except in some instances when $x = \frac{1}{3}$) transparent melt which was immediately chilled between stainless steel plates. The glasses obtained were colourless except in the cases of copper and nickel derivatives which were blue and yellowish green respectively. All these derivatives (when $x = \frac{2}{3}$), except the barium derivatives, were soluble in water, but the solubility as well as the rate of solution becomes less for derivatives with $x = \frac{1}{2}$. Only copper, zinc and lead derivatives were found to be soluble when $x = \frac{1}{3}$, but even in these cases, the rate of dissolution of derivatives of the last two metals was very slow.

SYNTHESIS OF COMPLEX POTASSIUM AND SODIUM POLYMETAPHOSPHATE GLASSES FROM SOLUTION

The observed water-soluble nature of the complex potassium polymetaphosphate can explain many earlier observations about the increased

solubility of potassium Kurrol salt in salt solutions of many cations other than potassium.

According to Madorsky and Clark⁷⁶, the solubility of potassium Kurrol salt in water is less than 0.004 g/100 ml at 25°C. Ohashi *et al.*⁵³ have more recently reported its solubility as 0.007–0.009 g/100 ml at 20°C. Volkerding and Bradfield⁷⁷ reported that the solubility of potassium Kurrol salt is much greater in salt solutions of alkali (other than potassium) and alkaline earth metals. Iler⁷⁸ has prepared its solution free of foreign anions by dissolving it in aqueous suspension of sodium bound cation exchange resin. It has therefore, been suggested that the above dissolutions involve ion-exchange phenomena. The exchange of bivalent and trivalent metal ions has been reported by Ohashi and co-workers⁵³ to occur to the extent of 82–94 per cent and 51–52 per cent in potassium and sodium Kurrol salts respectively. Malmgren and co-workers^{10, 13, 79} studied the sedimentation velocity, dialysis, electrophoresis and dilute solution viscosity of $(\text{KPO}_3)_n$ in the presence of a number of swamping electrolytes and found it to be a high molecular weight chain phosphates.

The species which must be getting formed in the above experiments^{10, 13, 79} when $(\text{KPO}_3)_n$ is shaken with solutions of other electrolytes must be complex polymetaphosphates of the type synthesized by fusion technique as described above. Even in Iler's method⁷⁸, the species brought into solution should have been $(\text{NaPO}_3)_x$, if the exchange was complete or in the case of incomplete exchange, it could have been expected to be $(\text{K}_x\text{Na}_{1-x}\text{PO}_3)_n$. In view of the above, attempts were made to prepare a few soluble potassium complex metaphosphates also under the mild conditions employed by the above workers.

It was observed that a clear solution could be obtained by shaking six formula weights of $(1/n)(\text{KPO}_3)_n$ with a solution of one gram mole of chlorides of calcium, strontium, zinc or lead. On adding excess alcohol to these concentrated solutions, viscous liquids were precipitated which on drying under reduced pressure yielded derivatives corresponding to $\text{K}_{2/3}\text{M}_{1/6}(\text{PO}_3)_n$. In some of these cases, it was difficult to remove completely from the final product, the anion of the bivalent salt originally taken. In order to overcome this difficulty, four formula weights of potassium polymetaphosphate were shaken with one formula weight of the bivalent metaphosphate, $\text{M}(\text{PO}_3)_2$. The bivalent metaphosphates were prepared by adding sodium polymetaphosphate to solutions of bivalent chlorides in the molar ratio of 2:1. The bivalent metaphosphates which separated as oily precipitates were obtained in the solid form by adding alcohol to the oily precipitates to extract as much water out of them as possible and then drying under reduced pressure at room temperature. Although both these metaphosphates are individually insoluble in water, a mixture of these two, when shaken vigorously in water, went gradually into solution; the time required for mutual dissolution differed from metal to metal, ranging from 12 hours for lead to 120 hours for strontium. The complex derivatives could be separated from the solution by the addition of alcohol and drying at room temperature under reduced pressure⁸⁰.

Most of the samples of bivalent phosphates $[\text{M}(\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}]_n$ and of the complex potassium polymetaphosphates $[\text{K}_4 \cdot \text{M}(\text{PO}_3)_6 \cdot 2\text{H}_2\text{O}]_n$ were found

to be associated with two molecules of water of crystallization. For the sake of comparison, a number of sodium complex metaphosphates, $[\text{Na}_4\text{M}(\text{PO}_3)_6 \cdot 2\text{H}_2\text{O}]_n$, where $\text{M} = \text{Ca}, \text{Sr}, \text{Cd}$ and Pb , were also prepared by similar methods.

The conductances of solutions of these complex metaphosphates at different dilutions as well as that of $(\text{NaPO}_3)_n$ were measured under similar conditions. The observed conductances of the solutions of these complex derivatives, prepared from solution, are of the same order, although they are generally lower than those of the samples obtained by fusion. Also, the plot of conductance versus concentration is similar in nature to that observed for sodium polymetaphosphates and complex polymetaphosphate derivatives^{55, 71}. The nature of these curves is also similar to those observed for other synthetic polyelectrolytes by Fuoss and Fitzgerald⁸¹ and confirms the polyelectrolytic behaviour of all these simple and complex polymetaphosphates.

SYNTHESIS OF SIMPLE AND COMPLEX POLYMETAPHOSPHATES OF LITHIUM AND CAESIUM

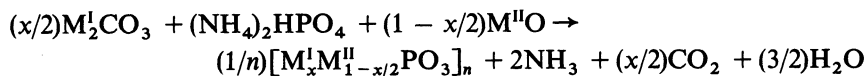
It is well known that although lithium belongs to the alkali metal group of the periodic table, it has many properties similar to those of alkaline earth metals; e.g. lithium orthophosphate is insoluble in water. It may also be mentioned that lithium Kurrol salt is soluble in water and has a distinct structure in the solid state, which consists of extended chains with alternating PO_4 tetrahedra.

Caesium, on the other hand, shows quite a close resemblance to potassium in many of its properties. Caesium polymetaphosphate, although it is isomorphous with potassium polymetaphosphate, is soluble in water, unlike the latter.

Thermal dehydration of lithium and caesium dihydrogen phosphates to yield lithium and caesium polymetaphosphates has been studied by several workers^{82, 83}, who have shown that the respective pyrophosphates are obtained around 180–183°C and the polymetaphosphate begins to be formed around 277°C in the case of lithium and at about 233°C in the case of caesium. The polymetaphosphates melt at about 600° in the case of lithium and at 700°C for caesium.

Unlike the sodium system, there appears to be no formation of trimetaphosphates in these systems.

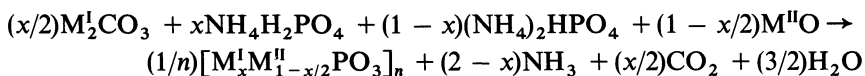
In view of the above, it was considered of interest to make a study of the complex polymetaphosphates of lithium and caesium^{84, 85} also. The preparation of these derivatives was, therefore, attempted by heating together the following reaction mixtures:



where M^{I} is Li or Cs and M^{II} is Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Ni or Pb and $x = 1, \frac{2}{3}, \frac{1}{2}, \frac{1}{3}$.

In some cases where x is more than one half, the amount of frothing in the above procedure was excessive. Hence, in these cases, a mixture of alkali

carbonate and the required quantity of ammonium dihydrogen phosphate was initially heated at a low flame till frothing had subsided and then a mixture of the bivalent metal oxide (or carbonate), with equivalent amount of diammonium hydrogen phosphate was added, followed by heating gradually till a clear melt was obtained. This melt was then placed in a muffle furnace at $800 \pm 25^\circ\text{C}$ for one hour. The reactions in these cases could be represented as:



A clear melt was obtained in almost all cases which on chilling between two stainless steel plates gave clear glasses, except in the case of $(\text{CsPO}_3)_n$, which was obtained as an opaque mass. However, all the complex polymetaphosphates of lithium and even caesium were obtained as clear glasses on chilling the melts in the usual manner. The yields in all cases corresponded within experimental errors to the values calculated on the basis of the above equations. This was confirmed also by following a few typical reactions on a thermogravimetric balance.

In one case (i.e. a lithium calcium derivative), a number of derivatives $(\text{Li}_x\text{Ca}_{1-x/2}\text{PO}_3)_n$ were prepared, in which x was gradually changed as $1/1$, $1/1.25$, $1/1.5$, $1/1.75$, $1/2$, $1/2.5$, $1/3$ and $1/4$. These were all obtained as transparent glasses. However, it was found that the samples with $x < 1/3$ dissolved too slowly for the preparation of a solution of reasonable strength. In view of the above, three convenient values were chosen arbitrarily for x , namely $\frac{2}{3}$, $\frac{1}{2}$ and $\frac{1}{3}$ so that a comparative study could be made of the samples with different alkali metals.

As stated above, all the complex metaphosphates were obtained as transparent glasses, which were colourless except those of copper and nickel, in which cases the colour deepened with the increase in percentage of these two coloured ions. All the derivatives with the composition $(\text{M}_{2/3}^{\text{I}}\text{M}_{1/6}^{\text{II}}\text{PO}_3)_n$ were soluble in water. The lithium derivatives were harder to dissolve than the corresponding caesium derivatives; the nickel and magnesium derivatives comparatively showed the lowest rates of dissolution. All the glasses were hard to powder; caesium glasses could, however, be powdered with greater ease than the corresponding lithium derivatives.

Derivatives with the general formula $(\text{M}_{1/2}^{\text{I}}\text{M}_{1/4}^{\text{II}}\text{PO}_3)_n$ were also all transparent glasses, more difficult to dissolve in water in general than the derivatives with the general formula, $(\text{M}_{2/3}^{\text{I}}\text{M}_{1/6}^{\text{II}}\text{PO}_3)_n$. In the cases of lithium, magnesium, barium and lead, complex derivatives of this composition were insoluble. Derivatives of lithium and caesium with the general formula, $(\text{M}_{1/3}^{\text{I}}\text{M}_{1/3}^{\text{II}}\text{PO}_3)_n$ were all transparent glasses. Out of the derivatives studied, those of calcium, zinc, cadmium and copper were soluble, but those of strontium, barium and lead were insoluble in water.

For sake of comparison, a few complex derivatives with the general formula $[\text{M}_4^{\text{I}}\text{M}^{\text{II}}(\text{PO}_3)_6 \cdot 2\text{H}_2\text{O}]_n$ were also prepared from aqueous solution (where $\text{M}^{\text{I}} = \text{Li}$ or Cs and $\text{M}^{\text{II}} = \text{Sr}$, Cd or Pb). These were prepared by treating salt solutions of these bivalent metals with lithium or caesium polymetaphosphates in 1:6 molar ratio, followed by precipitation with alcohol

and drying under vacuum. The properties of these complex derivatives prepared from solution were almost parallel to the sodium and potassium complex derivatives, described earlier⁸⁰.

POLYMERIC NATURE OF SIMPLE AND COMPLEX POLYMETAPHOSPHATE GLASSES OF GENERAL COMPOSITION $(M_x^+M_{1-x/a}^{a+}PO_3)_n$

As mentioned earlier, extensive work¹⁰⁻²¹ carried out on Graham's salt showed its highly polymeric character. Van Wazer and Holst⁸⁷ concluded early from their pHmetric and x-ray studies that branching units are comparatively much less stable (antibranching rule) and get fissioned on dissolution, sometimes causing an initial drop of viscosity. Similar studies^{10, 13, 79} on sedimentation velocity, dialysis, electrophoresis and dilute solution viscosity of potassium Kurrol salt in the presence of swamping electrolytes have shown it to be a high molecular weight chain phosphate; the species formed in solution during these studies, should have the general composition $(K_xM_{1-x/a}^{a+}PO_3)_n$ where a is the valency of the metal ions M^{a+} , used as the swamping electrolyte.

In view of the above, attempts have been made to throw light on the nature of the products synthesized during the course of our investigations by determination of their molecular weights, i.r. and n.m.r. spectra and by a study of their chromatographic and metachromatic behaviour. Finally, a detailed study of their conductivity has shown that the complexes are poly-electrolytes like Graham's salt.

The number average molecular weights of Graham's salt have been determined by end-group titrations^{12, 20, 88} and weight average values have been determined by light scattering¹⁵, dialysis and diffusion^{10, 11} techniques. Flory⁸⁹ introduced a new term 'viscosity average molecular weight'. Using Staudinger's method, molecular weights of Graham's salt have been determined by a number of workers^{15, 50, 72, 73, 90, 91, 92}. Both the end group titration as well as intrinsic viscosity methods have been used for estimating the molecular weights of the simple and complex metaphosphates described above.

End group titration

In the simple chain structure (*Figure 1*) of sodium polymetaphosphate, all the chain hydrogens would be strongly acidic titratable in the pH range around four, whereas the two terminal hydrogens would be much weaker in acidic behaviour and would be titrated at pH around nine. As suggested by Gustavsson and Larrson⁸⁸, a dilute hydrochloric acid solution was added to bring the pH of the polymer solution up to 3.0 to 3.5. On titration with alkali, two breaks were obtained at pH values around 4 and 9 and from this titre value, the number average molecular weight (M_n) of the polymer can be calculated by the formula:

$$M_n = \frac{2000 \times \text{wt of polymer dissolved in solution}}{\text{ml of } N \text{ NaOH required}}$$

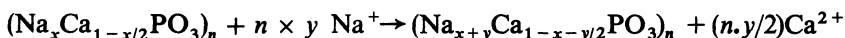
The initial addition of HCl was not considered⁸⁴ necessary with most of the complex lithium polymetaphosphates, as the pH of their solutions themselves was around 3.5. Values of M_n obtained for various simple and complex metaphosphates range generally between 4000 and 5000 for most of the complex derivatives except for those of caesium⁸⁶ which tend to be somewhat higher both for the simple as well as for the complex polymetaphosphates. The points of inflection were not quite sharp in the cases of complexes incorporating less-electropositive metal ions like Be^{2+} , Ni^{2+} , Zn^{2+} and in these cases the values of M_n also calculated from the observed titre values were exceptionally low. This might be explained on the possibility of consumption of some alkali by these less electropositive metal ions, if they are not strongly sequestered.

Determinations of weight average molecular weights (M_w) by viscosity measurements

The weight average molecule weights of Graham's salt have been determined by light scattering and viscosity measurements. Strauss *et al.*^{50, 93} observed that the weight average molecular weights of Graham's salt are proportional to intrinsic viscosity (η) of the sample in 0.035N sodium bromide solution. The value of M_w can, therefore, be calculated from the equation

$$(\eta) = K M_w$$

In the above equation, K is a constant and its value was found¹⁵ to be 1.76×10^{-5} when 0.035N sodium bromide solution is used as the theta solvent. The above constant K appeared to be unaffected by the nature of the anion of the electrolyte used as a solvent; Mehrotra and Gupta^{57, 59, 91} determined the viscosity of a number of samples of $(\text{NaPO}_3)_n$ in 0.035N sodium bromide and sodium chloride, and found the same value for η . Hence, the M_w values for simple and complex polymetaphosphates of lithium⁹², sodium⁵⁹, potassium^{71, 72} and caesium⁸⁶ were determined in 0.035N sodium chloride solutions. With lithium⁹² derivatives, lithium chloride and bromide were also sometimes employed as theta solvents. All these determinations did confirm the highly polymeric nature of these new complex derivatives. As expected, the values of M_w were higher than those of M_n for simple polymetaphosphates, but for some complex derivatives, this relationship appeared to be reversed. It was further observed that sodium chloride lowers the viscosity of solutions of complex polymetaphosphate, say $(\text{Na}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$ much more than that of solutions of simple sodium polymetaphosphate $(\text{NaPO}_3)_n$. Similarly, calcium ions (calcium chloride) were found to lower the viscosity of $(\text{NaPO}_3)_n$ solutions much more than sodium ions (sodium chloride). It has, therefore, been suggested⁹¹ that the anomalous behaviour of complex metaphosphates, like that of calcium, showing lower values for M_w than for M_n arises as the bivalent cations produced in equilibria of the following type reduce the observed viscosity of the metaphosphate solution quite markedly

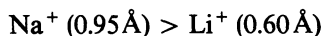


The correctness of this assumption is proved by the observation that the reduced viscosities of solutions of $(\text{NaPO}_3)_n + \text{CaCl}_2$ and $(\text{Na}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$

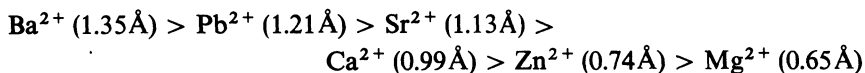
+ NaCl are almost identical, if the formal concentrations of the individual ions, i.e. of Na^+ , Ca^{2+} , Cl^- and $(\text{PO}_3)^-$ in the two cases are the same.

Effect of cations on the viscosity of polymetaphosphate solutions

As mentioned above, the viscosity of polymetaphosphate solutions is decreased by monovalent as well as by polyvalent cations, but the lowering is much more pronounced⁹¹ with the latter. It has been found that the order of change produced in reduced viscosity corresponds to the order of decreasing ionic radii of cations in the same valency state:



and



This simple relationship between ionic radii and the effect produced on reduced viscosity of a solution of Graham's salt appears to emphasize the physical picture of the phenomena as pointed out by Thilo⁷. The anion of the swamping electrolyte (for example, use of ZnSO_4 in place of ZnCl_2), does not appear to alter the effect⁴.

General conclusions from molecular weight measurements of polymetaphosphates

The main conclusions drawn from molecular weight measurements on simple and complex polymetaphosphates can be summarized:

(i) The reduced viscosity of simple as well as complex metaphosphate solutions shows a rise towards higher dilutions. This behaviour can be easily explained on the basis of the uncoiling of the chain due to the repulsion of charge centres in the polymers. This uncoiling effect could well be expected to be less pronounced for complex polymetaphosphates on the basis of structures of the type IIa; the actual experimental results corroborate this expectation fully.

(ii) Observed molecular weights of complex derivatives are comparatively lower than those of the corresponding simple alkali polymetaphosphates. This can be explained as being due to the following factors:

(a) The hydrolytic degradation of polyphosphate chains might take place in the presence of polyvalent cations, as has been observed by several workers^{94, 95}. Further, due to hydrolysis, the pH of the solution is lowered, requiring a larger volume of alkali in the end group titration method. Thus, M_n values of derivatives of Be, Mg and Ni are exceptionally low (of the order of 1500–2000), as the initial pH values of their solutions are also quite low, i.e. 2.6, 3.0, 2.8 respectively.

(b) Another reason for the low values of M_n obtained for complex derivatives may be due to extensive crosslinking in their structures, as is also indicated by the extremely slow rate of dissolution of these glasses in water, even when they are finely powdered. Recently, a study of the polyphosphate polymers: homopolymers containing Li^+ , Na^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} and Cd^{2+} and counter-ion copolymeric systems such as $\text{Na}^+ \text{La}^{3+}$; $\text{Na}^+ \text{Ca}^{2+}$; $\text{Na}^+ \text{K}^+$; $\text{K}^+ \text{Li}^+$ in the glass transition range by Eisenberg⁹⁶ has revealed

that the di-ionic chains possess crosslinking character as compared to those in which the repeat unit contains only one type of cations.

POLYELECTROLYTIC CHARACTER OF COMPLEX POLYMETAPHOSPHATES

Conductance measurements have been used as a valuable tool for establishing the polyelectrolytic nature of Graham's and Kurrol's salts. Davies and Monk¹⁶ found marked differences in electrolytic conductance behaviour of the cyclic sodium trimetaphosphate $(\text{NaPO}_3)_n$ and Graham's salt $(\text{NaPO}_3)_n$. The former behaves as a 1-3 valent electrolyte whereas the behaviour of the latter resembles that of polyelectrolytes. The conductances at different dilutions of a few typical polymetaphosphates of sodium⁵⁵⁻⁵⁹, potassium^{71, 72}, lithium⁸⁴ and caesium⁸⁶ have been published in a number of papers from our laboratories in recent years. The results have been well illustrated, in almost all cases, by the plots of (i) specific conductance against formal concentration; (ii) equivalent conductance (λ) against square root of concentration, i.e. λ versus \sqrt{c} ; and (iii) $\log \lambda$ versus $-\log c$. These plots have been shown to be characteristic of polyelectrolytes; similar curves have already been reported for some organic polyelectrolytes⁹⁷⁻⁹⁹. The results have been interpreted on the basis of the Fuoss model¹⁰⁰ for polyelectrolytes.

Thilo and co-workers¹⁰¹ had shown in 1960 that with the increasing chain length of the polyphosphate, $\text{Na}_{n+2}\text{P}_n\text{O}_{3n+1}$, the degree of dissociation first decreases rapidly and then more slowly to a limiting value at a chain length of about 100. The same general trend is observed in the conductance values of the simple and complex polyphosphates described above. Except in the cases of derivatives of nickel and magnesium, the molecular weights and chain lengths of which are quite low, molecular weights of the same species show only a slight upward trend with the temperature of preparation and the conductances of the higher molecular weight samples tend to be only slightly lower.

The conductances of complex polymetaphosphate solutions are generally in the same range (within 10-15 per cent) of the values for the solutions of the corresponding alkali polymetaphosphates, except in those cases where the chain length appears to assume an exceptionally low value. For example, the conductances of complex sodium polymetaphosphates^{46, 47, 55-59} are generally of the same order as those of simple sodium polymetaphosphate (Graham's salt). This appears to indicate that the mobilities of the anions $[\text{Na}_x(\text{PO}_3)_y]_n^{(y-x)-}$ are not affected by the partial or complete substitution of sodium atoms by bivalent atoms like calcium, strontium, barium, zinc, copper or lead. As discussed earlier also, this is in conformity with the structures suggested for these simple and complex polymetaphosphates by the author^{46, 47} in 1948. Wall and Doremus⁶⁴ had also shown in 1954 that the ionic mobilities of polyanions in the solutions of $(\text{NaPO}_3)_n$ and $(\text{Na}_{1/2}\text{Sr}_{1/4}\text{PO}_3)_n$ are of the same order.

If allowances be made for differences in lengths of polyphosphate chain, the conductances of equivalent solutions of simple and complex polymetaphosphate derivatives from different alkali metals follow the order of their

ionic mobilities: $Cs > K > Na > Li$, which is the reverse of the order of site-bonding shown for alkali metals with polyphosphate chains by Strauss and co-workers⁵⁰.

Thus the conductance measurements demonstrate clearly the poly-electrolytic nature of the simple and complex polymetaphosphates and the results are in conformity with the simple configurations shown in *Figures 1 and 2*.

METACHROMATIC REACTIONS OF POLYMETAPHOSPHATES

The absorption maxima of certain dyes which do not obey Beer's law are shifted to lower wavelengths in the presence of polyelectrolytes. This property has been termed 'metachromacy' by Michaelis and Granick¹⁰². The metachromatic effect of Graham's salt on toluidine blue was studied by Wiame¹⁰³. It has been found that the simple and complex polymetaphosphates, synthesized during the course of the present investigations, also shift^{104, 105} the absorption band of toluidine blue from 630 to 530 m μ . Further, it has been observed that the metachromatic effect of Graham's salt is unaffected in the presence of calcium or barium chloride. Similar effects have been observed for thionine and methylene blue, absorption bands of which are shifted from 590 to 510 m μ and 665 to 575 m μ respectively by various simple and complex polymetaphosphates of lithium, sodium, potassium and caesium.

The metachromatic effect on these dyes has been found to be independent not only of the nature of the above polymetaphosphates, but of their molecular weights¹⁰⁶. These effects have been explained by Michaelis and Granick¹⁰² and by Wiame¹⁰³ on the basis of the change in the degree of polymerization of the dye. Walton and Ricketts¹⁰⁷, however, found that in the cases of sulphonated dextrans, the reactive groups on the dextrans are responsible for metachromacy. Levine and Schubert¹⁰⁸ followed by Mckay and Hillson¹⁰⁹ have explained the origin of the metachromatic effects on the association of the dye molecules with the counter anions.

PAPER CHROMATOGRAPHIC STUDIES ON POLYMETAPHOSPHATES

Paper chromatography has in recent years proved useful in the separation of phosphate mixtures. A number of studies have been made by several workers^{18, 19, 110-112} and the subject has been reviewed by Thilo¹¹³ and by Hettler¹¹⁴. Morey¹¹⁵ in 1952 described the preparation of $Na_4Ca(PO_3)_6$ which was later shown by Ohashi and Van Wazer¹¹⁶ to be a trimetaphosphate derivative $Na_4Ca(P_3O_9)_2$. Thilo and co-workers¹¹⁷ have been able to separate quantitatively ring and chain phosphates by two-dimensional chromatography. Griffith and Buxton¹¹⁸ have been able to detect chain phosphates having chain lengths of up to eight phosphorus atoms and ring phosphates up to twelve-membered rings by this technique. Similarity in the nature of complex sodium¹¹⁹ and other alkali metal¹⁰⁵ polymetaphosphates with that of Graham's salt has been elucidated by recent paper chromatographic studies of Mehrotra and coworkers.

INFRA-RED AND NMR SPECTRA OF POLYMETAPHOSPHATES

Infra-red spectra

Chain and ring phosphates give characteristic i.r. vibrational frequencies in phosphates^{74, 75, 120}. The i.r. technique has also been used^{121, 122} for identifying the products of thermal dehydration of various metal phosphates. The i.r. spectral data of complex polymetaphosphates are given in Table 2. Those for sodium and sodium potassium trimetaphosphates⁷³ have also been included for comparison.

The following characteristics are discernible from these i.r. data :

(i) The absorption frequencies observed for alkali metal polyphosphates are in agreement within experimental error with the values reported in the literature^{74, 75}. The spectra of complex derivatives are almost similar to those of the corresponding alkali metal polymetaphosphates.

(ii) The strong and sharp absorption in the region $1300\text{--}1250\text{ cm}^{-1}$ in all the polymetaphosphates except in $(\text{KPO}_3)_n$ where it is observed as a doublet, is ascribed to P=O stretching, $\nu_{\text{as}}(\text{P=O})$. In almost all complex polymetaphosphates, the position of P=O stretching is not affected, indicating that the P=O bond characteristics are not changed by the substitution of monovalent metal ions by divalent metal ions.

(iii) A comparison of the spectra of complex polymetaphosphates shows the absence of strong and broad absorption in the region $1000\text{--}950\text{ cm}^{-1}$ characteristic of cyclic phosphates as well as of a strong sharp doublet at 745 cm^{-1} and a sharp peak at 770 cm^{-1} due to asymmetric and symmetric stretching of the P—O—P bond. Instead of these, vibrations at $895\text{--}860\text{ cm}^{-1}$ and $785\text{--}710\text{ cm}^{-1}$ are observed which have been ascribed to P—O—P chain vibrations. Corbridge and Lowe⁷⁴ have shown that the P—O—P chain causes characteristic vibrations at 900 cm^{-1} and due to its harmonics at 700 cm^{-1} , the frequency at 900 cm^{-1} is shifted to lower values, with increasing chain length. With $(\text{NaPO}_3)_n$, $\nu_{\text{as}}(\text{P—O—P})$ is observed at 868 cm^{-1} whereas in the case of complex derivatives, it is observed around $900\text{--}870\text{ cm}^{-1}$. This shift seems to be reasonable in view of the low molecular weight of the complex derivatives. Absence of splitting in $\nu_{\text{as}}(\text{P=O})$ vibrations and a number of other salient differences observed in the spectra of these complex derivatives from those of cyclic phosphates indicate their long chain character. Comparison of spectra of these derivatives with those of triphosphate reported by Corbridge also indicate their long chain characteristics. In the case of triphosphates, the strongest absorption is in the region $1170\text{--}1100\text{ cm}^{-1}$. In addition, a strong absorption in the region $1250\text{--}1085$, two absorptions at $1040\text{--}995$ and two at $775\text{--}690\text{ cm}^{-1}$ have been observed. However, in the case of these complex derivatives, the strongest absorption is in the region $1300\text{--}1250\text{ cm}^{-1}$ and only one absorption due to $\nu_{\text{as}}(\text{P—O—P})$ is observed in the region $900\text{--}860\text{ cm}^{-1}$.

The two absorption bands at $900\text{--}870$ and $1030\text{--}990\text{ cm}^{-1}$ in the case of $(\text{NaPO}_3)_n$ and $(\text{KPO}_3)_n$ have been assigned by Gehrke and Bues⁷⁵ to the coupling of two asymmetric stretching vibrations. The spectra of simple alkali polymetaphosphates prepared by us also show the two frequencies due to $\nu_{\text{as}}(\text{P—O—P})$. However, in the case of complex derivatives, this absorption is very weak and the second band could not be identified.

The band around $785\text{--}710\text{ cm}^{-1}$ also shows many variations in complex polymetaphosphates. No definite correlation between the nature of positive ions and $\delta(\text{P—O—P})$ is observed. It can be generalized that all absorptions which result due to the coupling vibrations of the bond in the chain or due to harmonics are very weak in complex derivatives because of their amorphous nature. In amorphous polymetaphosphates, the PO_4 chain is in a more disorganized state. It may be quite possible that couplings of various bond vibrations of the phosphate chain are really not very effective. This seems to be reasonable in view of the presence of the band at 677 cm^{-1} in $(\text{KPO}_3)_n$ and crystalline $(\text{NaPO}_3)_n$. The absence of this frequency has been reported also in the case of Graham's salt.

From the above discussion it can be said that these complex polymetaphosphate derivatives are similar in nature to amorphous polymeric Graham's salt.

Nuclear magnetic resonance studies

Condensed phosphates consist of PO_4 structural units which are distinguished from each other as the end, middle and branching groups. The polymetaphosphates are characterized by the presence of end and middle group only, whereas cyclic phosphates like trimetaphosphates have got only middle groups in their structure. Van Wazer *et al.*¹²³ have observed that each of the above-mentioned structural groups gives characteristic signals at different fields in ^{31}P resonance spectra of condensed phosphates in solution. More recently Crutchfield and Irani¹²⁴ have studied complexing between Li^+ , Ca^{2+} and Mg^{2+} ions and polyphosphates.

The chemical shift values¹²⁵ for complex polymetaphosphates, recorded in Table 1, show a sharp peak at 22 ± 1.5 p.p.m. and a weak peak at 12 ± 1.5 p.p.m. The former corresponds to the middle groups ($-\text{O—P—O—P—O—}$) whereas the latter is due to the end groups. The chemical shifts corresponding

Table 1. ^{31}P resonance spectra of a few complex polymetaphosphate derivatives

Complex polymetaphosphate	Chemical shifts		Complex polymetaphosphate	Chemical shifts	
	(p.p.m.) 85%	(reference H_3PO_4)		(p.p.m.) 85%	(reference H_3PO_4)
$(\text{NaPO}_3)_n$	11.35	20.42	$(\text{K}_{2/3}\text{Cd}_{1/6}\text{PO}_3)_n$	10.60	22.40
$(\text{LiPO}_3)_n$	11.47	21.90	$(\text{Li}_{2/3}\text{Cd}_{1/6}\text{PO}_3)_n$		23.40
$(\text{CsPO}_3)_n$	12.00	22.40	$(\text{K}_{2/3}\text{Li}_{1/3}\text{PO}_3)_n$	11.00	22.30
$(\text{K}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	11.10	22.10	$(\text{Li}_{2/3}\text{Pb}_{1/6}\text{PO}_3)_n$	11.20	22.70
$(\text{Li}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	12.80	23.40	$(\text{Cs}_{2/3}\text{Mg}_{1/6}\text{PO}_3)_n$	12.00	22.70
$(\text{Cs}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	11.20	22.70			

to middle and end groups are characteristic of long chain phosphates. These values are in agreement with those reported by Van Wazer *et al.*¹²³. The end group resonance could not be observed in those cases where the line due to the middle groups was of less intensity. This is expected since the intensity ratio of the end group line to the middle group line would be of the order of 1:40 when the degree of polymerization, n is 80. The intensities of end and middle group peaks depend very much upon the average chain length.

The above observations are in good agreement with those of Van Wazer *et al.* These are also in accord with the views of Eisenberg⁹⁶ about the extensive crosslinking in these products. The breaking of crosslinks in aqueous solution would form low molecular weight species. Therefore, in such cases the intensity of the middle group peak is expected to be low in comparison to the longer chain species.

Table 2. The i.r. spectral data of alkali polymetaphosphates and their complex derivatives

Compounds	$\delta(\text{P-O-P})$	$\nu_{\text{as}}(\text{P-O-P})$	$\nu_{\text{s}}(\text{PO}_2)$	$\nu_{\text{as}}(\text{PO}_2)$	
$(\text{LiPO}_3)_n$	792vwb	869vwb	1093mvb	1150vw	1258sb
$(\text{Li}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$	758vwb	893vwb	1099mb	1149vw	1250sb
$(\text{Li}_{2/3}\text{Ba}_{1/6}\text{PO}_3)_n$	758vwb	893vwb	1099mb	1150vw	1266sb
$(\text{Li}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	747vwb	893vwb	1099mb	1149vw	1250sb
$(\text{Li}_{2/3}\text{Cd}_{1/6}\text{PO}_3)_n$	758vwb	893vwb	1099mb	1149vw	1258sb
$(\text{Li}_{2/3}\text{Mg}_{1/6}\text{PO}_3)_n$	758vwb	893vwb	1081mb	1149vw	1258sb
$(\text{Li}_{2/3}\text{Ni}_{1/6}\text{PO}_3)_n$	758vwb	909vwb	1099mb	1151vw	1263sb
$(\text{Li}_{2/3}\text{Cu}_{1/6}\text{PO}_3)_n$	745vwb	901vwb	1070mb	1149vw	1250sb
$(\text{NaPO}_3)_n$	772wb	869sb, 995wb	1087s	1149w	1266ss
$(\text{Na}_{2/3}\text{Pb}_{1/6}\text{PO}_3)_n$	770wb	869sb	1085s	1149w	1258ss
$(\text{Na}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	763wb	885sb	1081s	1149w	1258ss
$(\text{Na}_{1/3}\text{Zn}_{1/3}\text{PO}_3)_n$	749wb	901sb	1053s		1266s
$(\text{Na}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$	769wb	877sb	1093s	1149w	1266ss
$(\text{Na}_{1/2}\text{Ca}_{1/4}\text{PO}_3)_n$	769wb	885sb	1093s	1149w	1266ss
$(\text{Na}_{1/3}\text{Cd}_{1/3}\text{PO}_3)_n$	769wb	889sb	1081s	1149w	1256ss
$(\text{KPO}_3)_n$	769w 677*	865ss 1025b	1093s	1149s	1265ss 1285ss
$(\text{K}_{2/3}\text{Pb}_{1/6}\text{PO}_3)_n$	781wb	887sb	1081s	1149w	1258ss 1282ss
$(\text{K}_{1/2}\text{Pb}_{1/4}\text{PO}_3)_n$	757wb	887sb	1081s	1143w	1258ss
$(\text{K}_{1/3}\text{Pb}_{1/3}\text{PO}_3)_n$	746wb	885sb	1087s	1150w	1266ss
$(\text{K}_{2/3}\text{Ba}_{1/6}\text{PO}_3)_n$	757wb	885sb	1085s	1149w	1258ss
$(\text{K}_{1/2}\text{Ba}_{1/4}\text{PO}_3)_n$	747wb	877sb	1081s	1149w	1266ss
$(\text{K}_{1/3}\text{Ba}_{1/3}\text{PO}_3)_n$	757wb	862b	1085s	1149w	1258ss
$(\text{K}_{2/3}\text{Ca}_{1/6}\text{PO}_3)_n$	764wb	870sb	1087s	1143w	1266ss
$(\text{K}_{1/3}\text{Ca}_{1/3}\text{PO}_3)_n$	769wb	885sb	1093s	1143w	1266ss
$(\text{K}_{2/3}\text{Na}_{1/3}\text{PO}_3)_n$	763wb	866sb	1087s	1149w	1266ss
$(\text{K}_{1/2}\text{Na}_{1/2}\text{PO}_3)_n$	767wb	870sb	1093s	1143w	1274ss
$(\text{K}_{2/3}\text{Li}_{1/3}\text{PO}_3)_n$	758wb	874s	1081s	1149w	1282ss
$(\text{K}_{1/2}\text{Li}_{1/2}\text{PO}_3)_n$	775wb	877s	1087s	1163w	1266ss
$(\text{K}_{1/3}\text{Li}_{2/3}\text{PO}_3)_n$	772wb	885s	1087ss	1163w	1266ss
$(\text{K}_{2/3}\text{Cu}_{1/6}\text{PO}_3)_n$	758wb	881s	1093s	1156w	1258ss
$(\text{K}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$	758wb	881sb	1087s	1143w	1266ss
$(\text{K}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$	763wb	891sb	1081s	1149w	1258ss
$(\text{K}_{2/3}\text{Cd}_{1/6}\text{PO}_3)_n$	768wb	874sb	1087s	1156w	1266ss
$(\text{K}_{2/3}\text{Ni}_{1/6}\text{PO}_3)_n$	754wb	881sb	1087s	1149w	1266ss
$(\text{K}_{1/2}\text{Ni}_{1/4}\text{PO}_3)_n$	744wb	877sb	1075s	1149w	1258ss
$(\text{CsPO}_3)_n$	794ms	885sh 1005mb	1081sb	1149wsh	1263s
$(\text{Cs}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$		854sb 1010mb	1081mb	1150wsh	1266sb
$(\text{Cs}_{2/3}\text{Cd}_{1/6}\text{PO}_3)_n$	766vwb	870wb 1010wb	1085mb	1149vw	1266s
$(\text{Cs}_{2/3}\text{Pb}_{1/6}\text{PO}_3)_n$	763vwb	870wb 1010wb	1085mb	1149vw	1266s

Table 2 (contd.)

Compounds	$\delta(\text{P-O-P})$	$\nu_{\text{as}}(\text{P-O-P})$	$\nu_{\text{s}}(\text{PO}_2)$	$\nu_{\text{as}}(\text{PO}_2)$	
$(\text{Cs}_{2/3}\text{Sr}_{1/6}\text{PO}_3)_n$		877wb 1010wb	1087mb	1150vw	1266s
$(\text{Cs}_{2/3}\text{Mg}_{1/6}\text{PO}_3)_n$		877vwb 1000m	1081mb	1148vw	1266s
$(\text{Cs}_{2/3}\text{Ni}_{1/6}\text{PO}_3)_n$		877vwb 1000m	1081mb	1149vw	1258s
$(\text{Cs}_{2/3}\text{Cu}_{1/6}\text{PO}_3)_n$		877vb	1087mb	1150vw	1266s

v = very; w = weak; b = broad; s = strong; ss = strong sharp and sh = shoulder.

* $\delta(\text{P-O-P})$.

δPO_2 , ν_{s} (ring) and $\nu(\text{P-O-P})$ for $\text{Na}_3\text{P}_3\text{O}_9$: (510, 520, 525) sb, 640 s and 690 cm^{-1} respectively; for $(\text{Na}_4\text{K}_2\text{P}_6\text{O}_{18})$: (513, 520, 525) sb, 640 and 690s cm^{-1} respectively.

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