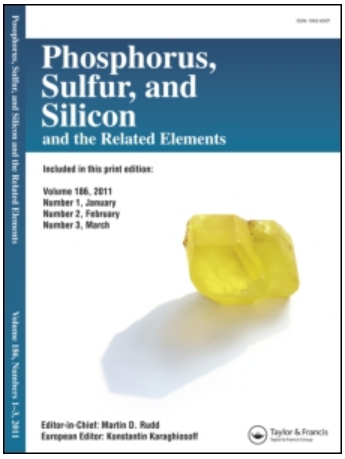

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EFFECT OF MAGNESIUM COMPLEXATION ON THE ^{31}P MIDDLE-GROUP CHEMICAL SHIFTS OF CHAIN AND RING PHOSPHATES

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For pure sodium polyphosphates, $Na_{n+2}P_nO_{3n+1}$, exhibiting 3 through 6 phosphorus atoms per molecule, the ^{31}P chemical shift of the middle group phosphorus atoms as measured in aqueous solution (0.1 M in P) at pH 7 was seen to increase with increasing magnesium ion concentration until there was one Mg atom per polyphosphate molecule, after which the chemical shift decreased. Finally the rate of decrease diminishes and precipitation occurs. For the longer-chain phosphates, $Na_{n+2}P_nO_{3n+1}$ with n = 8, 9, 10, or an average of 100, as well as for the ring phosphates, $Na_nP_nO_{3n}$ for n ranging from 3 through 10, an increase in magnesium concentration simply leads to a decrease in chemical shift which diminishes at the higher concentrations. These data lend additional support to the concept that polymerized phosphate anions in solution exist in preferred conformations which depend on the nature of the counteraction.

INTRODUCTION

The ^{31}P chemical shifts of phosphorus compounds have proven to be a valuable source of information relating to molecular[1-3] and electronic structures[1,4] as well as to conformational effects.[5,6] For example, in a recent paper[7] both end- and middle-group ^{31}P chemical shifts, as well as coupling constants, were used to demonstrate that the molecule adenosine triphosphate exists in a folded conformation in non-aqueous solutions having the polyphosphate side-chain adjacent to the plane of the adenine aromatic ring. In another paper, these same parameters were employed in a pH titration to determine the apparent acidity constants of tripolyphosphoric acid.[8] In the work reported here, these concepts are carried farther by interpreting chemical-shift changes upon adding a complexing cation to a phosphate solution in terms of families of complexes having defined ratios among their component ions.

RESULTS

Phosphorus-31 chemical shifts are reported as positive *downfield* from the standard in accord with the requirements of this Journal and the recently announced recommendation of the International Union of Pure and Applied Chemistry. Despite the problems inherent in such a convention change and the fact that this author and many of his colleagues have consistently used the older and now discarded ^{31}P shift convention, we advocate use of the new convention and hope that acceptance of the new convention will meet with a minimum level of resistance.

The changes in ^{31}P chemical shift at pH 7 of the phosphate middle groups upon adding increasing amounts of 0.1 M aqueous magnesium chloride to aqueous solutions of the various pure ring meta- and chain polyphosphates originally present at a phosphorus concentration of 0.1 M are shown in Figure 1; in the figure the ring metaphosphates are designated by (m) and the chain polyphosphates by (p). For the shorter-chain polyphosphates ($3 \leqslant n < 7$, where n is the number of phosphorus atoms per molecule), the chemical shift first increased in a linear manner, then curved to decrease linearly, and finally decreased less than linearly shortly before initiation of precipitate formation. The septapolyphosphate (7p) curve also exhibited a break; however, in this case all shift changes were negative. The larger chain polyphosphates (n = 8-10 and *ca.* 100) as well as the ring metaphosphates (trimeta- through octametaphosphate) exhibited only an initial linear decrease in this chemical shift which then flattened off.

It is important to note that the crossing points of the extrapolated two straight-line regions of the curves for the shorter chain phosphates correspond to Mg/P mole ratios exactly equivalent to one magnesium atom per polyphosphate molecule. Similar stoichiometric

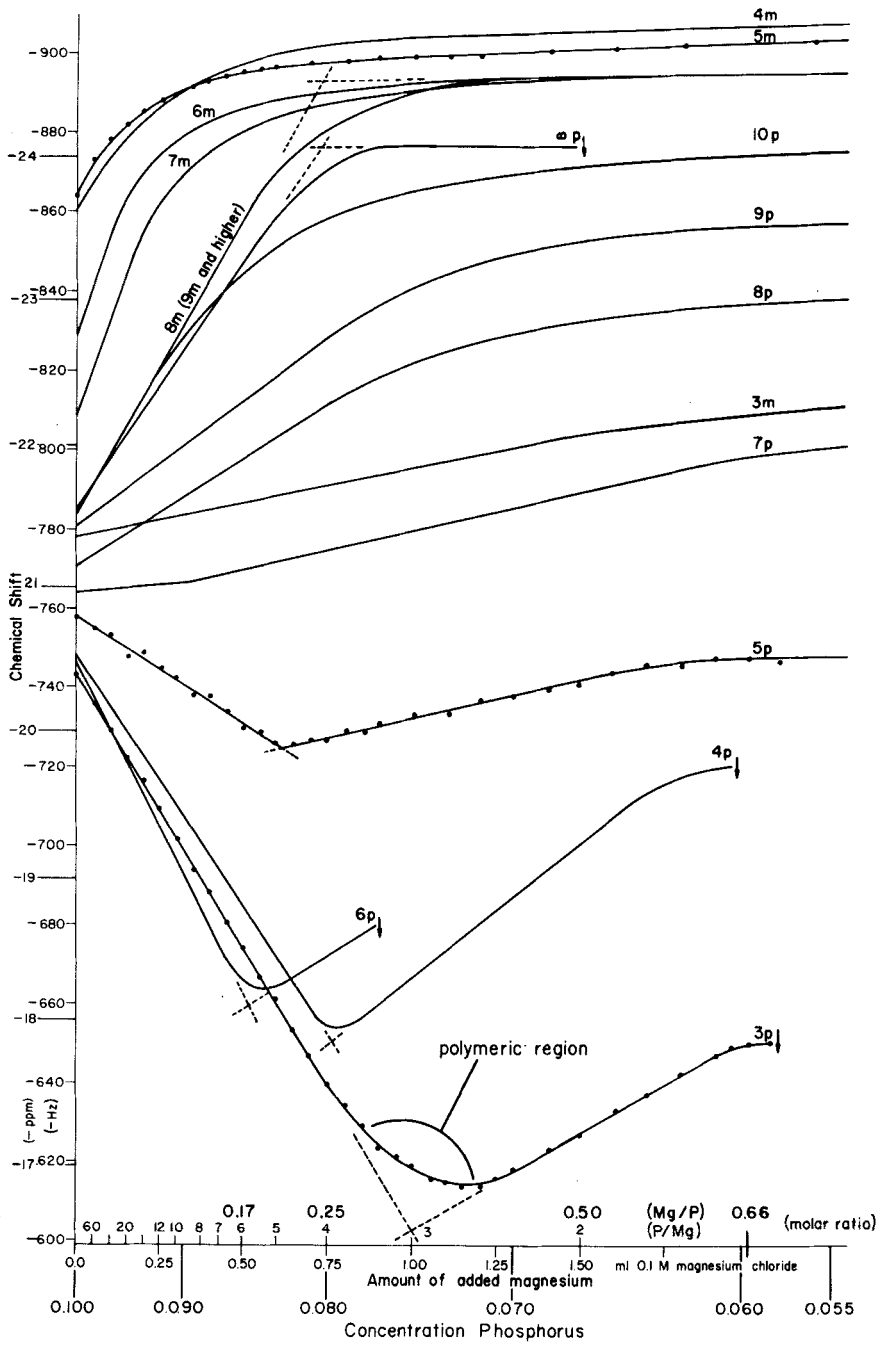

FIGURE 1 The ^{31}P chemical shift of condensed phosphate middle groups as a function of added magnesium ion. (NOTE: In this figure the ^{31}P shifts are plotted on the ordinate in accord with the newer ^{31}P shift convention in which positive numbers increase downfield. The absolute values of the shifts can be compared directly with previously published work from this laboratory since the same reference was used; only the sign of the shift is different.) The pure sodium phosphates were separately dissolved in deionized water to a total phosphorus concentration of 0.1 molar: tri- through decapolyphosphates, 3p–10p; long chain polyphosphate with an average chain length of 100.8 units, ∞P; cyclic metaphosphates, tri-nonametaphosphate, 3m–9m. One tenth molar magnesium chloride was added in small successive increments to 3.0 ml of these phosphate solutions, and the ^{31}P spectrum was taken after each

estimates of the Mg/P ratio can be made for the upper ends of these curves (corresponding to the higher magnesium concentrations) by finding the intercept between the linearly decreasing part of each chemical-shift plot and the horizontal straight line to which the final curved portion appears to be asymtotic. Although precipitate formation makes it very difficult to establish these Mg/P ratios, they seem to correspond to 2.0 for $n = 3$, 2.5 for $n = 4$, 3.0 for $n = 5$, and 5 for $n = 7$. Thus it seems that the tripolyphosphate anion (with sodium as counter alkali ion) forms two magnesium complexes, exhibiting respectively 1 and 2 Mg atoms per molecule. The larger oligomers up to the septaphosphate also exhibit a unique 1 : 1 magnesium complex although addition of further magnesium atoms per molecule does not seem to correspond to clearly distinguishable steps.

The plots in Figure 1 for the chain phosphates for which $n > 7$ as well as for the ring phosphates give no evidence for a 1 : 1 magnesium complex or indeed for any other specified complex. Instead they indicate an average number of complexed magnesium atoms per phosphate molecule of *ca.* 3.5 for the octa- and nonapolyphosphate chains, *ca.* 2 for the decapolyphosphate and *ca.* 24 for the centapolyphosphate. For the cyclic trimetaphosphate this average number seems to be *ca.* 2; whereas, for the larger cyclic phosphates up to the hexameta, it seems to be about 0.5, and for the heptameta- and larger metaphosphates it is bigger. Not surprisingly, the octameta- and nonameta- phosphates give curves in Figure 1 that approach that for the very long chain phosphate ($\bar{n} = 100$). The curves from these latter three polyanions exhibit an inflection corresponding to a phosphorus to magnesium ratio of 4/1.

The 1/1 magnesium tripolyphosphate complex when sedimented in the ultracentrifuge gave rise to a broad but readily observed Schlieren peak characteristic of a polydisperse material having a molecular weight range between 5 and 10 thousand. Such a complex would contain, on the average, 20 tripolyphosphate subunits.

DISCUSSION

In looking at the data of Figure 1, it appears that tri-, penta-, and septapolyphosphate comprise a set of polyanions which, upon the addition of magnesium ion, exhibit regular changes in the ^{31}P middle group chemical shift with progressive molecular weight. Tetra- and hexapolyphosphate shift changes with magnesium fall out of the pattern exhibited by tri-, penta-, and septapoly, with the hexapolyphosphate pattern being considerably different. The shifts of both tetra- and hexapolyphosphate increase rapidly with added magnesium to the point where the one-to-one phosphate to magnesium ratio is established, thereafter, they decrease almost as rapidly until precipitation occurs. It appears that the polyphosphate chain complexes with even numbers of phosphorus atoms may be structurally different from those having odd numbers of phosphorus atoms per chain.

The described ultracentrifuge experiment, which employed the tripolyphosphate anion, was designed to detect high molecular weight material since the unit sodium or magnesium tripolyphosphate complex, itself, is too light to be sedimented in the ultracentrifuge. Because the reference cell and the sample cell contained the same substances except for the magnesium ion, the Schlieren peaks observed for the 1 : 1 tripolyphosphato-magnesium complex must have resulted from a magnesium ion-induced polymerization of the phosphate, perhaps by a stacking process whereby each magnesium is sandwiched between two phosphate molecule-ions, or by a linear chaining process involving the phosphate chain end groups. The latter is the authors personal prejudice because it can neatly account for the formation of well defined 1/1 complexes with phosphate chains containing 3, 4, 5, 6, and 7 groups in the chain since, in a very large polymer formed from these phosphates, there will essentially be one magnesium ion for every phosphate end group.

The longer chain polyphosphates and the cyclic metaphosphates form another group of magnesium complexes characterized by having a diffuse stoichiometry. In this group the polyphosphates and the metaphosphates appear to represent the opposite wings of a continuum having as its central point the very high molecular weight poly- and metaphosphates.

The 4/1 stoichiometry exhibited by the high molecular weight poly- and metaphosphates in their chemi-

addition to produce the data of the Figure.[11] Except when precipitation of the salt occurred (indicated ↓) chemical shifts could be easily measured to within one Hz. Shifts are presented relative to 85% orthophosphoric acid; the ^{31}P resonance frequency was 36.43 MHz; and the spectrometer employed was a Bruker HFX5. Representative data are given for the tri- and pentapolyphosphates, 3p and 5p, and for the cyclic pentametaphosphate, 5m. The positions of the breaks in the curves are indicated by the crossed dashed lines. For all of the curves where precipitation is not indicated, data were accumulated with magnesium concentrations greater than the limits of the figure, and these extended curves were used to estimate the ratios of magnesium to phosphorus in the complexes involving more than one mole of magnesium per mole of phosphorus.

cal shift profiles is also exhibited in their corresponding ^{31}P line-width profiles, where a narrowing of the line-width occurs.[12] This may be interpreted to indicate that portions of the polymerized phosphate chain form a specific complex with each magnesium ion. In a number of earlier reports[5,7,12,13] it had been suggested that the condensed phosphate chain of high molecular weight polyphosphates existed as helixes in dilute aqueous solutions analogous to those which are known to exist in the crystalline state.[14] It was further suggested that the nature of the helix depended on the type of counter cation as well as the ionic strength of the medium and the polarity of the solvent.[5] A magnesium polyphosphate complex involving a helix having four phosphates per turn can best account for the stoichiometry shown in Figure 1 and the previously published line-width data.

EXPERIMENTAL

The cyclic metaphosphates,[5] the short-chain polyphosphates,[3,9] and the long-chain polyphosphate[10] ($\bar{n}$ = 100.8) were prepared as previously described. The preparation of the sodium salts, their titration with $MgCl_2$, and ^{31}P nuclear magnetic resonance (nmr) analyses were carried out according to a previous study.[11]

Ultracentrifuge experiments involving the 1/1 tripolyphosphato-magnesium complex were performed at 25° on a Beckman Model E ultracentrifuge equipped with the sector-cell assembly. A pH 7 stock solution of sodium tripolyphosphate was prepared by adding recrystallized sodium tripolyphosphate, $Na_5P_3O_{10}$, to deionized water, titrating the resultant solution to pH 7 with HCl, and then diluting with sufficient deionized water to obtain a solution 0.10 molar in phosphorus. The reference solution was prepared by adding 0.05 ml of a neutral 2 M NaCl solution to $1\frac{1}{2}$ ml of the stock solution; the sample was prepared by adding 0.05 ml of neutral 1 M $MgCl_2$ to $1\frac{1}{2}$ ml of the stock solution so that the ratio of Mg^{2+} ion to tripolyphosphate was 1/1. Solutions containing significantly less Mg^{2+} ion per phosphate did not yield measurable Schlieren peaks. Solutions containing Mg^{2+}/P ratios significantly greater than 1/1 or containing higher concentrations of phosphate precipitated in the course of the centrifuge run and yielded no interpretable information. The ultracentrifuge was operated at a speed of 59,780 rpm; an average run lasted 8 hours. These operations did not change the POP linkages in the tripolyphosphate since the characteristic tripoly ^{31}P nmr spectrum of the magnesium treated sample was exactly the same after centrifugation as before.

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