# Synthesis of α-, β-, and γ-Ketophosphonate Polymer-Supported Reagents: The Role of Intra-ligand Cooperation in the Complexation of Metal Ions

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ABSTRACT: Bifunctional ligands, viz., α-, β-, and γ-ketophosphonic acids, wherein a carbonyl group is systematically separated from a phosphoryl group with methylene moieties, have been immobilized on cross-linked polystyrene beads via the Arbusov and Perkow reactions. Studies with Eu(III), Cu(II), Pb-(II), Cd(II), Co(II), and Ag(I) in various acid solutions show that under conditions where coordination is the dominant mode of metal ion sorption, the α-ketophosphonate complexes greater levels of metal ions than the β-ketophosphonate and both complex far greater levels of ions than the γ-ketophosphonate. The latter performs in a manner comparable to the monofunctional phosphonic acid resin. The results are consistent with intra-ligand cooperation being an important factor in the design of polymer-supported reagents for the complexation of high levels of metal ions.

## Introduction

The selective complexation of metal ions by soluble and immobilized ligands is important in many enzymatic, chromatographic, and environmental processes.[1] The ion−ligand binding affinity is determined by a number of variables, including the acid/base strength of the interacting species and their polarizabilities.[2] This affinity is greater with ligands capable of chelation due to the presence of multiple binding sites and a minimum loss of entropy; thus, the binding constant for Cu(II) complexed with ethylenediamine is $10^{10.6}$ compared to $10^{7.7}$ for complexation with ammonia under identical conditions.[3]

Polymer-supported reagents have been prepared and utilized in chromatographic separations, the recovery of metal ions from water in the environment, and other applications.[4] Monofunctional cross-linked polymers with a single binding site per ligand include the sulfonic and carboxylic acid ion-exchange resins.[5] Greater ionic selectivity is observed with polymers to which chelating ligands are bound; for example, picolylamine-modified polystyrene has a very high affinity for Cu(II).[6] Bifunctional polymers, in which two different types of ligands are covalently bound to a cross-linked matrix, can also display high ionic affinities.[7] In one example, polystyrene modified with monoethyl- and diethylphosphonate groups had a distribution coefficient for Ag(I) from 4 N $HNO_3$ solutions of 2900; the monofunctional polystyrene matrices with monoethylphosphonate and diethylphosphonate ligands had Ag(I) distribution coefficients of 440 and 490, respectively.[8] The high metal ion affinity of the bifunctional polymer is attributed to the inter-ligand cooperation between two different functional groups in binding a given metal ion.

Intra-ligand cooperation allows for ionic affinities much higher than would be possible with inter-ligand cooperation alone due to metal ion chelate formation. For example, the gem-diphosphonate polymer (Figure 1a) has a distribution coefficient for $UO_2$(II) of $7 \times 10^5$ from 1 N $HNO_3$, while its monophosphonate analogue (Figure 1b) has a distribution coefficient of 900.[9]

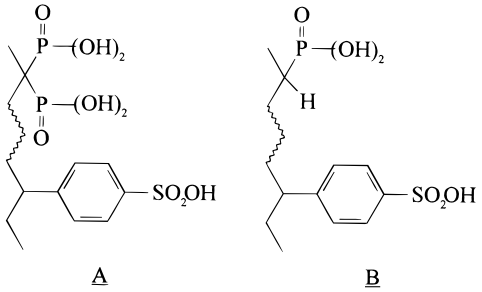

**Figure 1.** gem-Diphosphonate polymer (A) and its monophosphonate analogue (B).

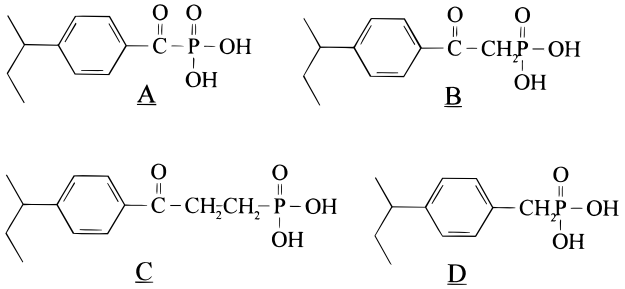

**Figure 2.** Styrene-based α-ketophosphonic acid (A), β-ketophosphonic acid (B), γ-ketophosphonic acid, and monofunctional phosphonic acid (D).

The objective of this report is to quantify the effect of intra-ligand cooperation within polymer-supported reagents on metal ion affinities. The ability of soluble diphosphonates and ketophosphonates to act as strong ion-complexing agents through a chelation mechanism has been studied.[10] The syntheses of styrene-based ketophosphonate polymers, viz., α-, β-, and γ-ketophosphonic acids (Figure 2a−c), were thus developed via the Arbusov and Perkow reactions. By increasing the distance between the binding sites (i.e., the carbonyl and phosphoryl groups), the extent of intra-ligand cooperation could be varied systematically while keeping other variables constant. Since the ligands are also capable of ion exchange, it was important to define the solution conditions where the background acidity was high

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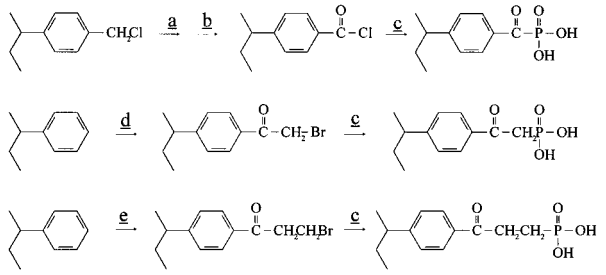

a: DMSO, $NaHCO_3$; 3 N $HNO_3$; 30% $H_2O_2$

b: $SOCl_2$

c: $P(OEt)_3$; conc. HCl

d: $BrCH_2C(O)Br$, $AlCl_3$

e: $BrCH_2CH_2C(O)Cl$, $AlCl_3$

**Figure 3.** Syntheses of the α-, *β*-, and *γ*-ketophosphonate resins.

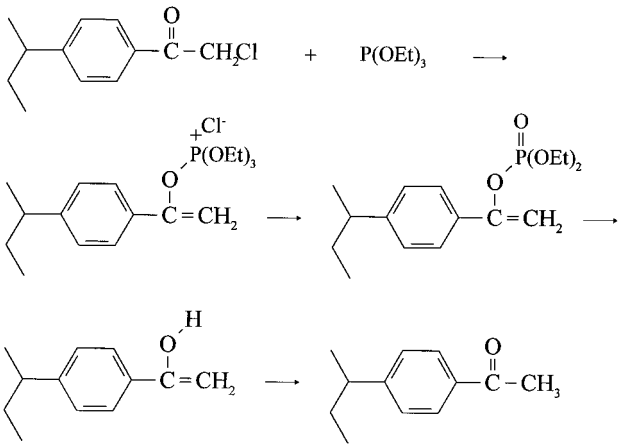

**Figure 4.** Mechanism of formation of acetyl-substituted polystyrene when chloroacetyl chloride is used as the acylating agent.

enough to counter the ion-exchange mechanism but low enough so that the ligands were not coordinated to the protons in solution. As a result, the ion complexation studies of Eu(III), Cu(II), Pb(II), Cd(II), Co(II), and Ag(I) were performed in 0.01, 0.10, and 1.0 N $HNO_3$ solutions. The distribution coefficient and percent complexed values were compared to those from the monofunctional phosphonic acid (Figure 2d).

## Experimental Section

The water content of the polymers, reported as percent solids ($(g_{dry}/g_{wet})100$), was measured by removing excess water from the beads by vacuum filtration and weighing before and after drying at 110 °C for 17 h.

The acid capacity was measured by contacting 1 g (dry weight) of the resin with 100 mL of 0.1000 N NaOH containing 5% NaCl for 17 h and back-titrating the excess base with 0.1200 N $H_2SO_4$.

Phosphorus elemental analysis was carried out by digesting 20 mg of resin with 15 mL of perchloric/nitric acid solution followed by reaction with amidol and ammonium molybdate.[11]

**Copolymer Synthesis.** Copolymers were synthesized as microporous (i.e., gel) and macroporous (MR) beads by suspension polymerization and cross-linked with 2% and 5% divinylbenzene (DVB) based on the total monomer weight. All chemicals were from Aldrich Chemical Co. unless otherwise noted.

In a typical preparation, the aqueous phase consisted of 1.93 g of gelatin (Knox Gelatin Co.), 23.68 g of poly(diallyldimethylammonium chloride) (Calgon Corp.), 1.26 g of boric acid, and 634 g of water adjusted to pH 10 with 50% NaOH. The monomer phase consisted of 286.7 g of styrene, 10.3 g of technical grade (55.4 wt %) DVB, and 3.0 g of benzoyl peroxide. A stir speed of 250 rpm gave beads with mostly 0.25−0.42-mm diameter. Higher stir speeds were used to obtain beads of smaller diameter. The vinylbenzyl chloride (VBC) beads were prepared in a similar manner except for the monomer weights. The gels were prepared with 114.70 g of VBC and 4.33 g of DVB, while the MRs were prepared with 107.97 g of VBC, 10.83 g of DVB, and 120 g of 4-methyl-2-pentanol as the porogen; 1.20 g of benzoyl peroxide was also added to each. Polymerizations were carried out by heating the suspension over a 2-h period to 80 °C, and the temperature was held for 10 h. Complete polymerization is ensured by heating the gels at 100 °C for 2 h. With the MRs, a 6-h steam distillation to remove the alcohol replaced the final 2-h heating period employed with the gels. The beads were washed four times with water and dried.

**Polymer-Supported Phosphonic Acid Resin.** Ten grams of poly(vinylbenzyl chloride) gel beads (2% DVB) was functionalized by refluxing with 100 mL of triethyl phosphite for 24 h. This was followed by hydrolysis at reflux with 100 mL of concentrated HCl for 24 h. After cooling to room temperature, the beads were filtered and washed with distilled water. The resin was placed in a fritted glass funnel and conditioned with 1 L each of $H_2O$, 1 N NaOH, $H_2O$, 1 N HCl, and $H_2O$, at 1 h/L. The resin had a phosphorus capacity of 4.83 mequiv/g (theoretical: 4.87 mequiv/g), 57.9% solids, and an acid capacity of 9.34 mequiv/g. The FTIR spectrum showed a broad peak at 1250 $cm^{-1}$ (P═O). The solid-state $^{31}P$ NMR spectrum showed the expected peak at 32.6 ppm.[12]

**Polymer-Supported α-Ketophosphonic Acid Resin.** Ten grams of poly(vinylbenzyl chloride) beads (2% DVB gel and 5% DVB MR; 0.25−0.42-mm diameter) was added to a mixture of 200 mL of dimethyl sulfoxide and 30 g of $NaHCO_3$. The mixture was stirred at reflux for 24 h. After cooling to room temperature, the beads were filtered and washed with ethanol and water. The beads were then swollen in 60 mL of 70% aqueous dioxane for 1 h followed by the addition of 130 mL of 3 N $HNO_3$. The mixture was heated at reflux for 24 h. After cooling to room temperature, the mixture was filtered. The beads were swollen in 60 mL of dioxane and heated at 80 °C with 130 mL of a 30% $H_2O_2$ solution for 24 h. The beads were recovered by filtration, washed with water, and conditioned by placing in a fritted glass column, as above. The gel and MR resins had acid capacities of 5.76 and 6.17 mequiv/g, with 34.0% and 27.1% solids, respectively. The carboxylic acid resin thus obtained was azeotropically dried with heptane and stirred with 150 mL of $SOCl_2$ at reflux for 48 h. Chlorine elemental analysis showed that high conversion to the acid chloride was possible only with the 5% DVB MR copolymer (4.63 mequiv/g; theoretical: 5.30 mequiv/g). The 2% DVB gel resin did not exceed 60% conversion and thus was not used in the subsequent reaction. The MR beads were filtered and washed with toluene three times followed by the addition of 100 mL of triethyl phosphite. The mixture was stirred and heated under nitrogen followed by hydrolysis with concentrated HCl, both of which were carried out at reflux for 24 h. The resin was filtered, washed with water several times and conditioned by placing in a fritted glass column, as noted earlier. The resin was further purified by extracting it with water for 17 h in a Soxhlet apparatus and reconditioned. Phosphorus elemental analysis showed a capacity of 3.76 mequiv/g (theoretical: 3.82 mequiv/g), 26.7% solids, and an acid capacity of 9.69 mequiv/g. Conversion of the acid chloride to the target ligand is 75%, with the remainder present as COOH groups. The weakly acidic ligands do not interfere in the ion-complexing studies due to the highly acidic background solutions used. The FTIR spectrum shows a peak at 1700 $cm^{-1}$ (C═O) and a broad peak at 1235 $cm^{-1}$ (P═O). The solid-state $^{31}P$ NMR shows a peak at 20.4 ppm, which is significantly more upfield compared to the peak position of the phosphonic acid.

**Polymer-Supported *β*-Ketophosphonic Acid Resin.** Ten grams of polystyrene beads (0.075−0.15-mm diameter) cross-linked with 2% DVB was swollen in 40 mL of $CS_2$.

**Table 1. Affinities of Immobilized Ligands for Eu(III) Ions from Nitric Acid Solutions**

| resin | 0.01 N $HNO_3$ | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ |
|---|---|---|---|
| $CH_2PO(OH)_2$ | ∞[a] (100%)[b] | 4070 (98.8%) | 9.43 (16.5%) |
| $COPO(OH)_2$ | ∞ (100%) | ∞ (100%) | 2060 (98.7%) |
| $COCH_2PO(OH)_2$ | ∞ (100%) | 7690 (99.5%) | 291 (88.6%) |
| $CO(CH_2)_2PO(OH)_2$ | ∞ (100%) | 3310 (98.9%) | 21.8 (40.5%) |

[a] Distribution coefficient. [b] Percent complexed.

**Table 2. Affinities of Immobilized Ligands for Cu(II) Ions from Nitric Acid Solutions**

| resin | 0.01 N $HNO_3$ | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ |
|---|---|---|---|
| $CH_2PO(OH)_2$ | 3610[a] (98.7%)[b] | 18.3 (27.8%) | 0 (0%) |
| $COPO(OH)_2$ | ∞ (100%) | 224 (89.5%) | 5.17 (15.8%) |
| $COCH_2PO(OH)_2$ | ∞ (100%) | 64.0 (63.0%) | 1.07 (5.12%) |
| $CO(CH_2)_2PO(OH)_2$ | 2430 (98.7%) | 15.1 (29.6%) | 2.03 (5.34%) |

[a] Distribution coefficient. [b] Percent complexed.

**Table 3. Affinities of Immobilized Ligands for Pb(II) Ions from Nitric Acid Solutions**

| resin | 0.01 N $HNO_3$ | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ |
|---|---|---|---|
| $CH_2PO(OH)_2$ | 1070[a] (95.7%)[b] | 59.8 (55.6%) | 0 (0%) |
| $COPO(OH)_2$ | ∞ (100%) | 1060 (97.5%) | 6.61 (19.4%) |
| $COCH_2PO(OH)_2$ | 2690 (98.6%) | 366 (90.7%) | 5.06 (11.2%) |
| $CO(CH_2)_2PO(OH)_2$ | 2290 (98.6%) | 40.8 (53.1%) | 1.17 (3.14%) |

[a] Distribution coefficient. [b] Percent complexed.

Bromoacetyl bromide (25.19 g; 124.8 mmol), $AlCl_3$ (40 g; 300 mmol), and 40 mL of $CS_2$ were added to the flask, and the mixture was stirred for 48 h at 0 °C. The beads were washed with an ice−ethanol mixture, water, acetic acid, and ethanol and dried in vacuo at 70 °C. They were refluxed with 100 mL of triethyl phosphite followed by hydrolysis with 100 mL of concentrated HCl, also at reflux, for 24 h. The beads were filtered and washed with water several times followed by conditioning in a fritted glass column, as above. They had a phosphorus capacity of 3.50 mequiv/g (theoretical: 4.26 mequiv/g), 48.2% solids, and an acid capacity of 6.83 mequiv/g. The FTIR spectrum is similar to the α-ketophosphonate with key peaks at 1680 and 1240 $cm^{-1}$. The solid-state $^{31}P$ NMR shows a peak at 23.8 ppm.

**Polymer-Supported γ-Ketophosphonic Acid Resin.** Ten grams of 2% DVB polystyrene beads (0.075−0.15-mm diameter) was swollen in 40 mL of $CS_2$. 3-Bromopropionyl chloride (21.43 g; 125 mmol), $AlCl_3$ (40 g; 300 mmol), and 40 mL of $CS_2$ were added to the flask, and the mixture was stirred for 48 h at 0 °C. The beads were washed with an ice−ethanol mixture, water, acetic acid, and ethanol and dried in vacuo at 70 °C. The dried beads were reacted with 100 mL of triethyl phosphite followed by hydrolysis with 100 mL of concentrated HCl, both of which were carried out at reflux for 24 h. The beads were filtered and washed with water several times followed by conditioning in a fritted glass column. The phosphorus capacity was 3.60 mequiv/g (theoretical: 4.01 mequiv/g), 46.7% solids, and the acid capacity was 7.27 mequiv/g. The FTIR spectrum is similar to the other ketophosphonates. The solid-state $^{31}P$ NMR shows a peak at 35.7 ppm.

**Metal Ion Contact Studies.** Metal ion analyses were carried out by contacting enough resin to give 1.0 mmol of ligands (as determined by phosphorus elemental analysis) with 10 mL of $10^{-4}$ N metal nitrate solution in 0.01, 0.10, and 1.0 N $HNO_3$ for 24 h. The metal ion left in solution was measured by atomic emission or absorption with a Perkin-Elmer 3100 atomic absorption spectrometer. The results are reported in terms of the percent $M^{n+}$ complexed and the distribution coefficient, $D$, defined as ([mequiv of $M^{n+}]_{resin}/g_{resin}$)/([mequiv of $M^{n+}]_{soln}/mL_{soln}$). The affinities of the resins toward Eu(III), Cu(II), Pb(II), Cd(II), Co(II), and Ag(I) were determined.

## Results and Discussion

The syntheses of the α-, β-, and γ-ketophosphonate resins are summarized in Figure 3. Immobilization of the α-ketophosphonate ligand was first carried out on a 2% DVB gel copolymer support. Though a very high conversion to the carboxylic acid was achieved, the subsequent reaction with thionyl chloride could not be made to proceed in greater than 60% conversion (3.00 mequiv of Cl/g; theoretical (based on the acid capacity of the precursor): 4.94 mequiv/g). Accessibility must thus be a variable because the same reaction with a 5% DVB MR copolymer gave 87% conversion (4.63 mequiv of Cl/g; theoretical (based on the acid capacity of the precursor): 5.30 mequiv/g). The α-ketophosphonate resin was thus prepared from the 5% DVB MR support. This does not affect the conclusions from the metal ion studies because the results at equilibrium are reported: the results at the 24-h contact time are identical with those at a contact time of 0.5 h.

Synthesis of the β-ketophosphonate resin was dependent on the initial acylation reaction. Reaction of the polystyrene beads with chloroacetyl chloride in $CS_2$ resulted in $C(O)CH_2Cl$ substitution (3.11 mequiv of Cl/g). The chloroacylated polystyrene was then reacted with triethyl phosphite; the resulting phosphorus capacity (2.33 mequiv/g) corresponded to complete reaction of the substituted sites. Hydrolyzing to the diacid, however, by refluxing with concentrated HCl resulted in a sharp drop in the phosphorus capacity (to 0.65 mequiv/g). Lowering the hydrolysis temperature to 40 °C did not reduce the loss of phosphorus. The IR spectrum of the polymer showed a peak in the carbonyl region (1690 $cm^{-1}$) and the absence of the strong P═O peak. The results thus suggest a mechanism wherein the phosphite reacts at the carbonyl oxygen to give a vinyl phosphate and hydrolysis leads to loss of phosphorus and the formation of acetyl-substituted polystyrene (Figure 4). This is supported by the strong similarity of the polymer's FTIR spectrum to that of acetophenone, especially at 1690 $cm^{-1}$ and the entire fingerprint region. Use of different solvents in the phosphite reaction (carbon tetrachloride, dioxane, ethanol, and 4-methyl-2-pentanol) did not obviate O-phosphorylation and continued loss of phosphorus was observed. An attempt to follow the reported synthesis of β-ketophosphonates from vinyl phosphates via 1,3-phosphorus migration using lithium diisopropylamide in dry THF[13] still yielded a product with low phosphorus capacity after hydrolysis (0.52 mequiv/g). The problem

**Table 4. Affinities of Immobilized Ligands for Cd(II), Co(II), and Ag(I) Ions from Nitric Acid**

| | Cd(II) | | Co(II) | | Ag(I) | |
|---|---|---|---|---|---|---|
| resin | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ | 0.10 N $HNO_3$ | 1.0 N $HNO_3$ |
| $CH_2PO(OH)_2$ | 31.3[a] (39.3%)[b] | 3.55 (6.85%) | 13.3 (21.6%) | 0 (0%) | 72.0 (59.9%) | 8.18 (14.5%) |
| $COPO(OH)_2$ | 248 (86.8%) | 3.36 (8.89%) | 71.6 (65.5%) | 0 (0%) | ∞ (100%) | 443 (92.2%) |
| $COCH_2PO(OH)_2$ | 100 (78.4%) | 2.96 (7.40%) | 37.4 (57.6%) | 0.21 (0.56%) | 36.9 (57.2%) | 5.57 (13.1%) |
| $CO(CH_2)_2PO(OH)_2$ | 30.6 (46.0%) | 2.76 (7.13%) | 10.3 (22.3%) | 0.67 (1.82%) | 20.8 (36.7%) | 6.89 (16.1%) |

[a] Distribution coefficient. [b] Percent complexed.

was circumvented by replacing chloroacetyl chloride with bromoacetyl bromide. The choice was based on the fact that bromide is a better leaving group than chloride in nucleophilic substitution reactions.[14] The bromoacylated beads had a phosphorus capacity of 3.50 mequiv/g after reaction with triethyl phosphite and hydrolysis with concentrated HCl at reflux; the corresponding acid capacity was 6.83 mequiv/g. The $\gamma$-ketophosphonate resin was then readily prepared from polystyrene beads with 3-bromopropionyl chloride.

The solid-state $^{31}$P NMR spectra of the three ketophosphonates show an effect of the carbonyl group on the peak position of the phosphorus. The standard phosphonic acid resin has a single peak at 32.6 ppm. The $\gamma$-ketophosphonate is most similar to it with a peak at 35.7 ppm. The chemical shift decreases to 23.8 ppm for the $\beta$-ketophosphonate and 20.4 ppm for the α-ketophosphonate. The similarity and differences noted here will have a parallel in the metal ion studies (vide infra).

The metal ion studies are reported in Tables 1−4. The results with Eu(III), Cu(II), and Pb(II) show that all polymers, including the phosphonic acid resin, complex metal ions nearly quantitatively from 0.01 N $HNO_3$ solutions. Ion exchange is thus the dominant sorption mechanism in this solution, and further studies with it were discontinued. The complexation of europium is > 98% from 0.10 N $HNO_3$ (Table 1). Important differences in europium affinities become evident from 1 N $HNO_3$, where ionic complexation is expected to occur by coordination rather than ion exchange: the distribution coefficient is greatest for the α-ketophosphonate (2057 (98.7% complexed)) followed by the $\beta$-ketophosphonate (291 (88.6% complexed)). The phosphonic acid and $\gamma$-ketophosphonate polymers show low affinities (9.43 and 21.8 (16.5% and 40.5% complexed, respectively)). The same trend is observed for the other metal ions, viz., Cu(II), Pb(II), Cd(II), Co(II), and Ag(I), from 0.10 N $HNO_3$ solutions (Tables 2−4). All polymers show low affinities for these ions from 1 N $HNO_3$.

The 0.10 N $HNO_3$ solution permits differences among the ligands to be observed for the transition-metal ions, while differences with Eu(III) are most evident in 1.0 N $HNO_3$. With all metal ion studies, however, the same trends are found: the α-ketophosphonate group shows the highest affinity toward a given metal ion followed by the $\beta$-ketophosphonate; the $\gamma$-ketophosphonate is either equivalent to or slightly better than the phosphonic acid ligand. These ionic affinities can be explained in terms of intra-ligand cooperation and the stability of the rings formed upon chelation. Ring formation as a variable in the complexation of metal ions has been identified with poly(pyrazolyl)borates[15] and polyamines.[16] In the present case, the high ionic affinity of the α-ketophosphonate ligand can be attributed to the formation of a stable five-membered ring[17] coupled with a relatively low loss of entropy upon chelation.[18] This is consistent with results obtained with the $\beta$-ketophosphonate where a still-favorable six-membered ring is formed but the loss of rotational entropy is expected to be higher, thus leading to a lower level of complexation. The $\gamma$-ketophosphonate ligand is much less likely to form a seven-membered chelate ring and so displays ionic affinities much like the phosphonic acid resin. The low metal ion affinities of the latter two ligands may thus be due to the absence of intra-ligand cooperation and coordination through a single site (the phosphoryl oxygen) for each ligand. Further studies aimed at quantifying these differences with binding constants are currently in progress.

## Conclusions

The syntheses of polymer-supported reagents with immobilized ketophosphonic acid ligands have been developed. Metal ion affinity studies lead to the conclusion that intra-ligand cooperation within sites capable of ionic complexation yields higher affinities. Complexation is greatest with the α-ketophosphonate ligand, followed by the $\beta$-ketophosphonate, most likely due to the formation of five- and six-membered chelate rings. It is expected that the size of the metal ion will also play a role in determining which of the chelate rings will be favored, and studies with actinide ions will be reported in due course.

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