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Immobilized Tris(hydroxymethyl)aminomethane as a Scaffold for Ion-Selective Ligands: The Auxiliary Group Effect on Metal Ion Binding at the Phosphate Ligand

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The metal ion affinities of a ligand in a polymer-supported reagent can be enhanced by the presence of a proximate group capable of hydrogen bonding. A new polymer-supported reagent has been synthesized by immobilizing tris(hydroxymethyl)aminomethane (Tris) onto cross-linked poly(vinylbenzyl chloride) and then phosphorylating the –OH moieties. The –NH– acts as the auxiliary group to increase the extent of complexation by the phosphate ligand. Additionally, Tris acts as a scaffold, wherein the phosphate ligands are in a known stereochemical arrangement. The Tris resin is mono-, di-, and triphosphorylated, depending on the concentration of the phosphorylating agent. The highest metal ion affinities are found with the resin having a phosphorus-to-nitrogen ratio of 2.36, consistent with one-third of the ligands being triphosphorylated and the remainder being diphosphorylated. The unphosphorylated Tris and phosphonate diester resins have no ionic affinities under the same conditions. Trivalent ions (Fe(III), Al(III), La(III), Eu(III), Lu(III)) are preferred over divalent ions (Pb(II), Cd(II), Cu(II), Zn(II)) from solutions at pH 2. The distribution coefficients of the divalent ions correlate with the Misono softness parameters, indicating that the polarizability of the phosphoryl oxygen is important to binding of the metal ions. The mechanism of complexation is probed with Fe(III) in 0.01–5 M HNO_3 and HCl. The high affinities are ascribed to activation of the P═O ligand toward metal ion binding by the N–H moieties acting as auxiliary groups, coupled with intraligand cooperation among the phosphate moieties at a given site. FTIR spectra show that the P═O band at 1261 cm^{-1} shifts as a function of the extent of hydrogen bonding. Binding at the P═O requires a balance between activation by hydrogen bonding and availability of the lone pair electrons to the metal ions.

Introduction

Polymer-supported reagents have numerous applications in synthesis, separations, catalysis, environmental remediation, and as sensors.[1] They can be prepared with different functional groups, as appropriate to the application. As sensors and in environmental remediation, a high affinity for a targeted metal ion is important, and the selection of suitable chelating ligands is essential to the design of a suitable polymer. Ligands oriented within a polymer framework through template polymerization can enhance metal ion selectivity.[2] The imprinted ions can be complexed from aqueous solutions with greater selectivity than other ions. However, the synthesis of template-bearing monomers can require a high level of cross-linking that can lead to low sorption capacities.[3] An alternative approach is to take advantage of the fact that many ions form stable complexes with multidentate ligands, and thus, it may be possible to enhance the selectivity of polymeric reagents by immobilizing ligands in positions where they can cooperate in binding to a given metal ion. Intraligand cooperation has led to much higher ionic affinities with diphosphonic acids relative to those with monophosphonic acid ligands.[4] The approach can be generalized to the use of scaffolds, wherein a molecule

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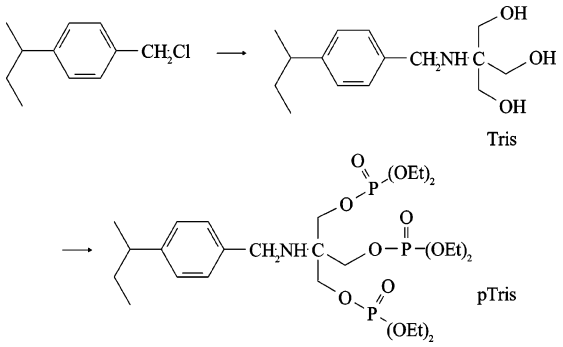

Figure 1. Synthesis of the pTris resin.

with a well-defined stereochemistry is modified with ligands whose resulting proximity allows cooperation in the binding of ions. Calixarenes are most often used as soluble scaffolds on which ligands, such as imidazole[5] and chelidamic acid,[6] are bound. Other scaffolds include modified porphyrins,[7] oligopeptides,[8] phosphazene,[9] trispyrazolylborate,[10] and trimethylbenzene.[11]

The use of scaffolds is one important approach to increasing metal ion affinity and selectivity. A new approach is to increase the affinity of an ion-binding ligand by activating it with an auxiliary group.[12] Activation of phosphate ligands through hydrogen bonding has been effective with −OH auxiliary groups. While the supported $-P(O)(OEt)_2$ ligand has a low affinity for metal ions from solutions at pH 2, that affinity markedly increases when it is proximate to hydroxy groups due to polarization of the P═O moiety through hydrogen bonding. In this report, the ability of amines to act as auxiliary groups is determined. Additionally, the auxiliary group is coupled to phosphate ligands on a scaffold in order to determine whether preorganization of the ligands has an additional effect. Tris(hydroxymethyl)aminomethane was chosen for these studies because it unambiguously reacts with poly(vinylbenzyl chloride) through its $-NH_2$ moiety and then has three $-CH_2OH$ groups that can react with an array of compounds. Proper choice of those compounds leads to substitution with ligands capable of complexing metal ions in a known stereochemical arrangement, and the reaction stoichiometry can be used to control whether the scaffold is mono-, di-, or trisubstituted. Immobilization of the phosphate ligand onto polymer-supported tris(hydroxymethyl)aminomethane by reaction with varying concentrations of diethylchlorophosphate (Figure 1) examines whether the ionic affinity of the phosphate in the scaffold is affected by amine or unsubstituted $-CH_2OH$ groups or by proximate ligands on the multiphosphorylated scaffolds. The affinity of the polymer for Fe(III), Al(III), La(III), Eu(III), Lu(III), Pb(II), Cd(II), Cu(II), and Zn(II) is quantified. The mechanism of complexation is probed with Fe(III) in order to separate the influence of the neutral salt from anionic species since Fe(III) remains as $Fe(NO_3)_3$ in HNO_3 at the acid concentrations used in this study but more readily forms $FeCl_4^-$ with increasing HCl concentration.

Experimental Section

Materials. A copolymer of vinylbenzyl chloride (VBC) and 2 wt % divinylbenzene (DVB) was prepared by suspension polymerization.[13] The resulting beads were placed in a Soxhlet extractor with toluene to remove any linear polymer, dried, and sieved to retain those with a particle size of 250−425 μm. All chemicals were purchased from the Sigma Aldrich or Acros companies.

Immobilization of Tris(hydroxymethyl)aminomethane. Four grams of polyVBC beads (24 mmol $-CH_2Cl$ groups) in 40 mL of *N*-methylpyrrolidone (NMP) was added to a solution of 30 g (248 mmol) of tris(hydroxymethyl)aminomethane, 100 mL of NMP, and 30 mL of H_2O in a 250 mL round-bottom flask fitted with a condenser and an overhead stirrer. The mixture was heated to 70 °C over 1 h and kept at 70 °C for 17 h. Excess solution was removed, and the beads were washed with 100 mL of NMP, NMP/H_2O (1:1 v/v), and H_2O.

Phosphorylation of Immobilized Tris(hydroxymethyl)aminomethane. Two grams of the tris(hydroxymethyl)aminomethane resin (7.94 mmol N) was swollen in 50 mL of pyridine for 2 h in a 250 mL round-bottom flask. Diethylchlorophosphate (DECP), in varying amounts depending upon the desired level of substitution (1.0−10.0 mL (6.92−69.2 mmol)), was added slowly, and the mixture was stirred at 25 °C for 17 h. The beads were washed with 100 mL each of methanol, methanol/H_2O (1:1, v/v), and H_2O, and they were then eluted with 1 L each of 1 M NaOH, H_2O, 1 M HCl, and H_2O.

Characterization.[14] The acid capacity was determined by contacting 0.5 g of Buchner-dried resin with 50 mL of 0.100 M NaOH containing 5 wt % NaCl for 17 h and then titrating a 10 mL aliquot with 0.100 M HCl. The phosphorus capacity was determined after mineralization of a 20 mg sample of resin in 10 mL of concentrated sulfuric acid containing 3.19 mg of copper sulfate and subsequent reaction with 10 mL of ammonium vanadate−molybdate. The color intensity was measured at 470 nm on a Milton Roy Spectronic 21D. The nitrogen capacity was determined by the Kjeldahl method after wet oxidation of 200 mg resin in 25 mL of concentrated sulfuric acid containing 250 mg of copper sulfate pentahydrate and 10 g of potassium sulfate.[15] The chlorine capacity was determined by combusting 100 mg of resin in an oxygen-filled bomb and titrating the resulting solution with silver thiocyanate. FTIR spectra were recorded with a Bomem spectrophotometer.

Metal Ion Affinities. Ionic affinities were determined by equilibration of the resins with 10^{-4} N metal salt solutions (Fe(III), Al(III), La(III), Eu(III), Lu(III), Pb(II), Cd(II), Cu(II), and Zn(II)) in 0.01−4 M HNO_3. (Note: The concentration of metal ions is given in terms of normality rather than molarity in order to emphasize that the same number of charges are present in solution,

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regardless of the valency of the ions, and to allow for comparisons of the coordination reactions at a constant ionic strength. The acid concentrations are given in molarity since HNO_3 and HCl are both monobasic. In subsequent studies that include H_2SO_4 and H_3PO_4, all concentrations will be reported in normality.) With Fe(III), the background solutions were 0.01−5 M HNO_3 or HCl. The effect of the electrolyte was studied by comparing results from 0.01 M HNO_3 and 0.01 M HNO_3/0.04 M $NaNO_3$. Enough Buchner-dried resin to give 0.50 mmol of phosphorus was pre-equilibrated with the appropriate background solution (three times, 15 min each) and then shaken with 5 mL of the metal ion solution for 17 h. Metal ion concentrations were determined by ICP−AES (Spectroflame M120E). The percent complexed was calculated from the initial and final concentrations. Distribution coefficients were also calculated (mmol of metal on resin per g_{resin}/mmol of metal in solution per mL_{soln}). All experiments were done in triplicate, and the log *D* values are valid to ±0.05.

Results

Polymer-supported amines are prepared by reaction of amines with immobilized $-CH_2Cl$ groups, often in dioxane as the solvent.[16] The reaction of tris(hydroxymethyl)aminomethane (Tris) on cross-linked polyVBC beads was thus first attempted in dioxane at reflux for 17 h. The Tris was in a 10:1 molar excess relative to the number of $-CH_2Cl$ moieties. The theoretical nitrogen capacity of the resulting resin is 4.05 mmol/g if there is complete conversion to $-CH_2$-Tris groups. The experimental nitrogen capacity, however, was 2.97 mmol/g. Slowly adding the beads to a hot, homogeneous solution of Tris in dioxane, followed by a 72 h reflux, gave an identical nitrogen capacity. Since there was no chlorine in the product resin, the secondary amine on the immobilized Tris must have reacted further with a neighboring $-CH_2Cl$ to form a tertiary amine. This type of secondary cross-linking occurs in the immobilization of dimethylamine.[17] In order to determine whether solvent polarity affects this reaction, the beads were contacted with Tris in *N*-methylpyrrolidone (NMP) at 70 °C. The product Tris resin had, within experimental error, the theoretical nitrogen capacity (3.97 mmol/g). Though NMP should not be sufficiently nucleophilic to react with the $-CH_2Cl$ groups, this was checked by contacting the beads with NMP at 80 °C; at the end of 17 h, the beads had no nitrogen content, and the FTIR spectrum was unchanged from that of polyVBC. After conditioning the resin with 1 L each of 1 M NaOH, H_2O, 1 M HCl, and H_2O, the acid capacity of the protonated amine was found to match the nitrogen capacity. The $-CH_2Cl$ moieties are thus quantitatively converted to Tris ligands, and all are accessible to ions in solution.

The hydroxyl groups on the immobilized Tris allow for subsequent functionalization with ligands such as phosphate. Tris serves as the scaffold on which varying levels of phosphate can be placed by reaction at the −OH groups. Those ligands would be proximate to the −NH− moiety, which could act as an auxiliary group to affect the ionic affinity of the phosphoryl oxygen through hydrogen bonding. Diethylchlorophosphate (DECP) is known to be an effective phosphorylating agent with molecules such as chitosan[18] and was used with the Tris resin in reactions at room temperature. In order to ascertain whether the secondary amine on the Tris would also react with the DECP, a primary amine resin prepared according to the Gabriel procedure[19] was contacted with DECP in pyridine; the product had no phosphorus capacity, and its nitrogen capacity was unchanged from that of the starting amine, indicating that the N−H moiety on Tris would remain unchanged after contact with DECP and subsequent washing with aqueous acid.

Table 1. Phosphorylation of the Tris Resin[a]

resin	DECP (mL)	DECP/Tris initial ratio	acid capacity (mmol/g)	nitrogen capacity (mmol/g)	phosphorus capacity (mmol/g)	P/N ratio
A	1.0	0.87	2.57	2.44	0.77	0.32
B	1.5	1.31	2.30	2.08	1.30	0.63
C	2.0	1.74	1.62	1.78	3.07	1.72
D	4.0	3.48	1.70	1.66	3.91	2.36
E	10.0	8.72	1.69	1.64	3.91	2.38

[a] Two grams of Tris resin in 50 mL of pyridine; 17 h at 25 °C.

In this research, varying degrees of phosphorylation were attempted by stoichiometric control of the initial DECP/Tris ratio. Pyridine was both solvent and base to remove the byproduct HCl. Contacting 2 g of Tris resin in 50 mL of pyridine with 1.0, 1.5, 2.0, 4.0, and 10.0 mL of DECP to give initial DECP/Tris molar ratios of 0.87, 1.31, 1.74, 3.48, and 8.72 gave phosphorylated Tris resins with P/N ratios of 0.32, 0.63, 1.72, 2.36, and 2.38, respectively, as the phosphorus capacities increased from 0.77 to 3.91 mmol/g (Table 1). The acid capacity of each resin matched its nitrogen capacity after conditioning with NaOH/H_2O/HCl/H_2O, indicating that phosphorylation occurs with no hydrolysis of the diester moieties and that the ligand is not hindered toward binding since the nitrogen is available for protonation.

A comparison of the FTIR spectra of resins with increasing phosphorus capacities (0.49, 1.49, 2.90, and 3.91 mmol/g) shows the region that distinguishes them is 1250−700 cm^{-1} (Figure 2). The left-most spectrum is that for a phosphorylated ethylene glycol resin[12] with a P═O band at 1261 cm^{-1}; that band drops to 1211 cm^{-1} for the monophosphorylated Tris and then increases to 1217, 1229, and 1230 cm^{-1} as phosphorylation increases. The peak at 1051 cm^{-1} in the resin with a phosphorus capacity of 0.49 mmol/g decreases to 1047, 1043, and 1040 cm^{-1} as phosphorylation increases. This peak is attributed to P−O(C).[20] Additionally, the region between 1150 and 950 cm^{-1} appears to broaden because a peak at ∼960 cm^{-1} grows relative to one at ∼1040 cm^{-1}, which remains of constant intensity. Tris has a similar peak at 1049 cm^{-1} and an adjoining peak at 1012 cm^{-1} that disappear upon phosphorylation (the resin with a phosphorus

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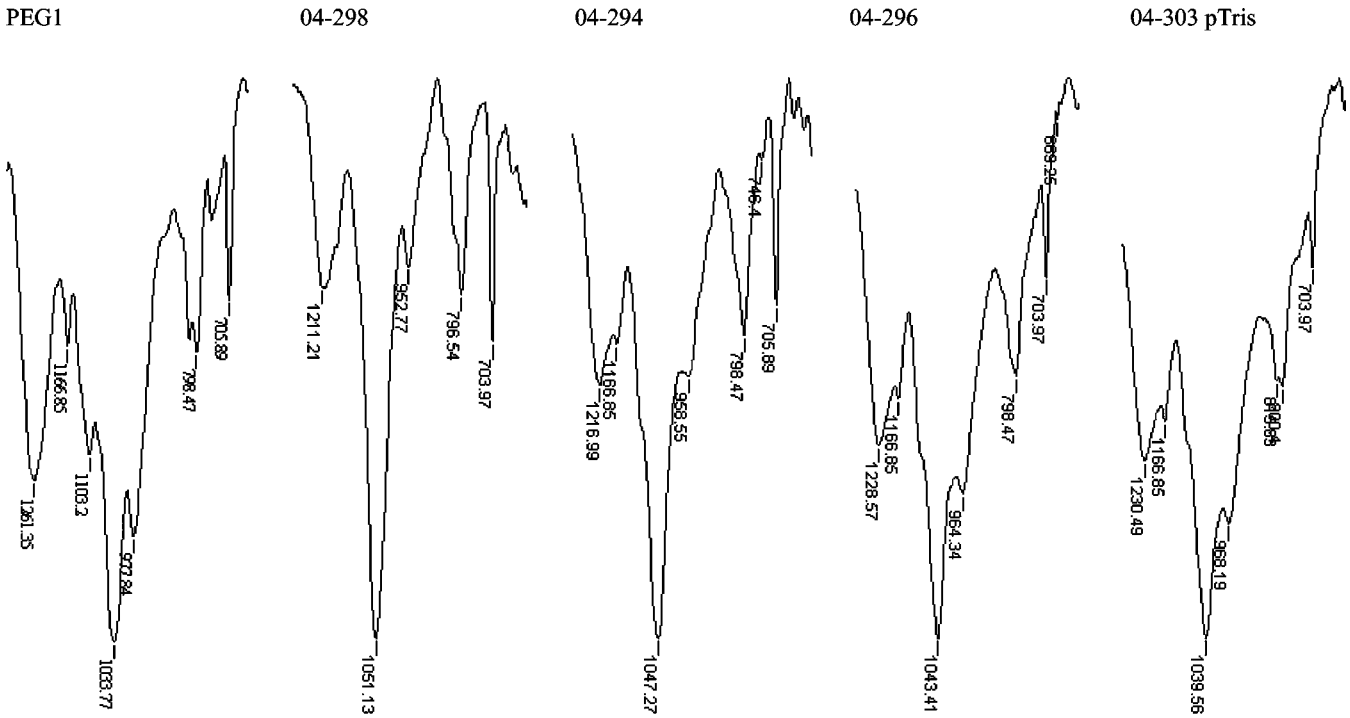

Figure 2. Infrared spectra for the phosphorylated ethylene glycol resin (PEG1) and Tris resins with phosphorus capacities of 0.49 (04-298), 1.49 (04-294), 2.90 (04-296), and 3.91 mmol/g (pTris).

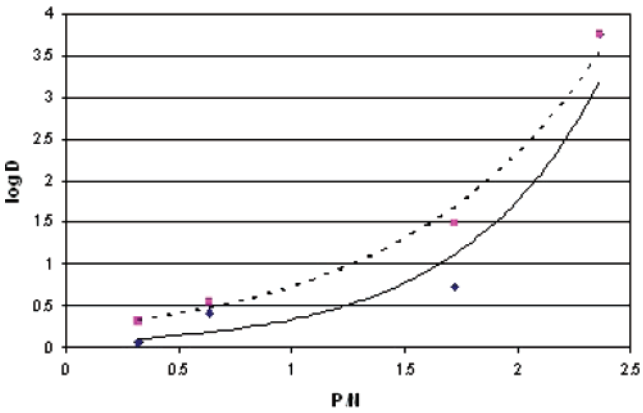

Figure 3. Correlation of log *D* versus P/N ratio (◆ 0.01 M HNO_3, ■ 1.0 M HNO_3).

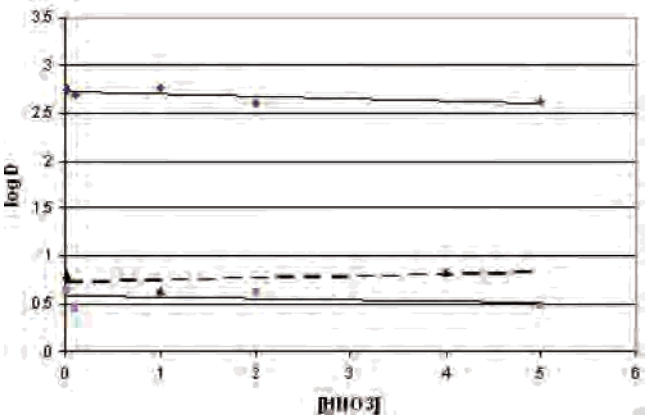

Figure 4. Correlation of log *D* versus [HNO_3] (◆ pTris, ■ PE, ▲ NR_2).

Table 2. Affinity of Trivalent Ions for the pTris Resin as a Function of Nitric Acid Concentration[a]

[HNO_3] M	Fe(III) %	Al(III) %	La(III) %	Eu(III) %	Lu(III) %
0.01	94.6 (2.75)	83.5 (2.32)	84.7 (2.37)	86.6 (2.43)	86.7 (2.44)
0.10	93.9 (2.68)	60.2 (1.62)	70.3 (1.86)		80.3 (2.05)
0.50		26.3 (1.04)	66.0 (1.78)	62.9 (1.69)	
1.0	94.8 (2.76)	13.2 (0.64)	51.2 (1.51)	43.2 (1.34)	56.4 (1.56)
2.0	92.7 (2.60)	8.3 (0.41)	30.7 (1.13)	31.3 (1.08)	32.3 (1.07)

[a] Percent complexed (log *D*).

capacity of 0.49 mmol/g shows the appearance of the ~960 cm^{-1} peak that grows as the P/N ratio increases). Thus, the key features of the FTIR spectra are that phosphorylation results in a shift of the peak originally at 1211 cm^{-1} to higher energy, a shift of the peak originally at 1051 cm^{-1} to lower energy, and the appearance of a peak at ~960 cm^{-1}.

The effect of the degree of phosphorylation on the affinity of a given ion was probed with 10^{-4} N solutions of Fe(III). An amount of resins A, B, C, and E to give 0.50 mmol of P complexed 11, 18, 21, and 95% Fe(III), respectively, from 0.01 M HNO_3, while, from 1 M HNO_3, the values were 18, 19, 56, and 95% Fe(III), respectively. The analogous log *D* values are plotted as a function of the P/N ratio in Figure 3. This behavior is also observed with La(III) and Eu(III); both are complexed to <5% from 0.01 M HNO_3 by resins A, B, and C, while complexation is >80% by resin E. There is <5% complexation when Eu(III) contacts resin C in 1 M HNO_3 and 1 M HCl. All subsequent studies are with resin E, and it will be referred to as the pTris resin.

The high level of complexation displayed by the pTris resin is not significantly dependent on the acidity of the background solution; it complexes >90% Fe(III) from a 0.01−5 M HNO_3 solution. Trivalent non-transition-metal ions, however, show a dependency on solution acidity (Table 2).

In order to understand the mechanism by which the pTris resin complexes metal ions, its affinity for Fe(III) was

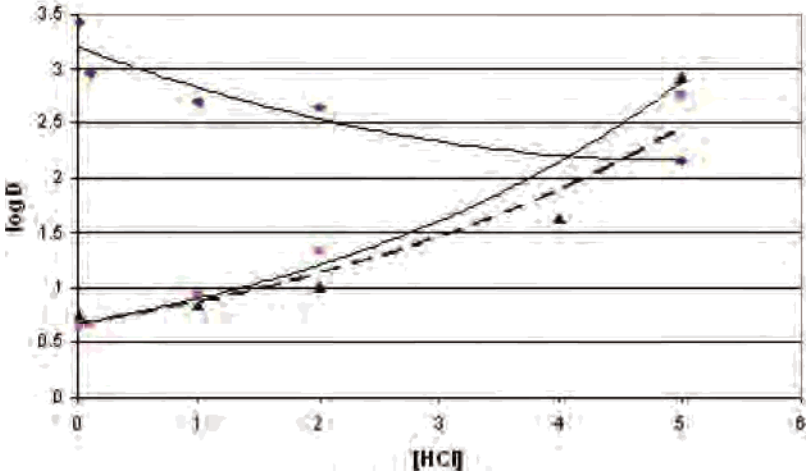

Figure 5. Correlation of log *D* versus [HCl] (◆ pTris, ■ PE, ▲ NR_2).

Table 3. Metal Ion Affinities of pTris,[a] Tris,[b] and PE[c] Resins Contacted with 10^{-4} N Metal Nitrate Solutions in 0.01 M Nitric Acid

	Fe(III) %	Al(III) %	La(III) %	Eu(III) %	Lu(III) %	Pb(II) %	Cd(II) %	Cu(II) %	Zn(II) %
pTris	94.6[d] (2.75)[e]	83.5 (2.32)	84.7 (2.37)	86.6 (2.43)	86.7 (2.44)	53.3 (1.62)	32.5 (1.27)	26.8 (1.13)	13.6 (0.75)
Tris	≤5	≤5	≤5	≤5	≤5	≤5	≤5	≤5	≤5
PE	≤5	≤5	≤5	≤5	≤5	≤5	≤5	≤5	≤5

[a] Phosphorylated tris(hydroxymethyl)aminomethane (P/N = 2.36). [b] Tris(hydroxymethyl)aminomethane. [c] Phosphonate diester. [d] Percent complexed. [e] Log(distribution coefficient).

compared to that of the dimethylamine (NR_2) and phosphonate diester (PE) resins. Both resins have little affinity for Fe(III) from a 0.01−5 M HNO_3 solution. The plot of log *D* as a function of HNO_3 concentration shows the resin affinities to be pTris ≫ PE, NR_2 (Figure 4).

Changing the acid from HNO_3 to HCl significantly affects the PE and NR_2 resins' affinity for Fe(III); complexation increases from <10% in 0.01 M HCl to >90% in 5 M HCl. Complexation by pTris is much less affected by the change to HCl with only a small decrease at 5 M compared to the value in HNO_3 (Figure 5).

The affinity of the pTris resin for divalent and trivalent ions was studied in 0.01 M HNO_3 (Table 3). Its affinity for Fe(III) is high and remains high for trivalent ions. The affinity is low for divalent ions, with only a moderate affinity for Pb(II). Both the Tris and PE resins do not complex metal ions from a 0.01 M HNO_3 solution, thus demonstrating the ineffectiveness of the −OH groups on Tris and the ester groups alone. A control experiment with the Tris resin shows no affinity for the divalent ions even at a final pH of 4.5.

Figure 6 shows that coordination to the pTris P═O moiety is sensitive to the solution pH, with increasing pH favoring divalent ion complexation; at pH 2.75, the uptake of Pb(II), Cd(II), Cu(II), and Zn(II) increases to 78.7, 46.6, 56.2, and 31.1%, respectively, from 53.3, 32.5, 26.8, and 13.6% at pH 2.0. The protons in solution effectively compete with the divalent ions for binding at the phosphoryl oxygen as the pH decreases below 2. However, the competition is more successful with the PE resin than it is for pTris; the former complexes <5% Pb(II) from a pH 2.1 solution.

Results with the trivalent ions are also sensitive to solution acidity (Figure 7). Starting at the levels reported in Table 2, complexation decreases as the acidity increases from 0.01 to 5 M HNO_3. Significant sorption of Al(III) requires a higher pH than the lanthanides. The PE resin has no affinity for the trivalent ions at solution pH values of 2 or less.

The effect of adding electrolyte to the solution was investigated by contacting solutions of divalent and trivalent ions in 0.01 M HNO_3 and 0.01 M HNO_3/0.04 M $NaNO_3$ with the pTris resin. Results show that the presence of sodium and nitrate ions increases the extent of complexation for all ions, except perhaps Fe(III) (Table 4). The increase is more pronounced with the divalent ions; at pH 2, complexation of Pb(II) increases from 53.3 to 68.8%, while Zn uptake increases from 13.6 to 24.5%.

Discussion

Degree of Phosphorylation. Increasing the DECP/Tris initial ratio increases the level of phosphorylation (Table 1). The extent of reaction on a group capable of multisubstitution can be controlled by the initial ratio of reactants; for example, the phosphorylation of chitosan increased as the amount of P_2O_5 in methanesulfonic acid increased,[21] and both phosphorylation and carbamidation of starch changed as the molar ratio of starch/H_3PO_4/urea was varied.[22] Complete phosphorylation of all Tris scaffolds gives a P/N ratio of 3. Assuming the scaffolds are first monophosphorylated before di- and triphosphorylation occurs, the P/N ratios show that resin A has one of every three Tris scaffolds monophosphorylated while two of every three are unphosphorylated, resin B has

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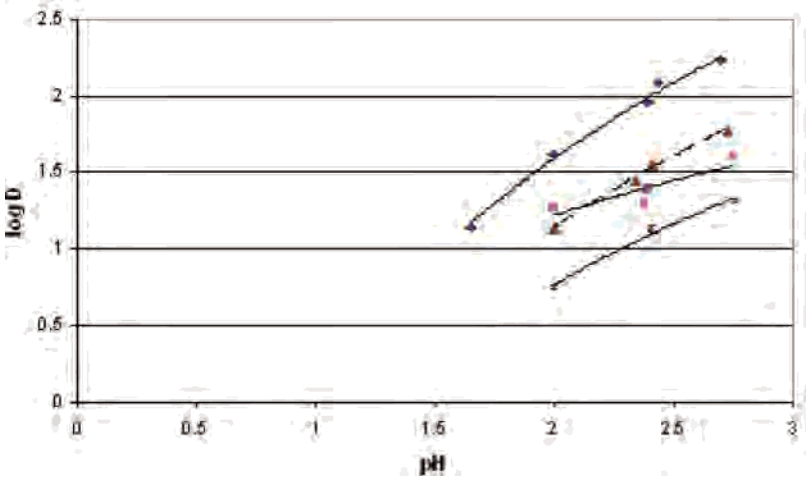

Figure 6. Correlation of log *D* versus pH of the solution in contact with the pTris resin (◆ Pb(II), ■ Cd(II), ▲ Cu(II), ∗Zn(II)).

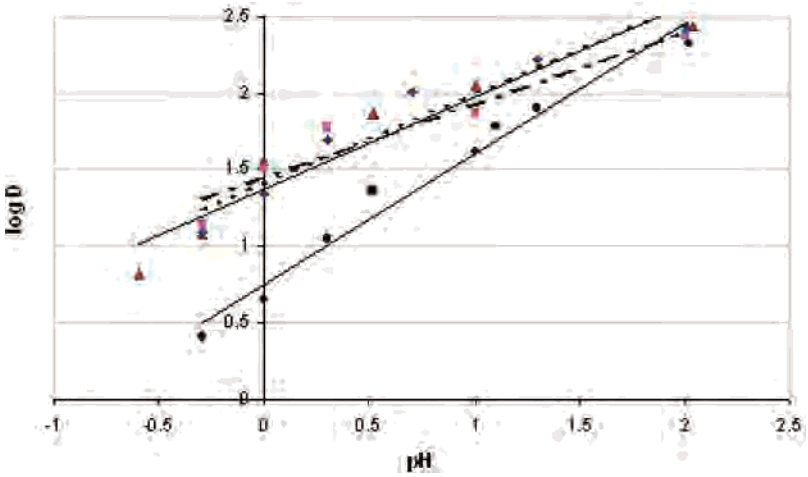

Figure 7. Correlation of log *D* versus pH of the solution in contact with the pTris resin (◆ Eu(III), ■ La(III), ▲ Lu(III), ● Al(III)).

two of every three Tris monophosphorylated while one of every three is unphosphorylated, resin C has two of every three Tris diphosphorylated while one of every three is monophosphorylated and resins D and E have two of every three Tris diphosphorylated while one of every three is triphosphorylated.

A plot of the final (P/N) ratio versus the initial (DECP/Tris) ratio shows the relationship of the variables (Figure 8a). A plot of the reciprocal values (Figure 8b) shows linearity between the initial Tris/DECP ratio and the final degree of functionalization down to a (N/P) value of 0.5 (equivalent to a P/N ratio of 2 (i.e., diphosphorylation)). At a given amount of Tris resin, as the Tris/DECP initial ratio decreases from unity, the amount of DECP increases, but phosphorylation is less than theoretical since the correlation has a slope greater than one. An increased level of DECP in solution is therefore required to drive the reaction forward until a ratio of 0.5 achieves the same final N/P ratio (i.e., diphosphorylation). This is consistent with uniform functionalization of the polymer beads from mono- through diphosphorylation. A further increase in DECP concentration gives additional phosphorylation so that approximately one-third of the ligands are triphosphorylated. The final resin has identical properties when the DECP/Tris initial ratio is 3.5 or greater. It may be expected that monosubstitution would be favored, as it is with β-cyclodextrin[23] due to steric hindrance,[24] but that the hindrance would be overcome by increasing the concentration of DECP in solution. However, the difficulty in achieving complete triphosphorylation is due not to steric hindrance but to a strong hydrogen bond between the third $-CH_2OH$ and the secondary amine. This was proposed in the etherification of tris(hydroxymethyl)aminomethane dissolved in THF and supported by the crystal structure of $(PhCH_2)_2NC(CH_2OH)(CH_2OCH_2$-(bromobipyridine))$_2$ which showed a short intramolecular N−H distance.[25] The current results suggest that one out of every three diphosphorylated Tris moieties has the $-CH_2OH$ group in a conformation that is not hydrogen bonded to the nitrogen (perhaps because the P═O are too closely associated with the N−H site) and is available to complete the phosphorylation.

pTris Resin Structure. The structural difference among the phosphorylated Tris resins was probed by contacting the

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Table 4. Effect of 0.04 M $NaNO_3$ on Metal Ion Extraction by the pTris Resin

	Fe(III)	Al(III)	La(III)	Eu(III)	Lu(III)	Pb(II)	Cd(II)	Cu(II)	Zn(II)
no $NaNO_3$[a]									
pH_f[b]	2.04	2.02	2.02	2.04	2.04	1.98	1.99	1.96	1.97
% complexed	94.6	83.5	84.7	86.6	86.7	53.3	32.5	26.8	13.6
log *D*	2.75	2.32	2.37	2.43	2.44	1.62	1.27	1.13	0.75
0.04 M $NaNO_3$[c]									
pH_f	1.99	1.94	1.94	1.95	1.97	2.01	2.02	1.99	2.01
% complexed	93.2	87.5	89.6	88.4	88.4	68.8	44.2	37.8	24.5
log *D*	2.76	2.46	2.56	2.51	2.49	1.92	1.46	1.35	1.07

[a] For divalent and trivalent ions, the background solution without $NaNO_3$ is 0.01 M HNO_3. [b] The final pH of the solution in contact with the pTris resin. [c] For divalent and trivalent ions, 0.01 M HNO_3 is also present.

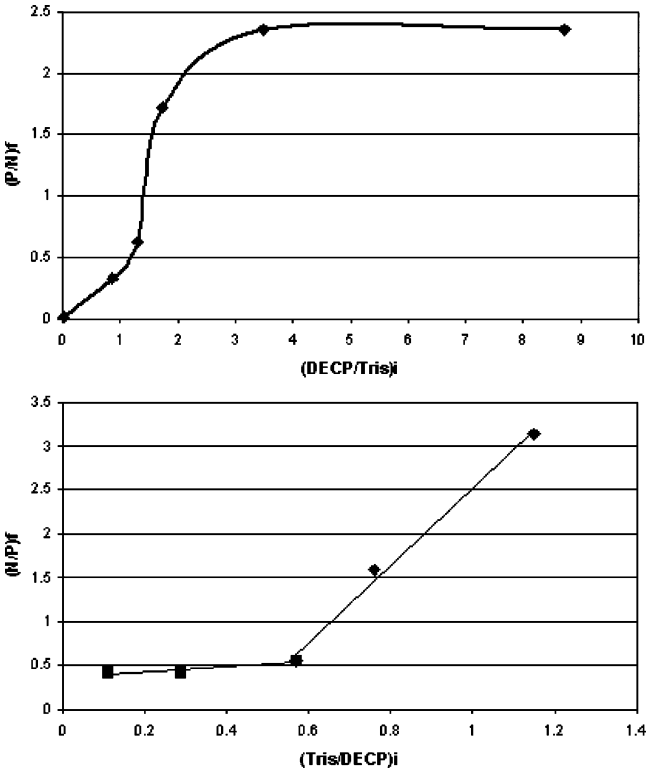

Figure 8. (a) Final ratio of phosphorus to nitrogen capacities, $(P/N)_f$, versus the initial ratio of DECP to Tris. (b) Final ratio of nitrogen to phosphorus capacities, $(N/P)_f$, versus the initial ratio of Tris to DECP.

Tris resin, a resin with a P/N ratio of 0.84, and the pTris resin with borate. Adjacent −OH groups give *N*-methyl-D-glucamine a high affinity for borate by forming a covalent complex.[26] Resins with immobilized glucamine ligands are commercially available for borate recovery.[27] *N*-Methyl-D-glucamine was immobilized on the same polymer support used for Tris (2% DVB polyVBC)[28] and found to complex 96.0% of the borate from a 10^{-4} M solution at pH 6.3. Under the same conditions, the unphosphorylated Tris resin complexes 97.2% borate, the resin with a P/N ratio of 0.84 complexes 97.0% borate, and the pTris resin complexes ≤5% borate. The pTris resin thus has no ligands with adjacent −OH groups, and the results are in line with expectations from the P/N ratio calculation, Figure 8, and the FTIR spectra (vide infra).

Ionic Affinity as a Function of Phosphorylation. The results summarized in Figure 3 indicate that affinity for the ferric ion increases as the P/N ratio increases. Monophosphorylated resins A and B have a low ionic affinity, the diphosphorylated resin C has a low to moderate ionic affinity, and the pTris resin, with significant triphosphorylation, has a high ionic affinity. The issue that thus need to be addressed is the reason for the much higher affinities of the pTris resin relative to resins with lower degrees of phosphorylation and whether those affinities are due to a scaffold effect, an auxiliary group, or both.

Resins A and B act similarly in 0.01 and 1 M HNO_3, consistent with both being monophosphorylated, an absence of a scaffold effect and an absence of auxiliary group activation. Resin C, even with a significant amount of diphosphorylation, has no Fe(III) affinity from a 0.01 M HNO_3 solution and a moderate affinity from a 1 M HNO_3 solution. Apparently, there is no auxiliary group effect and the two P═O moieties do not cooperate strongly enough in binding the $Fe(NO_3)_3$ from the 0.01 M HNO_3 solution. However, the diphosphorylated resin has an increased ionic affinity since complexation occurs from a 1 M HNO_3 solution; either the auxiliary group effect strengthens or intraligand cooperation by the diphosphorylated ligand is enhanced in this more acidic solution. The pTris resin (E), wherein one-third of the sites are triphosphorylated, complexes 95% of the Fe(III) in solutions of low and high acidities, indicating that the scaffold and/or auxiliary group effects are operative.

In order to explore the general nature of the results, La(III) and Eu(III) were studied with resins A, B, C, and E in 0.01 M HNO_3. Results identical to those with Fe(III) were obtained. Additionally, in comparing the Eu(III) affinities of resins C and E (with phosphorus capacities of 3.07 and 3.98 mmol/g, respectively), only resin E shows complexation from 0.01 M HNO_3, 1.0 M HNO_3, and 1.0 M HCl.

The difference between resins C and E is the extent of phosphorylation, and only resin E has a capacity high enough to allow triphosphorylation. While the ratio of phosphorus to nitrogen capacities suggests intraligand cooperation among three phosphoryl groups, as has been proposed with homogeneous phosphine-substituted neopentyl ligands,[29] a detailed

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examination of the results leads to the conclusion that the mechanism involves an auxiliary group effect onto which a scaffold effect is superimposed due to the proximity of the ligands.

Correlation with the Misono Softness Parameter. Research has shown that hydrogen bonding from −OH groups to the phosphate ligand has a significant effect on the affinity of the ligand for divalent ions.[12] The same ions were used to probe the affinity of the phosphate ligand on the Tris scaffold (Table 3); the distribution coefficients for Pb(II), Cd(II), Cu(II), and Zn(II) correlate with the Misono softness parameters[30] (correlation coefficient $<0.9992>$) to give a selectivity of 229 (a value comparable to the phosphorylated tris(hydroxymethyl)ethane resin). That the phosphoryl ligand is activated by the auxiliary −NH− group is thus supported by results with the divalent transition-metal ions and indicates that polarizability of the P═O ligand is an important determinant of ionic affinities. Activation of the phosphoryl oxygen results in complexation of the divalent ions where none is evident by the Tris and PE resins. The correlation with the Misono parameters is independent of pH (Figure 6), though Cd and Cu display similar affinities (as also found with the phosphorylated glycols).

Ionic Affinities of the pTris Resin: The Auxiliary Group Effect. Using Fe(III) to probe the binding mechanism of pTris, it was found that the resin has a uniformly high affinity for $Fe(NO_3)_3$, regardless of HNO_3 concentration (Figure 4). The PE resin, on the other hand, begins with a low affinity in 0.01 M HNO_3 that remains low as the acidity increases to 5 M. This is consistent with the behavior of tributyl phosphate (TBP), whose affinity for Fe(III) from HNO_3 is so low that ferric nitrate can be used as a salting-out agent for the extraction of other metal ions.[31] The amine resin also has no affinity for Fe(III) as $Fe(NO_3)_3$ due to insufficient basicity by the nitrogen for a direct interaction and the absence of $Fe(NO_3)_4^-$ for an ionic interaction. The high Fe(III) affinity by the pTris resin in HNO_3 is also evident in HCl (Figure 5). The PE and amine resins begin at the same low affinity in 0.01 M HCl as they did in HNO_3. However, their distribution coefficients increase as the HCl concentration increases, as would be expected from the behavior of TBP (extraction increases as the HCl concentration exceeds 2 M)[32] and soluble organophilic tertiary amines,[33] both of which complex Fe(III) from HCl as $HFeCl_4$. With regards to the phosphonate diester and amine resins, it is the formation of anionic complexes that provides the most notable difference between the behavior of Fe(III) in HNO_3 versus that in HCl. The P═O and R_3N moieties have low affinities for direct coordination to Fe(III) as $Fe(NO_3)_3$. The affinity is much greater for Fe(III) in HCl due to the formation of $FeCl_4^-$ and the subsequent ion exchange interaction with P═O(H^+) and $R_3N(H^+)$. Unlike the separate diester and amine ligands, the pTris resin again displays a uniformly high level of Fe(III) complexation.

Complexation of Al(III)[34] and La(III)[35] can occur only with neutral trinitrate salts from the HNO_3 solutions used in this study. The pTris resin displays an affinity for both only from the more dilute HNO_3 solutions (Table 2). The Tris and phosphonate diester resins show no affinity for these ions (Table 3). The affinity of the dimethylamine resin for Al(III) and La(III) from 0.01, 1.0, and 4.0 M HNO_3 is $<10\%$ for both; from 0.01, 1.0, and 4.0 M HCl, the percent of Al(III) complexed is 6.80, 8.79, and 15.6%, respectively, with similar values ($\pm1\%$) for La(III). This is consistent with: (1) Al(III) is not complexed by TBP from HNO_3;[34] (2) tertiary amines as the HCl salts[36] and organic phosphates[37] extract Fe(III) from HCl solutions containing Al(III); and (3) stability constants are significantly greater for hydroxide and ammonia with Fe(III) than they are for Al(III) and La(III).[38] There is thus a fundamental difference in the manner by which Fe(III) binds to ligands compared to Al(III) and La(III); the latter bind mainly through ionic interactions, while Fe(III) exhibits both ionic and covalent interactions. The pTris resin has an affinity for Al(III) and La(III) under more dilute acid conditions, suggesting a difference in binding ability relative to the phosphonate diester resin. Competition by HNO_3 displaces $Al(NO_3)_3$ and $La(NO_3)_3$, but not $Fe(NO_3)_3$, from the pTris resin in the more acidic solutions because the P═O ligand in the pTris resin binds more strongly with ions capable of covalent interactions.

Results with the pTris resin are best explained by an increased basicity at the phosphate ligand relative to the monofunctional amine and diester resins. The mechanism by which the pTris resin gains basicity was suggested by earlier research on the phosphate ligand bonded to polyols such as pentaerythritol, where it was determined that hydrogen bonding from the −OH groups increases the polarizability of the P═O ligand and thus increases its affinity for metal ions.[12] It is now proposed that the same phenomenon is operative with pTris; its high affinity for Fe(III) is due to tuning wherein the protonated amine functions as an auxiliary group and increases the polarizability of the P═O ligand by hydrogen bonding. Coordination is greater with trivalent rather than divalent ions (Figure 7) due to a greater electrostatic attraction. The increased basicity requires proximity of the −NH− group to the P═O ligand. A bifunctional resin wherein dimethylamine and diethyl phosphonate ligands are randomly placed along a polystyrene support (nitrogen and phosphorus capacities of 2.61 and 2.62 mmol/g, respectively) complexes $<10\%$ Fe(III), Al(III), and La(III) from 0.01 M HNO_3 and HCl; $<10\%$Fe(III) from 1 M HNO_3 and HCl; $<10\%$ Fe(III) from 4 M HNO_3; and

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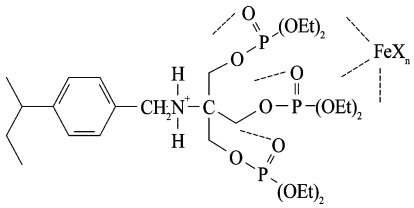

Figure 9. Interaction of phosphate ligands with the amine moiety through hydrogen bonding and with Fe(III).

88.3% Fe(III) from 4 M HCl (due to ion exchange with the amine sites).

FTIR Spectra. The spectra (Figure 2) support the concept of hydrogen bonding to the phosphoryl oxygens. This is the basis of the auxiliary group effect and the resulting increased ionic affinities. The phosphorylated ethylene glycol resin (PEG1), having no group with which to hydrogen bond the P═O ligand (and no divalent ion affinity from solutions at pH 2), has the P═O band at 1261 cm^{-1} and the P−OC band at 1034 cm^{-1}. Monophosphorylation of Tris results in a phosphate ligand with a significant shift of the P═O to 1211 cm^{-1} and a shift of the P−OC to 1051 cm^{-1}. Both are consistent with a strong hydrogen bond at the phosphoryl oxygen (decreased electron density between P═O, lengthening of the bond, lower energy needed to stretch; a shortening of the bond between P−OC, higher energy needed to stretch) and with a report on acidic poly(alkylene phosphate)s, which show the P═O at 1218 cm^{-1} and P−OC at 1058 cm^{-1}.[39] Hydrogen bonding decreases as phosphorylation increases in resins B, C, and E (the P═O band moves to 1230 from 1211 cm^{-1}, and the P−OC band moves to 1040 from 1051 cm^{-1}), perhaps because of the increasing number of phosphate ligands. The peak that increases in intensity at ∼960 cm^{-1} has been assigned to the P−O single bond[40] and is consistent with increasing phosphorylation. The concurrent broadening of the band at 1040−1050 cm^{-1} has been ascribed to hydrogen bonding in $(TBP)_2HFeCl_4$.[41] Moreover, intramolecular hydrogen bonding between −NH− and P═O moieties has been observed in soluble α-aminophosphonochloridates using FTIR and ^{31}P NMR spectroscopy.[42] The chemical effect of that hydrogen bonding (decreasing the electron density at the phosphorus and making it more prone to reaction with nucleophiles) is consistent with the conclusions reached in this research.

Results with the phosphorylated pentaerythritol (pPenta) resin[12] showed that hydrogen bonding need not be strong to activate the phosphate; the positions of its P═O and P−OC bands do not change from the PEG1 resin (1263, 1034 cm^{-1} for pPenta; 1261, 1034 cm^{-1} for PEG1), yet its hydrogen bonding is evident from a peak at ∼890 cm^{-1} and from solid state ^{31}P NMR spectra. While the hydrogen bonding is not pronounced (it is expected to be weaker with a $-CH_2OH$ group than with a protonated amine),[43] it is strong enough to result in significant divalent ion affinity from solutions at pH 2. Note that despite strong hydrogen bonding, the monophosphorylated resin has no ionic affinity; interaction with a hydrogen bond activates the P═O to metal ion binding but too strong of a bond precludes that binding. Since the addition of salts to solutions decreases hydrogen bonding,[44]the results in Table 4 with 0.04 M $NaNO_3$ may indicate that further decreasing the strength of the hydrogen bond to the phosphate ligand in the pTris resin leads to an increase in divalent ion affinity.

The Scaffold Effect. Resins A, B, and C show no metal ion affinity at pH 2 due to strong hydrogen bonding to the phosphate, not to a preference for H^+ since resin C has some Fe(III) affinity from 1 M HNO_3. The role of the scaffold effect in enhancing metal ion affinities may be indicated by the fact that, while resin E has a P═O bond peak at a slightly higher energy than resin C, it has a far greater affinity for metal ions. The amine group (protonated in the acidities used in this study) and its subsequent activation of the phosphoryl ligand provide the high affinities of the pTris resin due to a combination of the auxiliary group effect and the scaffold arrangement of ligands (Figure 9).

Conclusions

The ionic affinities of a series of phosphorylated polyols and phosphorylated tris(hydroxymethyl)aminomethane resins point to the conclusion that hydrogen bonding to the phosphate ligand is an important mechanism by which the ligand is activated toward binding metal ions. The hydrogen bonding from an auxiliary group must be strong enough to increase the polarizability of the phosphoryl oxygen but not strong enough to preclude further bonding to metal ions. FTIR is an important means of monitoring the extent of hydrogen bonding. Studies to be published with a new series of phosphorylated aminoethanols will illustrate the versatility of tuning the ligand's affinity through the extent of hydrogen bonding.

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