Synthesis and Ion-Binding Affinities of Calix[4]arenes Immobilized on Cross-Linked Polystyrene

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ABSTRACT: Calix[4]arene and its diphosphorylated derivative have been immobilized onto cross-linked polystyrene beads through an etherification reaction. The supported calixarene complexes 96.7% Cs(I) from a 10^{-4} N solution in 1 M NaOH. Poly(hydroxystyrene) complexes 35.6% Cs(I) from the same solution. Immobilization of the calixarene onto a polymer support thus does not affect its inherently high affinity for cesium ions. Substituting two of the three remaining hydroxyl groups on the calixarene with diethoxyphosphoryl moieties allows for quantitative complexation of Fe(III) and Pb(II) from 0.01 M nitric acid solutions. The unsubstituted calixarene complexes 6.00% Fe(III) and 7.36% Pb(II) while diethoxyphosphoryl-substituted poly(hydroxystyrene) complexes 10.0% Fe(III) and 3.76% Pb(II). The calixarene therefore acts as a platform on which ligands can be immobilized in close enough proximity to permit cooperative binding of metal ions.

Introduction

The design of molecules with high ionic affinities is important for numerous applications in chromatography,[1] catalysis,[2] and separations.[3] Immobilization of ion-selective ligands to form polymer-supported reagents results in an expanded set of applications.[4,5] Calixarenes are an important set of macrocycles formed by the condensation of para-alkylated phenols with formaldehyde.[6] Molecules with 4, 6, or 8 phenolic units within the macrocycle are most common. The selectivity of calix[4]arene for cesium ions has been reported.[7] Modifying the calixarenes with ion-complexing ligands changes the observed selectivity: calix[4]arene tetrasubstituted with phosphine oxide ligands has a high affinity for certain lanthanide ions.[8] This high affinity is ascribed to a cooperation among the four ligands in the binding of the ions. Calixarenes have been incorporated as units in soluble oligomers. For example, triketone-substituted calix[4]arene was bonded to oligomeric epichlorohydrin and found to complex lithium ions from a solution also containing sodium, potassium, silver, cobalt, nickel, copper, and cadmium ions.[9] Calixarenes have been incorporated into soluble step-growth polymers.[10] Calixarenes bonded to un-cross-linked polystyrene and polyacryloyl chloride were soluble in chloroform and selective for Fe(III) in aqueous solutions also containing copper, nickel, and cobalt ions.[11] The fluorescence properties of a water-soluble polymeric calixarene have been studied.[12] Calix[6]arene-*p*-hexasulfonate bonded to soluble poly(ethylene imine) was reported to have a high affinity for the uranyl ion.[13] A silica-bonded calix[4]arene modified with L-(−)-ephedrine has been used in enantioseparations.[14] Calix[4]arene tetrahydroxamic acid was bonded to silica particles and its affinity determined for different transition metal ions.[15] Cross-linked polymers have been formed from monomeric calixarenes bearing vinyl groups[16,17] and from the reaction between calixarenes bearing chloromethyl groups and poly(ethylene imine).[18] A polystyrene gel with calixarene groups has also been reported.[19]

Our research has focused on immobilizing ion-selective ligands onto cross-linked organic polymer beads.[20] The advantages of insoluble beads are well-known and include ease of handling and applicability to continuous processes. The current objectives were to define a procedure for immobilizing calix[4]arene onto cross-linked polystyrene beads and to determine whether its inherently high affinity for cesium ions would be retained. Additionally, it was important to examine whether the calixarene could be used as a platform for immobilizing ion-binding sites in a preorganized configuration that would allow for cooperative interactions leading to higher levels of metal ion complexation than would occur in the absence of this cooperation. Intraligand cooperation has been found to be important to the high ionic affinities displayed by polymers with covalently bound α- and β-ketophosphonates[21] as well as by diphosphonic acid ligands.[22] In the present study, diphosphorylation of the calixarene molecule was studied in order to determine whether the ligands would be close enough to cooperate in ionic binding. The method of immobilization was etherification by nucleophilic substitution of the $-CH_2Cl$ groups on poly(vinylbenzyl chloride) by the sodium salt of the calixarene (Scheme 1).

Experimental Section

Synthesis of the polymer support from vinylbenzyl chloride (VBC) by suspension polymerization has been described.[21] The microporous (gel) beads were cross-linked with 2% divinylbenzene (DVB), and the macroporous beads were cross-linked with 5% DVB. The particle size diameter was 75−150 μm for the former and 150−250 μm for the latter.

The tetra-*tert*-butylcalix[4]arene, calix[4]arene, and tribenzoyloxycalix[4]arene were prepared by procedures published by Gutsche and co-workers.[23] Bis(diethoxyphosphoryloxy)calix[4]arene was prepared by the procedure of Kal'chenko et al.[24] Yield data, melting points, mass spectra, and IR spectra were as reported in the cited publications. All chemicals were purchased from the Aldrich Chemical Co. FTIR spectra of samples were recorded as KBr pellets on a Bio-Rad FTS-7 spectrometer.

Polymer-Supported Phenol. A mixture of 1.45 g of NaH (as a 60% dispersion), 3.1 g of phenol, and 100 mL of anhydrous

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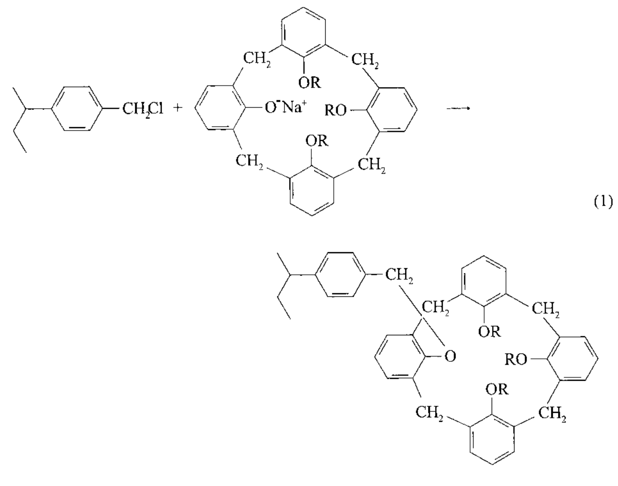
Scheme 1



R = PhC(O) tribenzoyloxycalix[4]arene resin (BzCR)

R = H hydroxycalix[4]arene resin (HCR)

R = (EtO)$_2$P(O), (EtO)$_2$P(O), H bis(diethoxyphosphoryloxy)calix[4]arene resin (BPCR)

dioxane were stirred in a 250 mL Erlenmeyer flask fitted with a Claisen adapter and gas inlet tube under a gentle nitrogen sweep for 1 h. Copolymer beads (2 g) were placed in a three-neck 250 mL round-bottom flask equipped with a condenser (fitted with a Drierite tube at the exit joint) and an overhead stirrer. The phenolate solution was transferred to the round-bottom flask and the mixture refluxed for 72 h. Excess solution was removed; the beads were washed with dioxane, water, and acetone (three times each) and vacuum-dried overnight at 80° C. The resins were characterized by chlorine elemental analyses (2.26 and 0.90 mmol/g for the gel and macroporous resins, respectively).

Tribenzoyloxycalix[4]arene Resin (BzCR). Macroporous copolymer beads (5 g) cross-linked with 5% DVB were swelled in 150 mL of dimethylformamide for 2 h in a three-neck 2 L round-bottom flask equipped with an overhead stirrer (fitted with a Drierite tube at the exit joint). Into a 1 L Erlenmeyer flask fitted with a Claisen adapter and gas inlet tube was added 57.0 g of tribenzoyloxycalix[4]arene, 750 mL of DMF, and 6.6 g of NaH under a gentle nitrogen sweep. Reaction proceeded for 2 h, after which time an orange colored solution was obtained. This was transferred to the round-bottom flask containing the beads and the mixture refluxed for 72 h. Excess solution was removed and the resin washed three times each with DMF, water, and acetone. It was vacuum-dried overnight at 90° C and characterized by FTIR (no phenolic O−H at 3300−3500 cm^{-1}; strong C═O at 1700 cm^{-1}) and chlorine elemental analysis (1.49 mmol/g).

Hydroxycalix[4]arene Resin (HCR). BzCR (5 g) was placed in a 500 mL round-bottom flask equipped with a condenser and overhead stirrer and swelled in 200 mL of THF for 2 h. A solution of 40 g of 50 wt % NaOH, 100 mL of water, and 200 mL of ethanol was added and the mixture refluxed for 48 h. Excess solution was removed, and the resin was washed three times with water and conditioned in a glass frit column by eluting with 1 L each of water, 4 wt % NaOH, water, 4 wt % HCl, and water. The resin was characterized by FTIR (phenolic O−H at 3300−3500 cm^{-1}; very weak C═O at 1700 cm^{-1}) and chlorine elemental analysis (1.86 mmol/g).

Bis(diethoxyphosphoryloxy)calix[4]arene Resin (BPCR). Into a 1 L Erlenmeyer flask fitted with a Claisen adapter and gas inlet tube was added 57.0 g of bis(diethoxyphosphoryloxy)calix[4]arene, 750 mL of DMF, and 6.6 g of NaH under a gentle nitrogen sweep. Reaction proceeded for 2 h. Macroporous copolymer beads (5 g) cross-linked with 5% DVB were swelled in 100 mL of DMF for 2 h in a 2 L three-necked round-bottom flask with a condenser (and attached Drierite tube) and an overhead stirrer. The calixarene solution was transferred to the round-bottom flask and the mixture refluxed for 72 h. Excess solution was removed, the resin washed three times each with DMF, water, dioxane, THF, and acetone, and the beads conditioned in a glass frit column by eluting with 1 L each of ethanol and water. The resin was characterized by FTIR (phenolic O−H at 3300−3500 cm^{-1}; no C═O; strong P═O at 1247 cm^{-1}) and phosphorus elemental analysis (1.78 mmol/g).

Polymerization of *p*-Acetoxystyrene. The organic phase was prepared by mixing 2.3 g of DVB (technical grade, 55.4% purity), 21.5 g of *p*-acetoxystyrene, and 1.2 g of benzoyl peroxide. The aqueous phase consisted of 54.0 g of water, 0.84 g of poly(vinyl alcohol) (molecular weight 150 000), and 13.4 g of CaCl$_2$. Both phases were sparged with nitrogen for 15 min and then transferred to a 250 mL three-neck round-bottom flask fitted with a condenser, overhead stirrer, and Claisen adapter. The stir speed was adjusted to give beads of the desired size. The temperature was controlled with a thermometer connected to a Therm-O-Watch sensor (Instruments for Research and Industry Corp., Cheltenham, PA). The suspension was heated to 85° C over a 2 h period and maintained at that temperature for 17 h. The beads were washed three times with water, extracted in a Soxhlet apparatus with toluene for 17 h, oven-dried at 60° C, and sieved.

Hydroxystyrene Resin (HSR). Poly(acetoxystyrene) beads (4 g) were placed in a 250 mL three neck round-bottom flask equipped with a condenser and overhead stirrer. A solution of 29.6 wt % ammonium hydroxide (100 mL) was added and the reaction heated at 85° C for 7 h. Excess solution was removed and the resin washed three times with water. The hydrolysis was repeated three additional times using 100 mL of ammonium hydroxide and reaction times of 17, 7, and 17 h. The resin was washed three times with water and conditioned in a glass frit column by eluting with 1 L each of water, 4 wt % NaOH, water, 4 wt % HCl, and water. The resin was characterized by FTIR (phenolic O−H at 3300−3500 cm^{-1}; no C═O).

Phosphorylated Ester Resin (PER).[25] HSR (4.5 g) was swelled with 60 mL of anhydrous THF and 16 mL of triethylamine in a 250 mL three-neck round-bottom flask equipped with a gas inlet tube and addition funnel. A solution of 19.8 g of diethylchlorophosphate in 30 mL of anhydrous THF was added dropwise under a nitrogen atmosphere while the contents were cooled in an ice bath. The reaction proceeded at ice-bath temperature for 2 h and at room temperature for 48 h. The resin was washed with dioxane, 2 wt % NaOH, water, ethanol, and acetone. After vacuum-drying overnight at 80° C, the resin was characterized by FTIR (no phenolic O−H; no C═O; strong P═O at 1275 cm^{-1}) and phosphorus elemental analysis (3.76 mmol/g; theoretical capacity assuming complete deacetylation of poly(*p*-acetoxystyrene) is 3.63 mmol/g).

Metal Ion Affinity Studies. An amount of Buchner-dried resin that would give 1 mmol of ligand was weighed into a 20 mL vial where it was preequilibrated four separate times (15 min each) with 10 mL of the appropriate background solution on a Burrell wrist-action shaker. The solution was removed using a pipet attached to an aspirator through a sidearm flask. The contact solutions were prepared with Nanopure water and reagent grade metal salts and acids. Stock solutions were prepared in concentrations of 0.001 N in a 1 L volumetric flask with 0.10 or 0.01 M nitric acid. Lower concentrations were prepared by subsequent dilutions. Contact solutions contained 10^{-4} N ferric, lead, copper, or nickel nitrate. The contact solution (10 mL) was pipetted into the vial and shaken for 24 h, after which time the solution was removed and transferred to a clean vial. The same procedure was followed when preparing and studying a solution of 10^{-4} N CsNO$_3$ in 1 M NaOH. The amount of metal ion complexed was determined on a Perkin-Elmer model 3100 atomic absorption/emission spectrometer.

Results and Discussion

The conditions appropriate for immobilization of the calixarene were approximated from reactions of poly-

(VBC) with phenol. Gel (2% DVB, 75−150 μm) and macroporous (5% DVB, 150−250 μm) copolymer beads were compared for their ability to be etherified with the phenolate ion. A dioxane solution of phenol was contacted with an equimolar amount of NaH and refluxed with the beads for 72 h. After washing and vacuum-drying, the final chlorine capacities for the gel and macroporous beads were 2.26 and 0.90 mmol/g, indicating degrees of functionalization of 56.5% and 80.3%, respectively. Since reactant accessibility seemed to limit the extent of reaction, the macroporous beads were used as the support for etherification reactions with calix[4]arene.

Preparation of the calix[4]arene salt was attempted by reacting a dioxane solution of the unsubstituted (i.e., tetrahydroxy) calixarene (THC) with NaH in a 1:4 molar ratio, but the product precipitated out of solution, perhaps because it was too ionic to be solvated by the dioxane. A precipitate was still observed when a solution of THC in toluene, toluene:THF (1:9 (v/v)), toluene:DMF (1:10), or dioxane:DMF (10:1) was reacted with 4 equiv of NaH. Reaction of THC with only a slight excess of NaH (1:1.11 mole ratio) in a solution of toluene:DMF (1:10) gave the same result. Though it is possible that the monoanion is insoluble under the conditions studied, it is also possible that the higher anions form, and these are what precipitate from solution.

A homogeneous solution was produced by modification of the calixarene. Benzoylation of THC results in a more organophilic compound when three of the four phenolic −OH groups are substituted.[23] Tribenzoyloxycalix[4]arene (BzC) was thus synthesized, dissolved in DMF, and contacted with NaH (1:1.11). The resulting homogeneous solution was refluxed for 72 h with poly(VBC) beads. Elemental analysis showed the chlorine capacity to decrease from 5.89 to 1.49 mmol/g, which calculates to 50 mol % functionalization. To ascertain whether the remaining $-CH_2Cl$ moieties were accessible for further reaction, the resin was refluxed with an excess of triethyl phosphite for 24 h (conditions under which the Arbusov reaction goes to completion with unfunctionalized poly(VBC) beads), followed by 24 h reflux in concentrated HCl so as to hydrolyze any phosphonate diester groups to phosphonic acid. The resin was extracted in a Soxhlet apparatus and then conditioned by eluting with water, 4% NaOH, water, 4% HCl, and water. Elemental analyses showed the resin to have a phosphorus capacity of 0.15 mmol/g and a chlorine capacity of 1.86 mmol/g, indicating only debenzoylation and little phosphorylation (consistent with the FTIR and increase in chlorine capacity). Hydrolysis of the benzoylated calixarene resin with NaOH in 37.5% aqueous ethanol gives a resin with a comparable chlorine capacity. The results thus show that the unreacted $-CH_2Cl$ groups are inaccessible to additional reactants due to unfavorable steric interactions with the calixarene.

Preparation of the immobilized calixarene with unsubstituted phenolic −OH groups allows for subsequent functionalization with ion-binding ligands. Reaction with diethylchlorophosphate in triethylamine/THF results in a resin with a phosphorus capacity of 1.74 mmol/g. Complete substitution at all hydroxy groups would have given a phosphorus capacity of 3.11 mmol/g. However, since it could not be established whether the calixarenes were uniformly substituted or whether the phosphorus capacity was an average of different degrees of substitution, it was decided to first prepare a well-characterized functionalized calixarene which could then be immobilized on the polymer support. As a result, bis(diethoxyphosphoryloxy)calix[4]arene was synthesized from dealkylated calix[4]arene and diethylchlorophosphate; two of the four −OH groups were substituted with diethyl phosphate moieties, and only the conformationally stable cone isomer was isolated.[24] The phosphorus capacity was 3.13 mmol/g, compared to a theoretical value of 2.87 mmol/g for disubstitution. After contact with NaH, it was immobilized on poly(VBC) beads. The FTIR spectrum showed the phosphoryl stretching peak at 1247 cm^{-1}. The phosphorus capacity was 1.78 mmol/g, compared to a theoretical value of 2.41 mmol/g for a completely functionalized resin.

Table 1. Complexation of Cs(I) from 10^{-4} N $CsNO_3$ in 1 M NaOH

resin	percent complexed	distribution coeff[a]
HCR[b]	96.7	1200
BPCR[c]	43.9	67.7
HSR[d]	35.6	27.7
PER[e]	8.10	2.28

[a] In (mequiv of Cs(I) in the resin per g_{resin})/(mequiv of Cs(I) in solution per mL_{soln}). [b] Hydroxycalix[4]arene resin. [c] Bis(diethoxyphosphoryloxy)calix[4]arene resin. [d] Hydroxystyrene resin. [e] Phosphorylated ester resin.

Ion binding affinities of the calixarene and bis(diethoxyphosphoryloxy)calixarene resins (HCR and BPCR, respectively) were quantified. To evaluate the mechanism of complexation, the results were compared to those from poly(hydroxystyrene) resin (HSR) and its phosphorylated diester derivative (PER), the latter resin isolating the effect of P═O coordination in the absence of any possible intraligand cooperation allowed by the calixarene ring. HSR was synthesized by suspension polymerization of *p*-acetoxystyrene with 5% DVB. Subsequent hydrolysis indicated complete deacetylation based on disappearance of the carbonyl peak coupled with appearance of the broad −OH peak at 3300−3500 cm^{-1}. Phosphorylation of HSR with diethylchlorophosphate in a THF/triethylamine solution gave PER. The resin had a phosphorus capacity of 3.76 mmol/g (theoretical capacity assuming complete deacetylation is 3.63 mmol/g).

Results from complexation studies with Cs(I) in 1 M NaOH at a 24 h contact time are reported in Table 1. HCR has a significantly greater affinity for the cesium ion than HSR (96.7% vs 35.6%, respectively), indicating the importance of the calixarene ring to the complexation. Computational studies and crystal structure determinations of the soluble calix[4]arene−Cs(I) complex have shown that the ion may be involved in polyhapto interactions with the aromatic rings as well as coordination to the phenolic oxygens.[26] The amount of Cs(I) complexed decreases significantly with HSR because the phenolic oxygen is the sole binding interaction. When this binding site is blocked by esterification to give the phosphate diester ligand, the amount of cesium complexed decreases still further (to 8.10% for PER), indicating further that the phosphoryl oxygens are not basic enough to complex cesium ions. Phosphorylating two of the three available phenolic oxygens in HCR to give BPCR results in a large decrease in cesium affinity (from 96.7% to 43.9%). The amount complexed is comparable to that for HSR, indicating that binding is solely through the single phenolic oxygen and that the phosphate diester groups prevent cesium from entering the calixarene cavity.

Table 2. Complexation of Metal Ions from 10^{-4} N Solutions in 0.01 M HNO_3

resin	Fe(III)	Pb(II)	Cu(II)	Ni(II)
HCR	6.00%^{a}(2.91)^b	7.36% (3.67)	13.6% (7.25)	7.50% (3.77)
BPCR	100% (∞)	100% (∞)	66.7% (166.)	37.5% (51.7)
HSR	10.0% (5.61)	12.1% (6.80)	4.78% (2.48)	8.39% (4.56)
PER	10.0% (5.65)	3.76% (1.99)	4.78% (2.56)	8.39% (4.43)

^{a} Percent complexed. ^{b} Distribution coefficient.

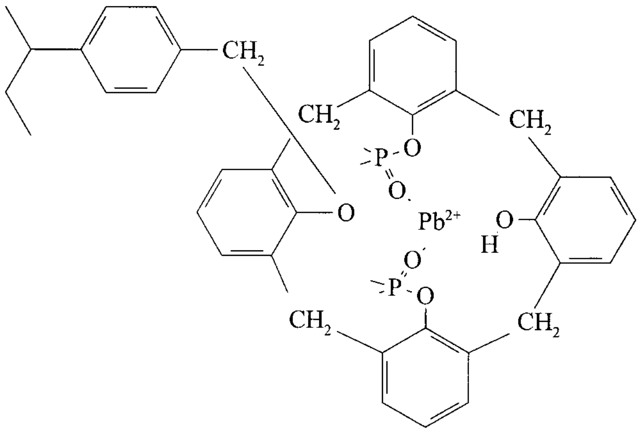


Figure 1. Pb(II) complexation by BPCR.

The affinities of transition metal ions in acidic solutions (0.01 and 0.10 M HNO_3) were quantified. Earlier research has shown that, in solutions of these acid strengths, the phosphonate diester ligand can be expected to complex metal ions; in solutions of higher acidity, the hydrogen ion concentration is high enough to compete with the metal ions for coordination to the phosphoryl oxygen while at lower acidity, precipitation of the ferric ion can occur.[27] The stability of the aryl−phosphate linkage in acidic solutions at room temperature was studied by deesterifying PER with bromotrimethylsilane in chloroform to give the phosphoric acid and then contacting that resin with 0.01, 0.10, and 1.00 M nitric acid for 24 h. Any loss of phosphorus capacity that results from the initial capacity of 4.46 mmol P/g would suggest cleavage of the phosphoric acid moiety from the polymer support. The final phosphorus capacities, however, were 4.55, 4.64, and 4.56 mmol/g for the resins from each of the three nitric acid solutions, indicating that the aryl−phosphate bond is stable under conditions used in studies with the transition metal ions.

Metal ion affinities from 0.01 M HNO_3 are presented in Table 2. HCR and HSR have low ionic affinities. BPCR, on the other hand, quantitatively complexes Fe(III) and Pb(II) with lower, though not negligible, levels of Cu(II) and Ni(II) (66.7% and 37.5%, respectively). That PER has a low ionic affinity indicates that the results are not due solely to the phosphate diester ligands. The high ionic affinities displayed by BPCR may thus be ascribed to preorganization of the coordinating ligands by the calixarene ring. Complexation by HCR, HSR, and PER shows that neither the cavity alone nor binding to phenolic or phosphoryl oxygens alone is responsible for the unique affinities displayed by BPCR. However, preorganization of the ligands around the cavity may allow for cooperation of the phosphoryl oxygens, resulting in the observed affinities (Figure 1). Results with HCR and BPCR from 0.10 M HNO_3 are consistent with those from the less acidic solution. Complexation by HCR remains low (2.47% Fe(III), 8.83% Pb(II), 5.36% Cu(II), and 5.49% Ni(II)) while BPCR retains its higher affinity for iron and lead ions (79.7% Fe(III), 68.1% Pb(II), 11.2% Cu(II), and 5.00% Ni(II)). Both HSR and PER complex very low levels of these ions (<5%) from 0.10 M HNO_3.

Conclusions

Calix[4]arene and its phosphorylated analogue have been immobilized onto cross-linked polystyrene. The phosphorylated calixarene complexes high levels of metal ions in a pH-dependent manner. Results are consistent with intraligand cooperation of the phosphoryl oxygens substituted at the phenolic rim. This is especially evident when the results are compared to those for the monophosphate ester resin which has a far lower metal ion affinity. Accessibility into the polymer network is unhindered, given the high cesium affinity displayed by HCR and iron/lead affinities displayed by BPCR. The calixarene ring is found to be an important platform on which ion-binding ligands can be preorganized, resulting in high ionic affinities and selectivities. Further studies with a wide array of ligands are in progress.

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