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Proton-ionizable acyclic dibenzopolyethers and their polymers for use in selective lead(II) separation

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2,2'-[1,2-Ethanediylbis(oxy)]bisbenzoic acid (1), 2,2'-[oxybis(1,2-ethanediyloxy)]bisbenzoic acid (2), 1,2-[2'-(acetoxy)phenoxy] ethane (3), and 1,5-[2'-(acetoxy)phenoxy]-3-oxopentane (4) have been prepared for use in selective Pb(II) separation. The extraction of Pb(II) and Cu(II) from buffered aqueous solutions of varying pH into chloroform by 1-4 is examined in relation to their molecular structure. Compound 1 with an ethylene glycol spacer unit exhibits excellent extraction selectivity for Pb(II) over Cu(II). Lengthening the spacer group to a diethylene glycol unit diminishes the extraction efficiency and selectivity. For 3 and 4, extraction was inefficient due to low lipophilicity and solubility of the ligands in chloroform. Condensation polymerization of compounds 3 and 4 with formaldehyde in formic acid provides stable chelating resins 5 and 6 which contain both ion-exchange and polyether binding sites for metal complexation. Resin 5 with an ethylene glycol spacer group is found to be an effective chelating resin for Pb(II) separation. The sorption mechanism and selectivity are studied and compared with the commercially available iminodiacetic acid resin CR-10.

INTRODUCTION

The development of chelating materials such as extractants and chelating polymers for selective separation and elimination of toxic heavy metal ions from the environment and from biological systems has received considerable attention.[1,2] Highly selective removal of Pb(II) for environmental remediation and in the treatment of acute and chronic lead poisoning remains as an important objective.[3-5] In the course of our study, we have been developing proton-ionizable crown ethers and their polymers for separation of alkali-metal and alkaline earth-metal cations from solution.[6-8] These proton-ionizable polyethers show a distinct advantage over neutral macrocycles in that the transfer of a metal ion into an organic medium, as well as into a polymer phase, do not require concomitant transport of an aqueous phase anion. Among heavy metal ions, some neutral macrocyclic polyethers are known to exhibit a specific interaction with Pb(II).[9] Therefore, the introduction of two proton-ionizable groups at such polyether binding sites is expected to provide effective chelators with a selective separation ability for Pb(II).

In this study, we designed and synthesized new acyclic dibenzopolyether dicarboxylic acids **1-4** for use in selective Pb(II) separation. The solvent extraction of Pb(II) from aqueous media into chloroform solutions of these compounds is examined in relation to their molecular structure. The results reveal that some of these extractants provide quite effective separation of Pb(II) from aqueous solutions. To utilize this function for practical Pb(II) separation, compounds **3** and **4** were converted into polymeric ligands **5** and **6**, and their separation selectivity and efficiency as a chelating resins assessed together with their sorption mechanism.

RESULTS AND DISCUSSION

Preparation of acyclic dibenzopolyether dicarboxylic acid monomers 1-4 and their polymers 5 and 6. The synthetic routes are shown in Scheme I. Compounds **1** and **2** were prepared from methyl salycilate and the appropriate glycol di-*p*-toluenesulfonates with potassium *tert*-butoxide, followed by hydrolysis of the resultant esters. Compounds **3** and **4** were synthesized by the reaction of the bisphenols **7** and **8** with bromoacetic acid. Structures of these compounds were confirmed by their ^{1}H-NMR and IR spectra and *elemental analysis*.

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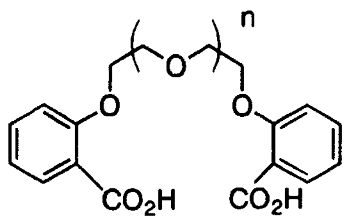
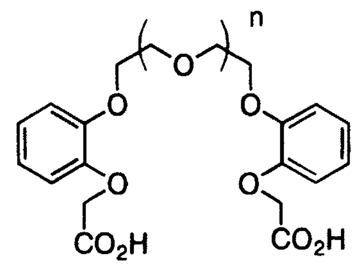
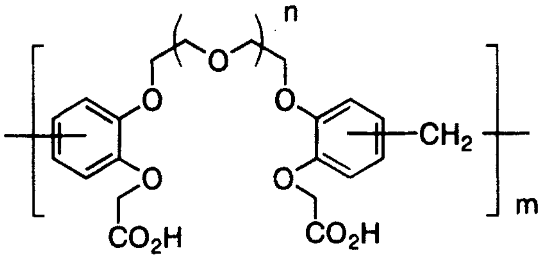


1 (n=0), **2** (n=1)

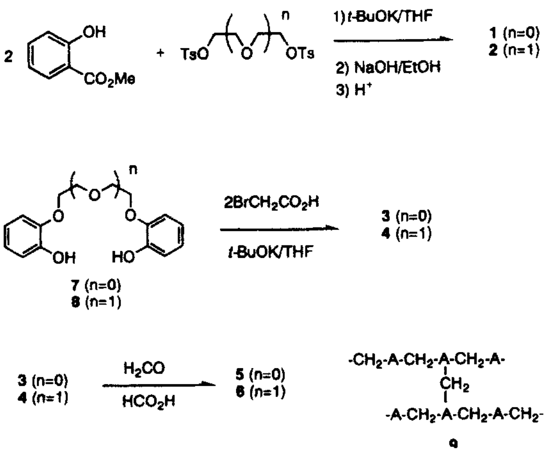


3 (n=0), **4** (n=1)



5 (n=0), **6** (n=1)

The polymeric ligands **5** and **6** were prepared by condensation polymerization of **3** and **4** with formaldehyde in formic acid. The absence of monomer decomposition during polymerization was verified by IR spectroscopy.[11] Structural representations **5** and **6** imply polymers with no crosslinking. This is most certainly an oversimplification since some level of crosslinking is anticipated. The elemental analysis results agreed with a partially crosslinked structure **9** in which A represents the polyether dicarboxylic acid unit in the resin. The product resins were washed, dried, and ground to finer than 60 mesh.



Scheme I

Solvent extraction of Pb(II) and Cu(II) by dibenzopolyether dicarboxylic acids 1-4. The properties of dibenzopolyether dicarboxylic acids **1-4** were first evaluated by solvent extraction of Pb(II) from buffered aqueous solution into chloroform. For conventional chelating reagents, Cu(II) generally shows the highest complexation in the Irving-Williams order.[12] Thus the extraction of Cu(II) under the same extraction conditions was compared with that of Pb(II) for estimation of the Pb(II) extraction selectivity.

A chloroform solution containing 1.0 mM ligand and a buffered aqueous solution containing 0.10 mM heavy metal ion was shaken for 1.0 hour. After phase separation, the ligand concentration in the organic phase, equilibrium pH and heavy metal ion concentration in the aqueous phase were measured by conventional methods. The percent extraction was calculated from the change of metal ion concentration in the aqueous phase before and after the extraction.

Figure 1 depicts results for the solvent extraction of Pb(II) and of Cu(II) from aqueous solutions of various pH into chloroform by *o*-methoxybenzoic acid (**10**) which is essentially one half of compound **1**. For **10**, negligible extraction was observed in the pH region from 1 to 6. The dashed line in the figure shows the ligand concentration in the chloroform phase. Above pH 4.5, the ligand concentration decreases due to a distribution of the proton-dissociated form of **10** into the aqueous phase.

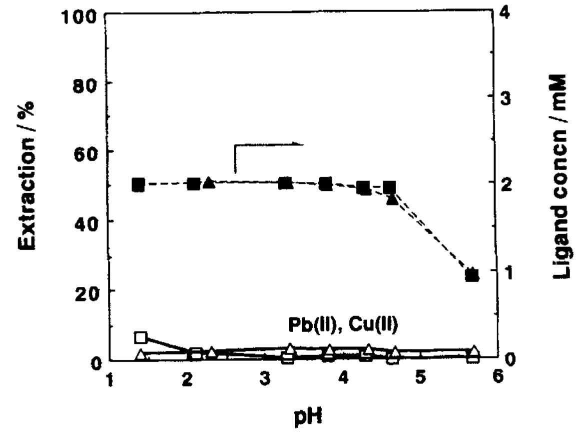
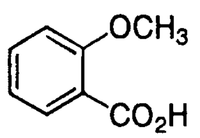


Figure 1 Extraction of Pb(II) and of Cu(II) from buffered aqueous solutions of varying pH into chloroform by **10**. □=Pb(II), △=Cu(II). The dashed lines denote the ligand concentration in the chloroform phase after the extraction (■,▲).



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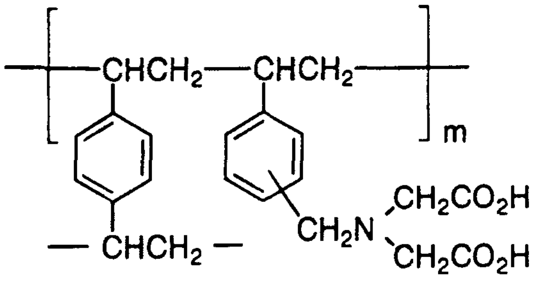

CR-10

In Figures 2a and 2b are shown the extraction behavior of Pb(II) and of Cu(II) by **1** and **2**, respectively. Compared with **10**, compound **1** exhibits an excellent extraction selectivity for Pb(II). This demonstrates that a bidentate structure is an important factor for selective Pb(II) recognition. The percent extraction of Pb(II) by **1** increased sharply at pH 3.5 and reached a maximum at pH 5.4. In the same pH regions, no extraction was noted for Cu(II) (Figure 2a). When the spacer group was changed from an ethylene glycol to a diethylene glycol unit, however, the extraction ability of Pb(II) decreased markedly (Figure 2b). This may be attributed to a greater flexibility of the diethylene glycol spacer in **2** compared with the ethylene glycol unit in **1**. Although compound **1** exhibited high Pb(II) extraction selectivity, the ligand concentration in the chloroform phase decreased significantly above pH 3.5 due to a low lipophilicity of the dissociated form.

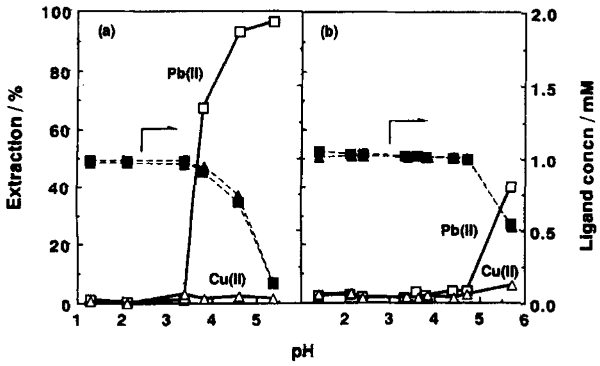

Figure 2. Extraction of Pb(II) and of Cu(II) from buffered aqueous solutions of varying pH into chloroform by (a) **1** and (b) **2**. □=Pb(II), △=Cu(II). The dashed lines denote the ligand concentration in the chloroform phase after the extraction (■,▲).

Compounds **3** and **4** are a second type of acyclic dibenzopolyether dicarboxylic acids and bear phenoxyacetic acid units as the ion-exchange site. Since compound **4** showed no appreciable solubility in chloroform, solvent extraction was investigated only with **3**. Figure 3 presents the extraction behavior of **3**. Due to low lipophilicity and solubility of **3** in chloroform, the extraction of Pb(II) and of Cu(II) exhibited a complicated behavior and very modest extractability was realized under the present conditions. In addition, white precipitation was noted at the interface between the two phases during the solvent extraction.

To avoid such loss of the extractant into the aqueous phase during the extraction and enhance the metal recognition ability, these ligands must be made more lipophilic or polymerized to form chelating resins.

Sorption of Pb(II) and of Cu(II) by dibenzopolyether dicarboxylic acid polymers 5 and 6. Blasius and coworkers synthesized a series of crown ether resins by condensation polymerization reactions of dibenzocrown ethers with formaldehyde.[13,14] These resins were used as stationary phases for the chromatographic separation of alkali-metal and alkaline earth-metal cations. This polymerization reaction has been employed in the preparation of acyclic dibenzopolyether resins also.[8] Thus compounds **3** and **4** were converted into polymeric ligands **5** and **6** and their sorption behaviors for Pb(II) and for Cu(II) were investigated.[10]

The resin (0.030 g) and 5.0 mL of buffered aqueous solution containing 1.0 mM Pb(II) or Cu(II) were shaken for 3 hours. In control experiments conducted with resin **5**, no significant variation in Pb(II) sorption was noted for shaking times which ranged from 0.5 to 5.0 hours. The aqueous mixture was filtered and the equilibrium pH and the metal ion concentration in the filtrate were

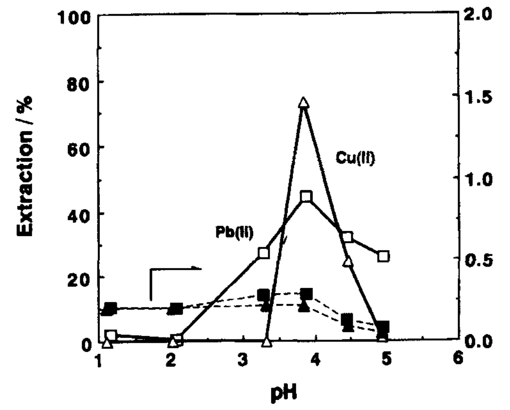

Figure 3 Extraction of Pb(II) and of Cu(II) from buffered aqueous solutions of varying pH into chloroform by **3**. □=Pb(II), △=Cu(II). The dashed lines denote the ligand concentration in the chloroform phase after the extraction (■,▲).

measured. The percent sorption was determined by the concentration change of metal ions in the aqueous solution before and after contact with the resin.

For comparison with a conventional chelating resin, the metal sorption by the commercially available iminodiacetic acid resin Diaion **CR-10** was first investigated. The results are shown in Figure 4. Both Pb(II) and Cu(II) sorption are enhanced as the pH of the aqueous phase increased. This indicates that ion-exchange sorption of the metal ions is facilitated by deprotonation of the carboxylic acid groups in the resin. The **CR-10** exhibited modest sorption selectivity for Cu(II) over Pb(II) in agreement with the reported selectivity.[15] Thus the percent sorption values at pH 2.0 were 82% for Cu(II) and 64% for Pb(II), respectively.

The sorption behavior of Pb(II) and of Cu(II) by resins **5** and **6** was studied under the same conditions. Figure 5a presents the sorption behavior for **5**. It is noted that resin **5** exhibits selective sorption for Pb(II) over Cu(II). Thus the percent sorption of Pb(II) exceeded 90% at pH 2.5, while copper sorption was less than 30% at this pH. This is the first instance in which a chelating resin exhibits efficient and selective Pb(II) recognition. The sorption behavior of **6** is shown in Figure 5b. When the spacer group was lengthened from an ethylene glycol to a diethylene glycol unit, the sorption efficiency and selectivity diminished, although resin **6** still exhibited Pb(II) selectivity below pH 5. This difference may be attributed to flexibility of the diethylene glycol spacer unit, which deforms the bidentate structure of the binding site during resin formation as compared with that in resin **5**.

Sorption mechanism. By use of **CR-10** and resin **5**, the sorption mechanism was investigated. When 1:1 complex formation takes place between the metal (M^{2+}) and the ligand (H_2L) in the resin, the following equilibria are considered below the pK_a of the resins in solution (K_a: proton dissociation constant):

$$(H_2L)_r+(M^{2+})_a \overset{K_d}{\rightleftharpoons} (ML)_r+2(H^+)_a \tag{1}$$

$$K_d=[ML]_r[H+]_a^2/[H_2L]_r[M^{2+}]_a \tag{2}$$

where K_d, the subscripts "r" and "a" denote the sorption constant and concentrations in the resin and the aqueous phase, respectively. By introducing the distribution ratio of the metal ion between the resin and the aqueous phase ($D = [ML]_r/[M^{2+}]_a$) into Equation 2, the sorption equilibrium is logarithmically expressed as:

$$\log\{D/([H_2L_t]_r-[ML]_r)\}=2pH+\log K_d \tag{3}$$

where $[(H_2L)_t]_r$ represents the ion-exchange capacity (mol/g). The ion-exchange capacities determined by the reported procedure[11] were 2.58 mmol/g for **CR-10** and 2.78 mmol/g for **5**, respectively. Equation 3 indicates that the plots of $\log\{D/([(H_2L)_t]_r - [ML]_r)\}$ against pH should show a straight line with a slope of 2. The results are shown in Figure 6. With the exception of Cu(II) sorption by resin **5**, the plots are all linear with a slope of 2. This indicates that complex formation as expressed in Equation 1 indeed takes place for Pb(II) sorption by resin **5**, similar to the conventional chelate formation observed for **CR-10**. For Cu(II) sorption by resin **5**, the observed slope was 1.0. Thus ion-exchange sorption accompanied by an anion from the aqueous phase must take place. Since resin **5** has an intrinsic pK_a value of 4.0, as determined by the pH titration method reported by Miyajima et al.,[16] ionization of the resin should also affect the Cu(II) sorption in the present system.

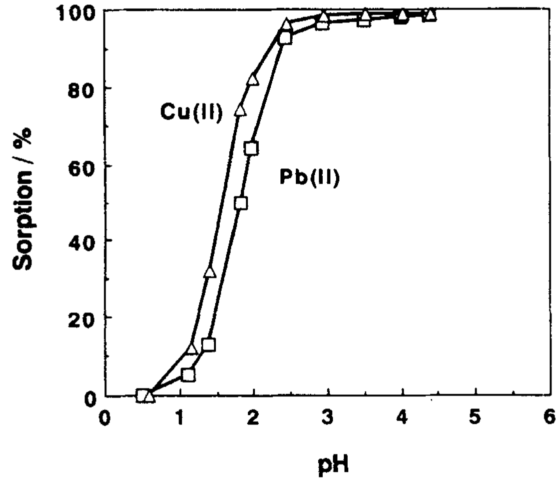

Figure 4 Sorption of Pb(II) and of Cu(II) from buffered aqueous solutions of varying pH by **CR-10**. □=Pb(II), △=Cu(II).

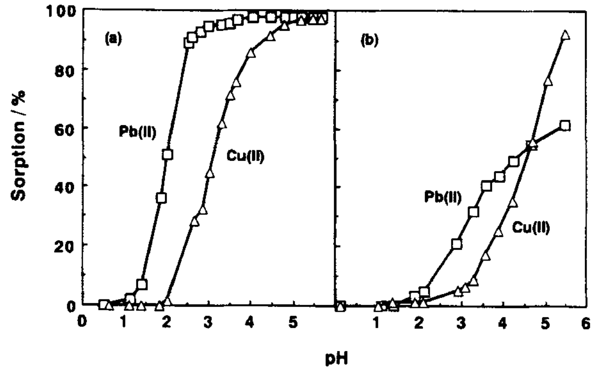

Figure 5 Sorption of Pb(II) and of Cu(II) from buffered aqueous solutions of varying pH by (a) **5** and (b) **6**. □=Pb(II), △=Cu(II).

CONCLUSIONS

In this study, the acyclic dibenzopolyether dicarboxylic acids with an ethylene glycol spacer unit were found to

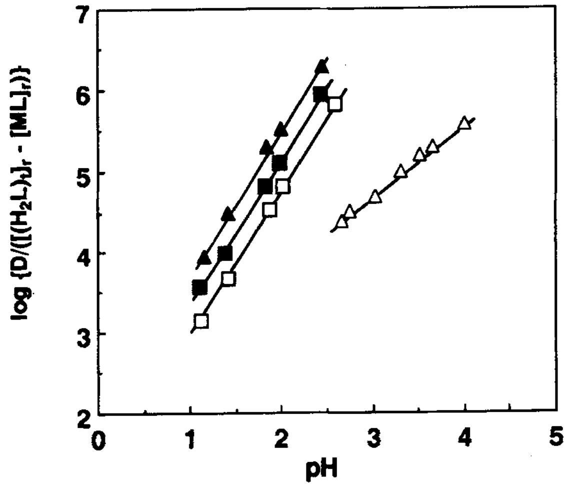

Figure 6. Correlation of log{D/([$(H_2L)_t$]$_r$ − [ML]$_r$)} and pH. Resin 5: □=Pb(II), △=Cu(II); **CR-10**: ■=Pb(II), ▲=Cu(II).

possess an effective binding site for selective Pb(II) separation. We have recently reported that a lipophilic polyether dicarboxylic acid, 1,2-bis[2-(o-carboxyphenyloxy)ethoxy]-4-tert-butylbenzene, exhibited uphill transport of Pb(II) ion in a liquid membrane system with high selectivity over monovalent and divalent metal ions.[17] Thus proper arrangements of "hard" polyether binding sites with ion-exchange functionality is expected to provide additional efficient and selective chelating materials for Pb(II) separation in solvent extraction, membrane transport, and resin separation systems. Further investigations are presently underway in our laboratories.

EXPERIMENTAL SECTION

Apparatus. ^{1}H-NMR spectra were taken with an IBM AF-200 nuclear magnetic resonance spectrometer. IR spectra were measured with Perkin-Elmer Model 1600 or Nicolet MS-X infrared spectrophotometers. Concentrations of Pb(II) and Cu(II) in the aqueous phases were determined with a Hitachi 170-30 atomic absorption spectrophotometer. pH measurements were made with an Orion Model 720A pH meter. A Yamato SA31 mechanical shaker was used to shake the aqueous solution-resin mixtures.

Reagents. 1,2-Di(2'-hydroxyphenoxy)ethane **7**,[18] 1,5-di(2'-hydroxyphenoxy)-3-oxopentane **8**,[19] and 1,2-[2'-(acetoxy)phenoxy]ethane resin **5**[10] were prepared by the reported procedures. Diaion **CR-10** resin was purchased from Mitsubishi Kasei Co. Ltd. Reagent-grade of Pb $(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$ were obtained from Wako Pure Chemical Industries, Ltd. Stock aqueous solutions of 5.0 mM $Pb(NO_3)_2$ and $Cu(NO_3)_2$ containing 0.1 M HNO_3 were stored in polyethylene bottles. Other inorganic and organic compounds were reagent-grade commercial products and were used as received.

Preparation of 2,2'-[1,2-ethanediylbis(oxy)]bisbenzoic acid (1). Under nitrogen, methyl salicylate (2.20 g, 14.5 mmol) was dissolved in 60 mL of dry THF and 2.00 g (17.8 mmol) of *t*-BuOK was added. The solution was heated to 40 °C and stirred for 30 minutes. A solution of the ethylene glycol di-p-toluenesulfonate[20] (2.42 g, 6.5 mmol) in 50 mL of dry THF was added and the reaction mixture was refluxed for two days. The reaction mixture was filtered, the filtrate was evaporated in vacuo and the residue was dissolved in EtOAc. The solution was washed with water (3 × 30 mL), dried over $MgSO_4$ and evaporated in vacuo. The crude diester was dissolved in 20 mL of EtOH, 10 mL of 10% aqueous NaOH was added and the mixture was refluxed for 12 hours. Most of the solvent was evaporated in vacuo, water (30 mL) was added to the residue and the solution was acidified to pH 1 with 6 N HCl. The mixture was extracted with CH_2Cl_2 (3 × 80 mL) and the combined extracts were washed with water (2 × 50 mL) dried over $MgSO_4$ and evaporated in vacuo to afford the dicarboxylic acid. After recrystallization from Et_2O, a 38% yield of white solid with mp 163–164 °C (lit[20] mp 150–153 °C) was realized. ^{1}H-NMR ($CDCl_3$ + $CD_3S(O)CD_3$): δ 4.45 (s, 4H), 7.03–7.17 (m, 4H), 7.45-7.58 (m, 2H), 7.92-8.02 (m, 2H). IR (deposit on a NaCl plate from $CHCl_3$ solution): 3424 (O-H), 1710 (C=O), 1245 (C-O) cm^{-1}.

Preparation of 2,2'-[oxybis(1,2-ethanediyloxy)]bisbenzoic acid (2). By the same procedure as that given for the synthesis of **1**, the title compound was synthesized. After recrystallization from Et_2O, a 34% yield of white solid with mp 103-104 °C was obtained. ^{1}H-NMR ($CDCl_3$): δ 3.96–4.09 (m, 4H), 4.41-4.52 (m, 4H), 7.03-7.21 (m, 4H), 7.50-7.63 (m, 2H), 8.11–8.22 (m, 2H). IR (deposit on a NaCl plate from $CHCl_3$ solution): 3283 (O-H), 1728 (C=O), 1240, 1126 (C-O) cm^{-1}. Elemental analysis, calculated for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found: C, 62.44; H, 5.25.

Preparation of 1,2-[2'-(acetoxy)phenoxy]ethane (3). To 12.08 g (49.5 mmol) of **7** in 500 mL of dry THF was added 27.7 g (0.245 mol) of *t*-BuOK. The solution was brought to reflux and a solution of 16.80 g (0.121 mol) of bromoacetic acid dissolved in 200 mL of dry THF was added during a 2-hour period. The reaction solution was refluxed for 2 days, water (300 mL) was added and the THF was evaporated in vacuo. After addition of water (100 mL), the aqueous mixture was extracted with EtOAc (4 × 70 mL). The aqueous solution was acidified to pH 1 with 6 N HCl and the mixture was filtered. The pale yellow solid was washed with cold water (3 × 50 mL) and dried in vacuo (1 torr) to give 6.82 g (38%) of the desired product with mp 153–154 °C. ^{1}H-NMR ($CDCl_3$ + $CD_3S(O)CD_3$): δ 4.40-4.46 (t, 4H), 4.64-4.68 (d, 4H), 6.89-7.05 (m, 8H), 7.48 (s, 2H). IR (KBr): 3426 (O-H), 1739 (C=O) cm^{-1}. Elemental analysis, calculated for $C_{18}H_{18}O_8$: C, 59.67; H, 5.07. Found: C, 59.52; H, 5.00.

Preparation of 1,5-[2'-(acetoxy)phenoxy]-3-oxopentane (4). By the same procedure as that given for the synthesis of **3**, a solution of bromoacetic acid (2.00 g, 14.4 mmol) in 40 mL of dry THF was added dropwise to a refluxing solution of 2.00 g (6.89 mmol) of **8** and 3.20 g (28.5 mmol) of *t*-BuOK in 100 mL of dry THF during a 1-hour period. After refluxing for 2 days and workup, the crude product was recrystallized from Et_2O to give 1.68 g (60%) of the desired product as a white solid with mp 126-128°C. ^{1}H-NMR ($CDCl_3$ + $CD_3S(O)CD_3$): δ 3.93-3.97 (t, 4H), 4.19-4.24 (t, 4H), 4.63 (s, 4H), 6.80-6.95 (m, 8H), 7.53 (s, 2H). IR (KBr): 3417 (O-H), 1732 (C=O) cm^{-1}. Elemental analysis, calculated for $C_{20}H_{22}O_9$: C, 59.11; H, 5.46. Found: C, 58.84; H, 5.43.

Preparation of 1,2-[2'-(acetoxy)phenoxy]ethane resin **5** was described previously.[10]

Preparation of 1,5-[2'-(acetoxy)phenoxy]-3-oxopentane resin (6). Compound **4** (0.57 g, 1.4 mmol) was dissolved in a solution of formic acid (5 mL) and formaldehyde (37% aqueous solution, 5 mL). The mixture was refluxed for 6 hours. Formaldehyde (5 mL) was added a second time and the mixture was refluxed for another 6 hours. To complete resin precipitation, another 5 mL of formaldehyde was added and the mixture was refluxed for 6 hours and cooled. The precipitated resin was collected, washed with deionized water, methanol, and finally dried at 80 °C. The resin was ground in powder form finer than 60 mesh. Yield 56%. IR (KBr): 3435 (O-H), 1742 (C=O) cm^{-1}. Elemental analysis, calculated for $\mathbf{9}\cdot 4H_2O$: C, 58.93; H, 5.44. Found: C, 58.79; H, 5.44.

Extraction procedure. A chloroform solution (9.0 mL) containing 1.0 mM ligand and 9.0 mL of buffered aqueous solution (0.010 M sodium acetate buffer) containing 0.10 mM Pb(II) or Cu(II) were mechanically shaken for 1.0 hour in a 50-mL centrifuge tube at room temperature (24-26°C). The aqueous and the organic phases were separated by centrifuging (2000 rpm) for 10 minutes, and the metal ion concentration and the equilibrium pH of the aqueous phase were measured. A portion of the organic phase (0.50 mL) was sampled and diluted with chloroform in a 5.0-mL volumetric flask. The UV-Vis spectrum at 273-278 nm was measured to determine the ligand concentration in the chloroform phase. The percent extraction (E) was calculated by the following equation:

$$E(\%)=100([M^{2+}]_i - [M^{2+}]_f)/[M^{2+}]_i \qquad (4)$$

where $[M^{2+}]_i$ and $[M^{2+}]_f$ are the initial and the final metal ion concentrations in the aqueous phase, respectively.

Sorption procedure. An aqueous solution (5.0 mL) of 1.0 mM metal ion with nitric acid or 0.20 M tetramethylammonium acetate buffer was mechanically shaken with 0.030 g of the resin for 3.0 hours in a 50-mL centrifuge tube. The aqueous phase was filtered and the metal ion concentration and the equilibrium pH were measured. The percent sorption (S) was calculated by the following equation:

$$S(\%)=100([M^{2+}]_i - [M^{2+}]_f)/[M^{2+}]_i \qquad (5)$$

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