Anal. Chem. **1997,** *69,* 3002−3007

Selective Liquid Membrane Transport of Lead(II) by an Acyclic Polyether Dicarboxylic Acid Ionophore

Kazuhisa Hiratani,*,† Toshikazu Takahashi,† Hideki Sugihara,† Kazuyuki Kasuga,† Kyoko Fujiwara,† Takashi Hayashita,‡ and Richard A. Bartsch§

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan, Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo, Saga 840, Japan, and Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

The effects of the chain structure and substitutents in six acyclic polyether dicarboxylic acids and one acyclic polyether carboxylic acid upon the efficiency and selectivity of pH-driven Pb^{2+} transport in a bulk chloroform membrane system have been assessed. Among the carriers, 1,2-bis[2-(*o*-carboxyphenoxy)ethoxy]-4-*tert*-butylbenzene (1) is found to exhibit high selectivity for transport of Pb^{2+} compared with alkali metal cations and a variety of other divalent metal ion species. Ionophore 1 also extracts Pb^{2+} from aqueous solution into chloroform with the loss of two protons. A 1:1 complex of Pb^{2+} with di-ionized 1 was isolated.

Selective removal of Pb^{2+} for environmental remediation and in the treatment of acute and chronic lead poisoning remains an important objective.[1−3] Attempts to remove toxic heavy metal ions (e.g., Cd^{2+}, Hg^{2+}, and Pb^{2+}) from the environment and from biological systems have utilized a variety of separation methods, such as adsorption, precipitation, and solvent extraction.

Compared with solvent extraction, liquid membrane transport systems have the advantage that the amounts of organic liquid and metal ion complexing agent are markedly reduced.[4−6] Selective transport of lead salts across bulk liquid membranes with dicyclohexano-18-crown-6 (DC18C6) has been reported by Lamb et al.[7] Since in this system both Pb^{2+} and one or more anions must be transported from the aqueous source phase through the chloroform membrane and into the aqueous receiving phase, the rate of Pb^{2+} transport is anion-dependent.

In earlier work, we observed that the acyclic polyether dicarboxylic acids **1** and **2** exhibit selectivities for Ba^{2+} and Mg^{2+}, respectively, in competitive proton-coupled transport of alkali metal and alkaline earth metal cations from a basic aqueous solution (source phase) through a chloroform membrane into an acidic aqueous solution (receiving phase).[8] For these di-ionizable carriers, transport of the divalent metal ions does not require concomitant transport of anions from the aqueous phase. Also, the pH gradient may be used to drive metal ion transport against its concentration gradient.

Recently we discovered that **1** and **2** also exhibit selectivity for Pb^{2+} transport from weakly acidic aqueous solutions through a chloroform membrane and into a strongly acidic aqueous solution.[9] To probe the influence of chain structure and substituents within the carrier upon the efficiency and selectivity of Pb^{2+} transport, the study has now been expanded to include four additional acyclic polyether dicarboxylic acids **3**−**6** and the acyclic polyether carboxylic acid **7**. In addition to Pb^{2+}, divalent metal ions of Ba^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, and Zn^{2+} were chosen for the following reasons: (i) Earlier, **1** was found to selectively transport Ba^{2+} across a bulk chloroform membrane;[8] (ii) Cd^{2+} is a different, toxic, divalent, heavy metal ion; (iii) Cu^{2+} is at the top of the Irving−Williams order;[10] (iv) Zn^{2+} is an important metal ion in biological systems; and (v) Hg^{2+} is a toxic, divalent heavy metal ion with approximately the same ionic radius as Pb^{2+}. In addition to the liquid membrane transport studies, the stoichiometry of the solvent extraction complex formed from Pb^{2+} and **1** has been determined and spectroscopic properties of the isolated complex have been examined.

While this research was underway, good selectivity for Pb^{2+} over Cu^{2+} in competitive transport across plasticized cellulose triacetate membranes containing acyclic polyether dicarboxylic acid **8** was reported.[11]

[†] National Institute of Materials and Chemical Research.

[‡] Saga University.

[§] Texas Tech University.

(1) Izatt, R. M..; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

(2) Hancock, R. D. *Pure Appl. Chem.* **1986**, *58*, 1445.

(3) Damu, K. V.; Shaikjee, M. S.; Michael, J. P.; Howard, A. S.; Hancock, R. D. *Inorg. Chem.* **1986**, *25*, 3879.

(4) *Liquid Membranes*; ACS Symposium Series 347; Noble, R. D., Way, J. D., Eds.; American Chemical Society: Washington, DC, 1987.

(5) Araki, T.; Tsukube, H. *Liquid Membranes: Chemical Applications*; CRC Press: Boca Raton, FL, 1990.

(6) *Chemical Separations with Liquid Membranes*; ACS Symposium Series 642; Bartsch, R. A., Way, J. D., Eds.; American Chemical Society: Washington, DC, 1996.

(7) Lamb, J. D.; Izatt, R. M.; Robertson, P. A.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 2452.

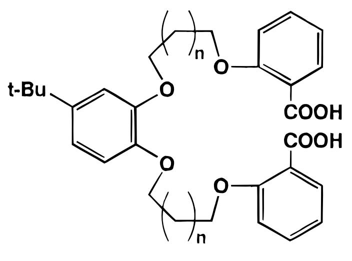
(8) Hiratani, K.; Taguchi, K.; Sugihara, H. *J. Membr. Sci.* **1991**, *56*, 960.

(9) Hiratani, K.; Sugihara, H.; Kasuga, K.; Fujiwara, K.; Hayashita, R.; Bartsch, R. A. *J. Chem. Soc., Chem. Commun.* **1994**, 319.

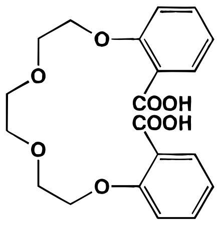
(10) Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192; *Nature* **1948**, *162*, 746.

(11) Hayashita, T.; Fujimoto, T.; Moriata, Y.; Bartsch, R. A. *Chem. Lett.* **1994**, 2385

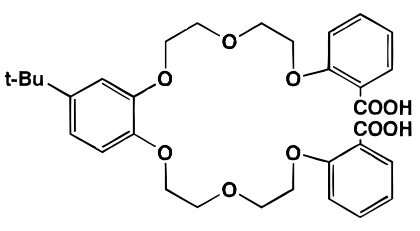
S0003-2700(97)00159-5 CCC: $14.00



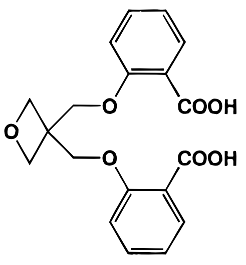
1: n = 0, **2**: n = 1



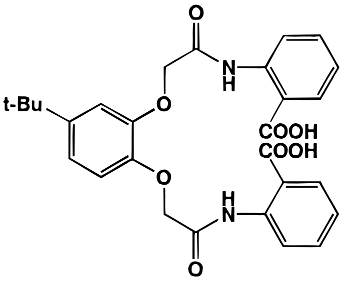
3



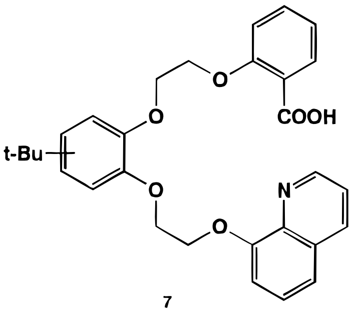
4



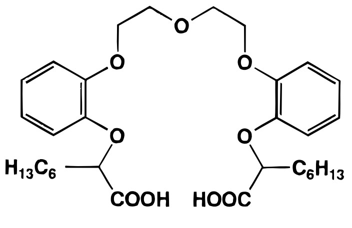
5



6



7



8

EXPERIMENTAL SECTION

Reagents. Inorganic and organic compounds were reagent-grade commercial products and were used as received. 1,2-Bis-[2-(*o*-carboxyphenoxy)ethoxy]-4-*tert*-butylbenzene (**1**),[8] 1,2-bis[3-(*o*-carboxyphenoxy)propoxy]-4-*tert*-butylbenzene (**2**),[8] 1,2-bis[2-(*o*-carboxyphenoxy)ethoxy-2-ethoxy]-4-*tert*-butylbenzene (**4**),[12] and 1-[(2-quinolyl-8-oxy)ethoxy]-2-[(*o*-carboxyphenoxy)ethoxy]-4(5)-*tert*-butylbenzene (**7**)[13] were prepared as previously reported.

Preparation of 1,8-Bis(*o*-carboxyphenoxy)-3,6-dioxaoctane (3). A mixture of 3.30 g (20 mmol) of ethyl salicylate, 0.50 g (20 mmol) of oil-free NaH, and 50 mL of DMF was stirred until it became homogeneous and 1.90 g (10 mmol) of 1,2-bis(2-chloroethoxy)ethane was added. The mixture was stirred at 70 °C for 24 h, cooled to room temperature, and poured into 300 mL of water. The mixture was extracted with benzene (200 mL), and the benzene layer was washed with water (3 × 100 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed on silica gel with chloroform as eluent to give 3.20 g (72%) of 1,8-bis[(*o*-ethoxycarbonyl)phenoxy]-3,6-dioxaoctane as a colorless liquid. A solution of this di(ethyl ester) (2.20 g) and 1.0 g of KOH in 30 mL of EtOH was refluxed overnight and evaporated in vacuo. Water was added to the residue, and the solution was acidified with concentrated HCl and extracted twice with chloroform. The combined chloroform layers were washed twice with water, dried over $MgSO_4$, and evaporated in vacuo. Recrystallization of the residue from benzene gave 1.20 g (62%) of **3** with mp 113−114 °C: ^1H NMR ($CDCl_3$) δ 3.76 (4H, s, OCH_2CH_2O), 3.92 (4H, t, $J = 4$ Hz, OCH_2CH_2O-Ar), 4.36 (4H, t, $J = 4$ Hz, OCH_2CH_2O-Ar), 7.02 (2H, dd, $J = 8$ and 8 Hz), 7.09 (2H, dd, $J = 8$ and 8 Hz), 8.10 (2H, d, $J = 8$ Hz) ppm; IR (KBr) 3264 (CO_2H), 1714 (C=O), 1244 (CO) cm^{-1}; UV ($CHCl_3$) λ_{max} 292 nm, ϵ 6180. Anal. Calcd for $C_{20}H_{22}O_8$: C, 61.53; H 5,68. Found: C, 61.63; H, 5.85.

Preparation of 3,3-Bis[*o*-(carboxyphenoxy)methyl]oxetane (5). In a manner similar to that described above for the synthesis of **3**, reaction of 3,3-bis(chloromethyl)oxetane with the sodium salt of ethyl salicylate in DMF followed by hydrolysis gave oxetane derivative **5** with mp 162−162.5 °C in 65% yield: ^1H NMR ($CDCl_3$) δ 4.57 (4H, s, cyclic-OCH_2), 4.75 (4H, s, Ar-OCH_2), 7.13 (2H, m), 7.55 (2H, m), 8.07 (2H, dd, $J = 2$ and 8 Hz) ppm; IR (KBr) 2665, 2558 (CO_2H), 1690 (C=O), 1250 (CO) cm^{-1}; UV ($CHCl_3$) λ_{max} 292 nm, ϵ 6650. Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06. Found: C, 63.39; H, 5.05.

Preparation of 1,2-Bis[*o*-(carboxyphenyl)aminocarbonylmethoxy]-4-*tert*-butylbenzene (6). To 1.60 g (5.0 mmol) of 1,2-bis[(chlorocarbonyl)methoxy]-4-*tert*-butylbenzene, which was obtained from the reaction of 1,2-bis[(hydroxycarbonyl)methoxy]-4-*tert*-butylbenzene with thionyl chloride, in 50 mL of benzene were added 1.70 g (10 mmol) of ethyl 2-aminobenzoate and 1.0 g (10 mmol) of triethylamine. The mixture was stirred at 70 °C for 24 h, cooled to room temperature, and poured into water (300 mL). The mixture was extracted with benzene (200 mL), and the benzene layer was washed with water (3 × 100 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed on silica gel with chloroform as eluent to give 2.30 g (79%) of 1,2-bis[(*o*-ethoxycarbonylphenyl)aminocarbonylmethoxy]-4-*tert*-butyl-benzene as a colorless liquid. A solution of this di(ethyl ester) (1.40 g) and 1.0 g of KOH in 30 mL of EtOH was refluxed overnight and evaporated in vacuo. Water was added to the residue, and the solution was acidified with concentrated HCl and extracted twice with chloroform. The chloroform layer was washed twice with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was recrystallized from benzene/cyclohexane (2:1) to give 0.80 g (67%) of **6** with mp 157−158 °C: ^1H NMR ($CDCl_3$) δ 1.21 (9H, s), 4.75 (2H, s), 4.78 (2H, s), 6.81 (1H,

---

(12) Hiratani, K.; Sugihara, H.; Taguchi, K.; Iio, K. *Chem. Lett.* **1983**, 1657.

(13) Hiratani, K.; Taguchi,; Sugihara, H.; Iio, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1976.

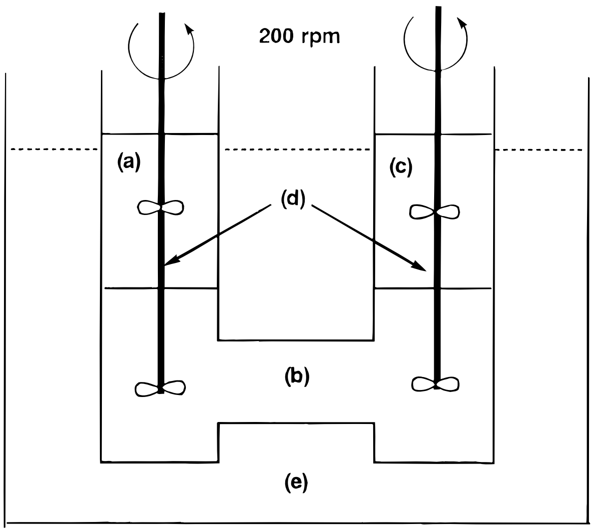


Figure 1. Cell for measuring metal ion transport across a chloroform membrane: (a) aqueous source phase, (b) chloroform membrane, (c) aqueous receiving phase, (d) glass stirrer, and (e) water bath at 25 °C.

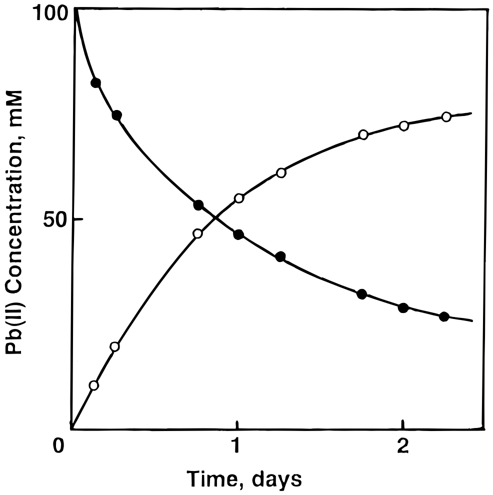


Figure 2. Pb^{2+} concentrations in the source phase (●) and receiving phase (○) vs time for transport across a chloroform membrane by carrier **1**. Initial conditions: source phase, 15 mL of 0.10 M Pb^{2+} in acetate buffer at pH 6.18; membrane phase, 30 mL of 5.0 mM **1** in chloroform; receiving phase, 15 mL of 0.10 M nitric acid.

d, $J = 8$ Hz), 6.92 (1H, d, $J = 8$ Hz), 6.95 (1H, m,), 7.18 (2H, m), 7.64 (2H, m), 8.05 (2H, dd, $J = 4$ and 8 Hz), 8.85 (2H, dd, $J = 4$ and 8 Hz), 11.64 (2H, s, NH) ppm; IR (KBr) 3194, 2616 (CO_2H), 1691 (C=O), 1235 (CO) cm^{-1}; UV ($CHCl_3$) λ_{max} 309 nm, ϵ, 9700. Anal. Calcd for $C_{28}H_{28}N_2O_8$: C, 63.51; H, 5.52; N, 5.29. Found: C, 64.43; H, 5.77; N, 5.25.

Preparation of the Pb^{2+} Complex of 1,2-Bis[2-(*o*-carboxyphenoxy)ethoxy]-4-*tert*-butylbenzene (1). Lead(II) acetate trihydrate (0.38 g, 1.0 mmol) was added to a solution of **1** (0.49 g, 1.0 mmol) in 2 mL of DMSO. The mixture was heated to obtain a solution which was allowed to cool to room temperature and stand gradually forming colorless crystals. The crystals were filtered and dried in vacuo at 100 °C overnight to give 0.51 g (71%) of the complex with mp 132−135 °C: ^1H NMR ($CDCl_3$) δ 1.20 (9H, s), 4.23 (4H, br m, OCH_2CH_2O), 4.50 (4H, br m, OCH_2CH_2O), 6.67 (2H, br, m), 6.90 (4H, br m), 7.04(1H, br s), 7.30 (2H, br m), and 7.70 (2H, br m) ppm; IR (KBr) 1588, 1556, 1520 (CO_2^-), 1219 (CO) cm^{-1}; UV ($CHCl_3$) λ_{max} 283 nm, ϵ, 7300. Anal. Calcd $C_{28}H_{28}O_8Pb{\cdot}H_2O$: C, 46.86; H, 4.21. Found: C, 46.51; H, 4.14.

Metal Ion Transport across Bulk Chloroform Membranes. Single species and competitive metal ion transport experiments were conducted in a U tube-type glass cell (Figure 1) thermostated at 25.0 ± 0.2 °C. Each phase was mechanically stirred at 200 rpm. The acetate buffer for the source phase was prepared from 195 mL of 1.00 M AcONa, 25 mL of 0.20 M AcOH, and 780 mL of deionized, distilled water. Compositions, concentrations, and volumes of the weakly acidic (pH 5.2−6.2) aqueous source phase, the chloroform membrane phase, and the more strongly acidic aqueous receiving phase are given in the table footnotes. The amounts of metal ions transported into the receiving phase and metal ions remaining in the source phase were determined by atomic absorption spectrophotometry.

Solvent Extraction of Pb^{2+} by 1. Into a 20-mL sample tube with a screw cap were added 8.0 mL of an aqueous 10 mM Pb^{2+} solution and 8.0 mL of a 1.0 mM chloroform solution of **1**. The pH of the aqueous solutions ranged from 4.57 to 6.28 as achieved by appropriate combinations of 1.0 M NaOAc and 1.0 M HNO_3. The mixture was shaken vigorously for 24 h at 25 °C, after which time both phases were clear in all cases. The concentration of Pb^{2+} in the aqueous solution was determined by atomic absorption spectroscopy, and the amount of extracted Pb^{2+} was calculated by difference from the concentration of Pb^{2+} in the original aqueous solution.

RESULTS AND DISCUSSION

Acyclic polyether dicarboxylic acids **1**−**6** each contain two ortho-substituted benzoic acid units with variation in the length of the spacer that joins the two carboxylic acid-containing end groups, as well as the number and type(s) of potential coordinating atoms. Compounds **1**,[8] **2**,[8] and **4**[12] form a series in which the length of the spacer and number of polyether oxygen atoms are systematically varied. **3** is an analog of **1** in which the *tert*-butylbenzo group of the latter has been replaced by an ethylene unit. Since the oxetane ring oxygen is directed away from the dicarboxylic acid groups, which should limit its role in metal ion coordination, **5** is a close analog of **3**. In **6**, two of the ether oxygens in **1** have been replaced by two amide groups. **7** was included to provide an example of an acyclic polyether with only one carboxylic acid group.

Transport of Pb^{2+} across Bulk Chloroform Membranes by Acyclic Polyether Dicarboxylic Acids 1−6 and Carboxylic Acid 7. The metal ion transport experiments were conducted in the U tube-type glass cell shown in Figure 1. The source phase "a" was a 0.10 M aqueous solution of Pb^{2+} in acetate buffer at pH 6.18. The membrane phase "b" was a 5.0 mM solution of the acyclic polyether dicarboxylic or carboxylic acid carrier in chloroform. In nearly all cases, the aqueous receiving phase "c" was 0.10 M nitric acid. All phases were stirred mechanically at 200 rpm. Samples of the aqueous receiving and source phases were removed periodically, and the Pb^{2+} concentrations were determined by atomic absorption spectrophotometry. In the absence of carrier, no Pb^{2+} transport was detected.

A plot of the Pb^{2+} concentrations in the aqueous source and receiving phases vs time for single-species transport by acyclic polyether dicarboxylic acid **1** is shown in Figure 2. After one day, the Pb^{2+} concentration in the receiving phase exceeds that in the source. Thus, proton-driven transport of Pb^{2+} against its

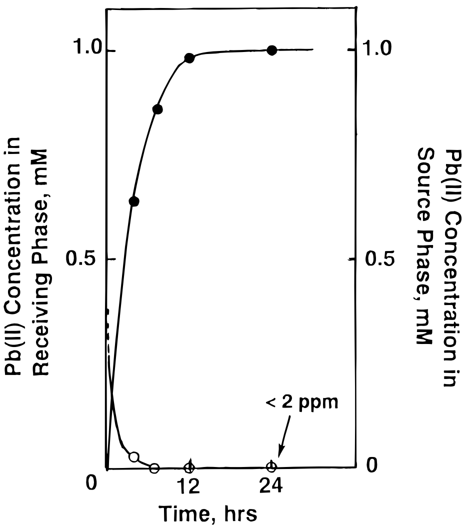


Figure 3. Pb^{2+} concentrations in the source phase (○) and receiving phase (●) vs time for Pb^{2+} transport across a chloroform membrane by carrier **1**. Initial conditions: source phase, 15 mL of 1 mM Pb^{2+} in acetate buffer at pH 6.18; membrane phase, 30 mL of 5.0 mM **1** in chloroform; receiving phase, 15 mL of 0.10 M nitric acid

Table 1. Transport of Pb^{2+} across Bulk Chloroform Membranes by Acyclic Polyether Carboxylic and Dicarboxylic Acids Carriers at 25 °C[a]

entry	carrier	initial Pb^{2+} transport rate × 10^6 (μmol h^{-1} cm^{-2})[b]
1	**1**	53
2[c]	**1**	54
3	**2**	20
4	**3**	34
5	**4**	24
6	**5**	<1[d]
7	**6**	29
8	**7**	9.2

[a] Initial conditions: source phase, 15 mL of 0.10 M Pb^{2+} in acetate buffer at pH 6.18; membrane phase, 30 mL of 5.0 mM carrier in chloroform; receiving phase, 15 mL of 0.10 M nitric acid. [b] Reproducibility was ±10% or less of the stated value. [c] Receiving phase was 0.20 M nitric acid. [d] A white precipitate formed in the chloroform membrane.

Table 2. Competitive Transport of Pb^{2+} and Cu^{2+} across Bulk Chloroform Membranes by Acyclic Polyether Carboxylic and Dicarboxylic Acids and by Dicyclohexano-18-crown-6 at 25 °C[a]

entry	carrier	pH of the source phase	initial transport rate ×10^6 (μmol h^{-1} cm^{-2})[b] Pb^{2+}	Cu^{2+}	Pb^{2+}/Cu^{2+} transport selectivity
1	**1**	5.27	46	0.48	96
2	**2**	5.27	20	1.3	15
3	**3**	5.27	26	0.66	40
4	**4**	5.27	13	4.0	3.3
5	**6**[c]	6.18	2	2	1
6	**7**	6.18	3.0	12	0.25
7	DC18C6[d]	6.18	0.1	<0.1	

[a] Initial conditions: source phase, 15 mL of 0.10 M Pb^{2+} and 0.10 M Cu^{2+} in acetate buffer; membrane phase, 30 mL of 5.0 mM carrier in chloroform; receiving phase, 0.10 M nitric acid. [b] Reproducibility was ±10% or less of the stated value. [c] The chloroform membrane became pale blue and turbid. [d] Dicyclohexano-18-crown-6.

concentration gradient is achieved. The transport rate decreases gradually with time, presumably due to a lowering of the source phase pH by the antiport of protons. Figure 3 shows a plot of the Pb^{2+} concentrations in the aqueous source and receiving phases vs time for single species transport by carrier **1** from a solution that was initially 1.0 mM in Pb^{2+}. As can be seen, Pb^{2+} transport from the source phase into the receiving phase is nearly quantitative after 12 h. The Pb^{2+} concentration in the source phase after 24 h is reduced to less than 2 ppm.

Initial rates of Pb^{2+} transport across the chloroform membrane by carriers **1**−**7** are recorded in Table 1. Identical Pb^{2+} transport rates by **1** into receiving phases of 0.10 and 0.20 M nitric acid (Table 1, entries 1 and 2, respectively) are consistent with transport through the chloroform membrane as the rate-limiting step. For the acyclic polyether dicarboxylic carriers, the rate of Pb^{2+} transport decreases in the order **1** > **3** ≥ **6** > **4** ≥ **2** with a variation of (5.3−2.0) × 10^{-5} μmol h^{-1} cm^{-2} for the series. Thus, the nature of the spacer that joins the two ortho-substituted benzoic acid units in the carrier is found to have a modest influence upon the rate of Pb^{2+} transport. For the oxetane polyether dicarboxylic acid **5**, a white precipitate formed in the chloroform membrane, suggesting that the Pb^{2+} complex of the dicarboxylate form of **5** is insoluble in chloroform. Therefore, no further attempts were made to study divalent metal ion transport by potential carrier **5**.

The acyclic polyether carboxylic acid **7** (Table 1, entry 8) is less effective in Pb^{2+} transport than the acyclic polyether dicarboxylic acids **1**−**4** and **6**. For **7**, transport of Pb^{2+} requires either two molecules of ionized carrier or one molecule of ionized carrier and a monovalent anion from the aqueous source phase for electroneutrality.

Competitive Transport of Pb^{2+} and Cu^{2+} across Bulk Chloroform Membranes. To explore the influence of structural variation within the carrier upon selectivity, competitive transport of Pb^{2+} and Cu^{2+} across chloroform membranes by **1**−**4** and **6**, **7**, and the crown ether DC18C6 was examined. The initial Pb^{2+} and Cu^{2+} transport rates for these carriers are presented in Table 2.

As can be seen, the nature of the spacer that joins the two ortho-substituted benzoic acid groups in the acyclic polyether dicarboxylic acid carrier has a profound influence upon the relative rates of Pb^{2+} and Cu^{2+} transport. The Pb^{2+}/Cu^{2+} selectivity ratios vary from 96 for carrier **1** to 1 for carrier **6**. The very high selectivity obtained with **1** is reduced somewhat when the *tert*-butylbenzo group in the spacer is replaced with a more flexible ethylene unit in **3**. Replacing two of the ethylene units in the spacer of carrier **1** with propylene units in **2** diminishes the selectivity to an even lower level than was observed for **3**. Replacing two of the ether linkages in carrier **1** with amide groups in **6** produces a profound diminution in the selectivity.

7 is found to transport Cu^{2+} more effectively than Pb^{2+}. Presumably this results from preferred interaction of Cu^{2+} with the quinolinyl unit in the carrier.

Compared with the nonionizable, cyclic polyether carrier DC18C6, pH-driven Pb^{2+} transport by carriers **1**−**4** and **6** is much more rapid (Table 2).

Single-Species and Competitive Metal Ion Transport across Chloroform Membranes by 1. Since **1** was found to provide the most efficient Pb^{2+} transport in single-species transport experiments and the greatest Pb^{2+}/Cu^{2+} selectivity in competitive

Table 3. Single-Species and Competitive Divalent Metal Ion Transport across Bulk Chloroform Membranes by Acyclic Polyether Dicarboxylic Acid 1[a]

entry	initial pH of source phase	initial transport rate × 10^6 (μmol h^{-1} cm^{-2})[b]						selectivity
		Pb^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ba^{2+}	Hg^{2+}	
1	5.80		9.2					
2	6.26	53		<0.07				$Pb^{2+}/Zn^{2+} \geq 760$
3	6.24	44			0.30			$Pb^{2+}/Cd^{2+} = 150$
4	6.47	35				0.46		$Pb^{2+}/Ba^{2+} = 87$
5	6.13	15					4.5	$Pb^{2+}/Hg^{2+} = 3.3$

[a] Initial conditions: source phase, 15 mL of 0.10 M metal ion (each) in acetate buffer; membrane phase, 30 mL of 5.0 mM **1** in chloroform; receiving phase, 15 mL of 0.10 M nitric acid. [b] Reproducibility was ±10% or less of the stated value.

transport experiments, the transport behavior of this carrier for alkali metal cations and several divalent metal cations was examined.

In single-species transport experiments conducted with carrier **1**, no transport of alkali metal cations was detectable.

The initial rate for the single-species transport of Cu^{2+} across the chloroform membrane by carrier **1** is presented in Table 3 (entry 1). The flux for Cu^{2+} is 9.2×10^{-6} μmol h^{-1} cm^{-2} compared with a single species Pb^{2+} flux of 53×10^{-6} μmol h^{-1} cm^{-2} (Table 1, entry 1). Based upon these single species transport behaviors, a competitive Pb^{2+}/Cu^{2+} transport ratio of ~5.5 is estimated. Although the single-species fluxes for Pb^{2+} and Cu^{2+} transport are not directly comparable due to somewhat differing source phase pH values, it appears certain that this estimated Pb^{2+}/Cu^{2+} transport selectivity is considerable less than the measured competitive selectivity ratio of nearly 100 (Table 2, entry 2). The primary causative factor for the considerable higher competitive Pb^{2+}/Cu^{2+} selectivity in competitive transport is a marked diminution of Cu^{2+} transport compared to that observed in the single-species transport experiment.

For competitive transport of Pb^{2+} and other divalent metal ion species (Table 3), selectivity ratios are $Pb^{2+}/Zn^{2+} \geq 760$, $Pb^{2+}/Cd^{2+} = 150$, $Pb^{2+}/Ba^{2+} = 87$, and $Pb^{2+}/Hg^{2+} = 3.3$. Thus, with the exception of Hg^{2+}, the Pb^{2+} selectivity in competitive transport is very high for carrier **1**.

Results for competitive transport by carrier **1** from a source phase solution 10 mM in Pb^{2+} and 1.0 M in Zn^{2+} are presented in Figure 4. Even though there was an initial 100-fold excess of Zn^{2+} in the source phase, 75% of the Pb^{2+}, but only 3% of the Zn^{2+}, was transported into the receiving phase after two days.

Solvent Extraction of Pb^{2+} by 1. To gain insight into the nature of the complex between carrier **1** and Pb^{2+} in membrane transport, solvent extraction experiments were conducted.

If extraction of Pb^{2+} with **1** (LH_2) occurs as follows

$$(Pb^{2+})_w + (LH_2)_o \Leftrightarrow (Pb^{2+}{\cdot}L^{2-})_o + (2H^+)_w \tag{1}$$

the extraction constant may be written as

$$K_{ex} = [Pb^{2+}{\cdot}L^{2-}]_o[H^+]^2_w/[Pb^{2+}]_w[LH_2]_o \tag{2}$$

where the subscripts "o" and "w" denote the organic and aqueous phases, respectively. The distribution coefficient may be written as

$$D = C_{M,o}/C_{M,w} = [Pb^{2+}{\cdot}L^{2-}]_o/[Pb^{2+}]_w \tag{3}$$

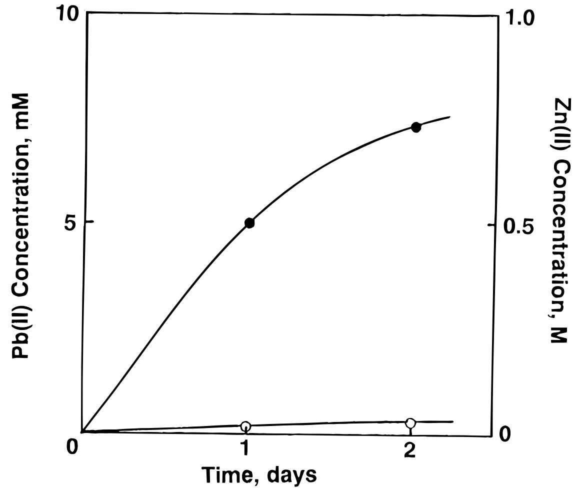


Figure 4. Concentrations of Pb^{2+} (●) and Zn^{2+} (○) in the aqueous receiving phase vs time for competitive transport across a chloroform membrane by carrier **1**. Initial conditions: source phase, 15 mL of 10 mM Pb^{2+} and 1.0 M Zn^{2+} in acetate buffer at pH 6.18); membrane phase, 30 mL of 5.0 mM **1** in chloroform; receiving phase, 15 mL of 0.10 M nitric acid.

where $C_{M,o}$ and $C_{M,w}$ denote the Pb^{2+} concentrations in the organic and aqueous phases, respectively. When the volumes of the organic and aqueous phases are the same and the concentration of $Pb^{2+}{\cdot}L^{2-}$ in the aqueous phase is negligible, the following relationships can be derived from eqs 2 and 3

$$D = K_{ex}[LH_2]_o/[H^+]^2_w \tag{4}$$

$$\log D = \log K_{ex} + \log[LH_2]_o - 2\log[H^+]_w \tag{5}$$

Thus if the extraction occurs according to eq 1, plots of log D vs $-\log[H^+]_w$ (= pH) at a constant $[LH_2]_o$ and of log D vs $\log[LH_2]_o$ at a constant pH would be straight lines with slopes of 2 and 1, respectively.

Data for the solvent extraction of Pb^{2+} from aqueous solutions into chloroform by **1** are shown in Figure 5. A plot of log D vs pH (Figure 6) shows a linear relationship with a slope of 1.9. Thus the formation of the extraction complex in solvent extraction of Pb^{2+} with **1** is accompanied by the loss of two protons. For extractions conducted at pH 6.28, a plot of log D vs $\log[LH_2]$ gives a straight line with slope 1.05 (Figure 7). These results verify the stoichiometry of the extraction complex as $Pb^{2+}{\cdot}L^{2-}$.

Further Investigation of the Complexation of Pb^{2+} by 1. Although lead(II) acetate is insoluble in chloroform, rapid dis-

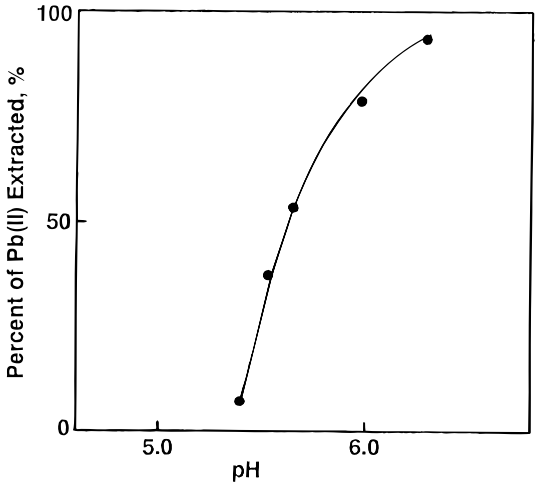


Figure 5. pH dependence for solvent extraction of 10 mM Pb^{2+} in acetate buffer with 1.0 mM **1** in chloroform.

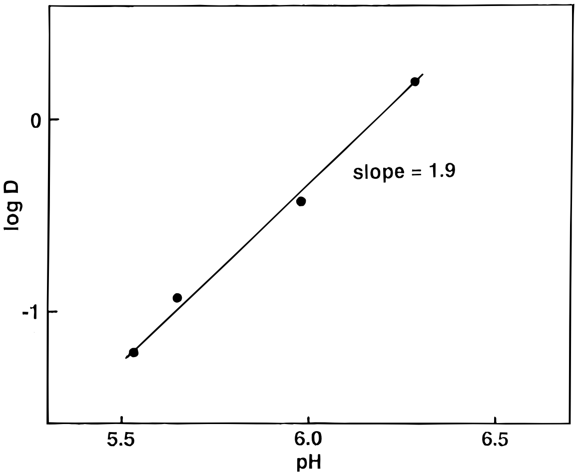


Figure 6. Plot of log *D* vs pH for solvent extraction of Pb^{2+} from aqueous solution into chloroform by **1**.

solution of lead acetate was observed in a solution of **1** in chloroform. To examine this process in a more quantitative fashion, ^1H NMR spectroscopy was utilized. The aromatic region of the ^1H NMR spectrum of **1** in deuteriochloroform is shown in Figure 8. Addition of a slight excess of lead(II) acetate and shaking for 10 min produced marked changes in these absorptions. Only limited further changes were noted after one day. Thus formation of the complex between Pb^{2+} and **1** is shown to be rapid.

From an equimolar solution of lead acetate trihydrate and **1** in dimethyl sulfoxide, a 1:1 complex of Pb^{2+} and the di-ionized form of **1** crystallized as a monohydrate. This complex was characterized by ^1H NMR and IR spectra and its composition verified by combustion analysis.

CONCLUSIONS

1 is shown to provide efficient and selective transport of Pb^{2+} across bulk chloroform membranes. Carrier **1** exhibits high selectivity for Pb^{2+} transport over Ba^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}, as well as over alkali metal cations. Solvent extraction of Pb^{2+} from aqueous solutions into chloroform occurs with formation of a 1:1 complex of Pb^{2+} and the di-ionized form of **1**.

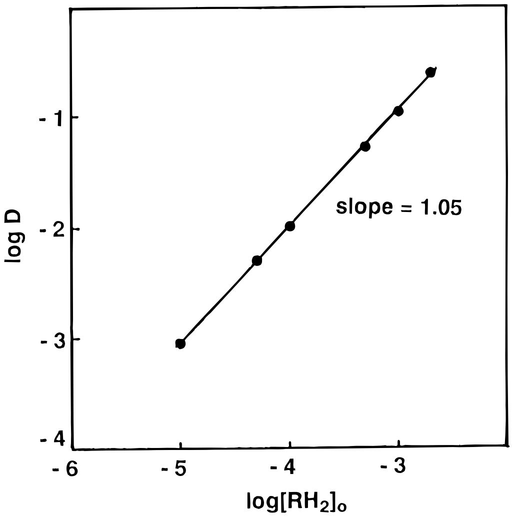


Figure 7. Plot of log *D* vs log [**1**] for solvent extraction of Pb^{2+} from aqueous solution at pH 6.28 into chloroform by **1**.

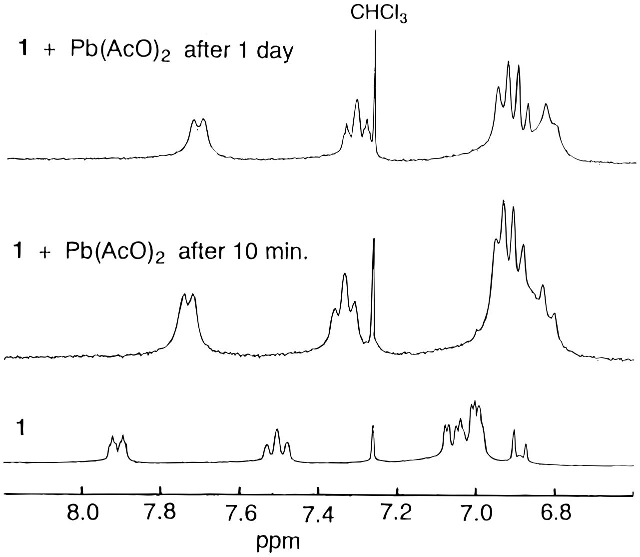


Figure 8. Aromatic region of the ^1H NMR spectrum of **1** in the absence and presence of lead(II) acetate.

ACKNOWLEDGMENT

R.A.B. gratefully acknowledges support by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy (Grant DE-FG03-94ER14416).

Received for review February 10, 1997. Accepted May 21, 1997.⊗

AC9701593

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.