

An Acyclic Polyether Dicarboxylic Acid Ionophore with High Selectivity for pH-driven Uphill Transport of Lead(II) Ion

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1,2-Bis[2-(*o*-carboxyphenoxy)ethoxy]-4-*tert*-butylbenzene transports Pb^{II} ion against its concentration gradient in a liquid membrane system with high selectivity over a variety of monovalent and divalent metal ions.

Several methods, such as solvent extraction, precipitation, and adsorption have been utilized in attempts to remove toxic, heavy metal ions (*e.g.* lead, cadmium and mercury) from the environment and from biological systems. Selective removal of Pb^{II} for environmental remediation and in the treatment of acute and chronic lead poisoning remains an important objective.¹⁻³

Selective transport of Pb^{II} across a liquid membrane using dicyclohexano-18-crown-6 (DCH18C6) as the carrier has been reported by Lamb *et al.*⁴ Here we describe the selective, proton-coupled transport of Pb^{II} through a liquid membrane by two acyclic polyether dicarboxylic acids, 1,2-bis[2-(*o*-carboxyphenoxy)ethoxy]-4-*tert*-butylbenzene **1** and 1,2-bis[3-(*o*-carboxyphenoxy)propoxy]-4-*tert*-butylbenzene **2**.⁵

In earlier work, we observed that ionophores **1** and **2** exhibited selectivities for transport of Ba^{II} and Mg^{II}, respectively, in competitive, proton-coupled transport of alkali and alkaline earth metal cations from a basic aqueous solution (source phase) across a chloroform liquid membrane into an acidic aqueous solution (receiving phase).⁵ We have now examined the transport of Ba^{II}, Cd^{II}, Cu^{II}, Pb^{II}, Zn^{II}, as well as alkali metal ions, from weakly acidic aqueous source phases (pH = 5.2–6.2) across a chloroform liquid membrane containing potential carriers **1** and **2** into strongly acidic aqueous receiving phases (pH = 1.2). In addition to Pb^{II}, the other divalent metal ions were chosen for the following reasons: (i) Ba^{II} has an ionic radius which is very similar to that of Pb^{II}; (ii) Cd^{II} is a different toxic, divalent, heavy metal ion; (iii) Cu^{II} usually exhibits the highest complexation in the Irving–Williams order,⁶ and, (iv) Zn^{II} is an important metal ion in biological systems.

A U-tube glass cell was utilized to study the single or competitive transport of metal ions.⁷ (See footnotes of Table 1 for compositions and volumes of the three phases.) The cell was thermostatted at 25.0 ± 0.2 °C and each phase was mechanically stirred at 200 rpm.⁷ Concentrations of metal ions transported into the receiving phase and remaining in the source phase were determined periodically by atomic absorption spectrophotometry.

Initial rates for both single species and competitive metal ion transport are summarized in Table 1. In control experiments conducted without **1** or **2** in the chloroform phase, it was confirmed that there was no divalent metal ion transport in the absence of carrier. In addition it was observed that alkali metal cations were not transported when **1** and **2** were present in the chloroform phase under the same conditions.

With ionophore **1** and only a single divalent metal ion species present in the aqueous source phase, the flux for Pb^{II} was 53 × 10⁻⁶ mol h⁻¹ cm⁻² (run 1, pH 6.18) and for Cu^{II} 9.2 × 10⁻⁶ mol h⁻¹ cm⁻² (run 6, pH 5.80). Based upon these single species results, the Pb^{II}/Cu^{II} transport selectivity is calculated to be about 5.5. However, when both Pb^{II} and Cu^{II} were present in the aqueous source phase (run 2, pH 5.27), the Pb^{II} flux remained approximately the same but the Cu^{II} flux was markedly diminished resulting in a Pb^{II}/Cu^{II} transport selectivity of nearly 100. Thus the competitive transport selectivity as measured in competitive experiments was found to be much higher than would have been predicted based upon the results of single species experiments. For competitive Pb^{II}–Cu^{II} transport by ionophore **2** the Pb^{II}/Cu^{II} selectivity under the same conditions was 15 (run 11). The reduced selectivity arises from a decrease in the Pb^{II} flux and an enhancement in the Cu^{II} flux. Thus **1** is found to be superior to **2** both in terms of Pb^{II} transport rate and selectivity. It should be noted that under our experimental conditions, DCH18C6, which is reported to be a highly selective Pb^{II} carrier,⁴ provided only a very low Pb^{II} flux in a competitive Pb^{II}–Cu^{II} transport experiment (run 12), because DCH18C6 could be significantly affected both by the concentration of Pb^{II} and the type of counter anions in the source phase.

The transport of Zn^{II} by **1** is very slow in both single species (run 7) and competitive Pb^{II}–Zn^{II} transport (run 3) producing very high Pb^{II}/Zn^{II} transport selectivity. This suggests that **1** may have the potential for removal of Pb^{II} from biological systems. The Cd^{II} flux was also very low in competitive Pb^{II}–Cd^{II} transport (run 4) leading to high Pb^{II}/Cd^{II} selectivity. Thus carrier **1** exhibits very good differentiation for

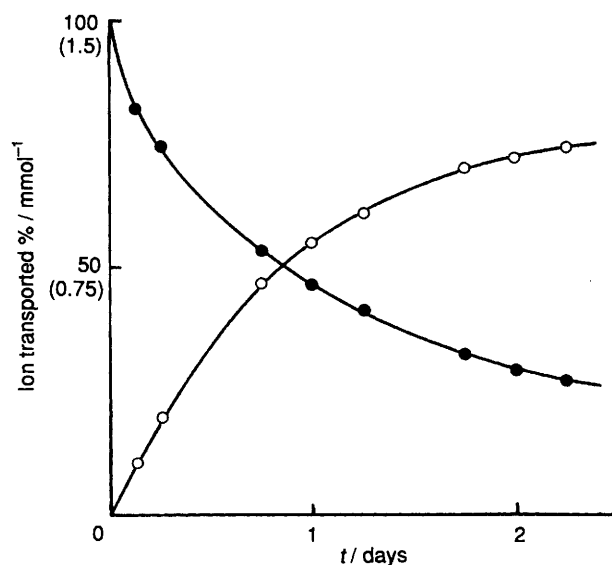


Fig. 1 Amount of Pb^{II} ion transported by **1** vs. time for run 1 (Table 1); ●—: Pb^{II} in the source phase, ○—: Pb^{II} in the receiving phase

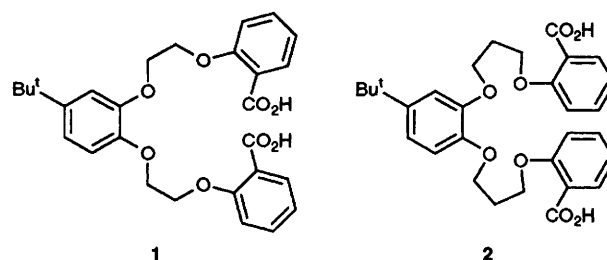


Table 1 Transport of metal ions through liquid membranes^a

Run	Ionophores	Initial pH in source phase ^b	initial transport rate/ $\mu\text{mol m}^{-2} \text{cm}^{-2} \text{h}^{-1}$					Selectivity
			Pb ^{II}	Cu ^{II}	Zn ^{II}	Cd ^{II}	Ba ^{II}	
1	1	6.18	53	—	—	—	—	—
2	1	5.27	46	0.48	—	—	—	Pb/Cu = 96
3	1	6.26	53	—	<0.07	—	—	Pb/Zn > 760
4	1	6.24	44	—	—	0.30	—	Pb/Cd = 150
5	1	6.47	35	—	—	—	0.46	Pb/Ba = 87
6	1	5.80	—	9.2	—	—	—	—
7	1	6.33	—	—	<0.03	—	—	—
8	1	6.56	—	—	—	—	0.30	—
9	1	6.18	54	—	—	—	—	—
10	2	6.18	20	—	—	—	—	—
11	2	5.27	20	1.3	—	—	—	Pb/Cu = 15
12	DCH18C6	6.18	0.1	<0.1	—	—	—	—

^a Initial transport conditions (25 °C): (source phase) 0.1 mol dm⁻³ (=M) of each metal ion, aqueous buffered solution, 15 ml, (chloroform phase) 0.15 mmol of carrier in 30 ml chloroform, (receiving phase) 0.1 mol dm⁻³ HNO₃ (pH 1.19) for runs 1–8 and 10–12 or 0.2 mol dm⁻³ HNO₃ (pH 0.78) for run 9, 15 ml. ^b Source phase is adjusted by the buffered solution composed of 195 ml of 1 mol dm⁻³ AcONa, 25 ml of 0.2 mol dm⁻³ AcOH, and 780 ml of water. ^c Reproducibility of the values is $\pm 10\%$ or better.

transport of Pb^{II} over another toxic, divalent, heavy metal ion. From the weakly acidic aqueous source phase, the flux of Ba^{II}, which is chemically most similar to Pb^{II}, was found to be very low in both single species transport (run 8) and in competitive Pb^{II}–Ba^{II} transport (run 5) yielding a high Pb^{II}/Ba^{II} transport selectivity.

A plot of the amount of Pb^{II} in the aqueous source and receiving phases for transport by ionophore **1** vs. time for run 1 in Table 1 is shown in Fig. 1. After one day, the concentration of Pb^{II} in the receiving phase is greater than that in the source phase. Thus proton-driven transport of Pb^{II} against its concentration gradient is achieved. The transport rate gradually decreased with time, presumably due to lowering of the source phase pH by the antiport of protons. A receiving phase of 0.1 mol dm⁻³ HNO₃ was found to be sufficiently acidic for release of the Pb^{II}, since the change to 0.2 mol dm⁻³ HNO₃ gave essentially the same rate of Pb^{II} transport (compare runs 1 and 9 in Table 1).

The structural difference between **1** and **2** is the number of methylene groups which join the ether oxygens. As previously reported, acyclic polyether carboxylic acid ionophores with trimethylene bridging unit, such as **2** form small cavities and exhibit selectivities for small ions, such as Li⁺ and Mg²⁺.⁵ It is assumed that the larger pseudocavity formed by the dimethylene bridging units in **1** fits Pb^{II}, which has nearly the same ionic radius as Ba^{II}. The complex of **1** with Pb^{II} was found to be readily soluble in chloroform. This is consistent with incorpor-

ation of Pb^{II} within the pseudocyclic cavity of the ligand to form a lipophilic complex.

Thus we have shown that the lipophilic acyclic polyether dicarboxylic acid **1** is an efficient and selective carrier for the separation by liquid chloroform membranes of Pb^{II} from weakly acidic aqueous solutions containing a variety of monovalent and divalent metal ions.

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References

- R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271.
- R. D. Hancock, *Pure Appl. Chem.*, 1986, **58**, 1445.
- K. V. Damu, M. S. Shaikjee, J. P. Michael, A. S. Howard and R. D. Hancock, *Inorg. Chem.*, 1986, **25**, 3879.
- J. D. Lamb, R. M. Izatt, P. A. Robertson and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102**, 2452.
- K. Hiratani, K. Taguchi and H. Sugihara, *J. Membr. Sci.*, 1991, **56**, 960.
- H. Irvin and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192; *Nature*, 1948, **162**, 746.
- K. Hiratani, I. Nozawa, T. Nakagawa and S. Yamada, *J. Membr. Sci.*, 1982, **12**, 207.
- K. Hiratani, *Chem. Lett.*, 1982, 1021; *Bull. Chem. Soc. Jpn*, 1985, **58**, 420.