Versatility of Kemp's acid imides as heavy metal ion carriers

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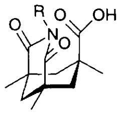
Kemp's acid imides transport transition-metal ions through a $CHCl_3$ liquid membrane, most effectively transporting Hg^{II} with high selectivities (Hg/Ag = 5, Hg/Cu = 14, and Hg/Pb = 86 for an aromatic imide).

In our previous study,[1] we reported that Kemp's acid imides are efficient carriers for alkaline-earth metal ions from a weakly basic aqueous solution across a chloroform liquid membrane to an acid solution. Unique for these ionophores is their ability to transport divalent alkaline-earth metal ions more efficiently than monovalent alkali-metal ions despite the presence of only one carboxyl group. To examine Kemp's acid imide versatility further, additional study on the transport ability was necessary for other metal ions.

The importance of transport through a liquid membrane, *i.e.* carrier-mediated continuous solvent extraction, of metal ions is well known and is used for environmental protection as well as recovery of natural resources.[2–4] Previously we developed several ionophores having quinoline moieties which can effectively extract or transport Cu^{II} [5,6] and/or Hg^{II}.[7] Here we report high transport ability of Kemp's acid imides for transition-metal ions, especially for Hg^{II}.

The synthesis of imides **1** and **2** from the reaction of Kemp's triacid anhydride acid chloride and primary amines was reported previously.[1] The metal ion transport ability of **1** and **2** was examined for several transition-metal ions, using a U-tube glass cell.[1,6,7] Negligible or non-existent ion transport was confirmed by control experiments with no imide acids in the chloroform phase (Table 1, runs 11 and 12). Concentrations of the transported and remaining metal ions in the receiving and source phases, respectively, were monitored by AAS (Shimadzu AA-680).



1: R = *p-n*-$C_4H_9C_6H_4$
2: R = *n*-$C_{18}H_{37}$

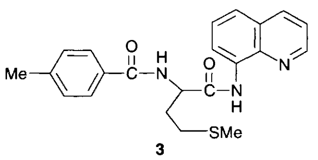


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Table 1 shows the transport ability of **1** for several transition metals examined by either competitive or single ion transport experiments. The imide acid **1** transported Cu^{II}, Pb^{II}, Hg^{II} and Ag^{I} very efficiently, but gave low transport ability for Ni^{II}, Co^{II}, Zn^{II} and Cd^{II}. Transport of Hg^{II} and Ag^{I} was almost completed after 24 h under present conditions (Table 1, runs 4 and 5). Taking into account the carrier concentration, the present data show that **1** (5 mmol dm^{-3}) is a more efficient Hg^{II} carrier than the previously reported compound **3** (10 mmol dm^{-3}),[7] which contains a sulfur atom. It is well known that the soft sulfur atom is an efficient coordinating atom for soft metal ions like Hg^{II} and Ag^{I}. In fact, many sulfur-containing mercury(II) ionophores have been developed.[7–10] For other transition metals[5,6,11–13] many compounds containing several oxygen and/or nitrogen atoms, such as macrocycles,[14] have been used for selective extraction and transport. By contrast, it is very interesting that **1** has only one carboxyl and one imide group which are possibly available for coordination to a metal ion. The aliphatic analogue, **2**, has similar but slightly lower transport ability than **1** (Table 1, runs 8–10).

The Hg^{II} selectivity over Cu^{II}, Pb^{II} and Ag^{I} was examined for **1** by dual ion competitive transport experiments and the results are summarized in Table 2. In order to know the transport profile, the time dependences of Hg^{II} and Ag^{I} concentrations of both the source and the receiving phases are shown in Fig. 1; indicating that the Hg^{II} concentration decrease of the source phase is faster than the concentration increase of the receiving phase, which means extraction of Hg^{II} at the interface of the source and organic phases is more efficient than release of it at the interface of the receiving and organic phases. In addition, the faster concentration decrease of Hg^{II} than that of Ag^{I} can be interpreted to mean **1** has a stronger affinity towards Hg^{II}, which

Table 1 Amount of transition-metal ions transported after 2 days[a]

		Metal ions transported to the receiving phase/mol%[b] (μmol)								
Run	Carrier	Cu^{II}	Pb^{II}	Zn^{II}	Ni^{II}	Co^{II}	Ag^{I}	Hg^{II}[c]	Cd^{II}	Selectivity
1	**1**	65 (98)	27 (40)	1 (1)	0	0	—	—	—	Cu/Pb = 2.5, Cu/Zn = 98
2	**1**	61 (92)	—	—	—	—	—	—	—	
3	**1**	—	63 (95)	—	—	—	—	—	—	
4	**1**	—	—	—	—	—	95 (143)	—	—	
5	**1**	—	—	—	—	—	—	100 (150)	—	
6	**1**	—	—	—	—	—	—	—	0.9 (1)	
7[d]	**1**	—	—	—	—	—	—	63 (945)	—	
8	**2**	49 (73)	35 (53)	2 (3)	0	0	—	—	—	Cu/Pb = 1.4, Cu/Zn = 24
9	**2**	—	—	—	—	—	71 (107)	—	—	
10	**2**	—	—	—	—	—	—	89 (134)	—	
11	none	~0	0	~0	0	0	—	—	—	
12	none	—	—	—	—	—	—	2–4	—	

[a] Initial transport conditions (25 °C): source phase; 10 mmol dm^{-3} metal acetate AcONa–AcOH buffered solution, pH *ca.* 6.0–6.4, 15 ml liquid membrane; 0.15 mmol of imide acid in 30 ml of chloroform. Receiving phase; 0.1 mol dm^{-3} HNO_3 15 ml. Each phase was mechanically stirred at 200 rpm. [b] mol% = 100 × (moles of ion M^{z+} transported)/(initial moles of ion M^{z+} in the source phase). [c] Data after 1 day. [d] 100 mmol dm^{-3} $Hg(OAc)_2$ solution and 0.2 mol dm^{-3} HNO_3 were used for the source and receiving phases, respectively.

leads to the high selectivity ratio of 5 : 1. The situations are similar for other ion combinations, such as for the Hg^{II}–Cu^{II} and Hg^{II}–Pb^{II} systems, which showed selectivity ratios of 14 : 1 and 86 : 1, respectively. Even after 12 h, almost complete transport of Hg^{II} was observed in every experiment. At this time the selectivity of Hg^{II} over Cu^{II} for **1** is improved (Table 2, run 2) from that of our previous carrier **3** (Table 2, run 7)[7] after 24 h. As the selectivity is time dependent (Fig. 1), it becomes higher when calculated at the earlier stage of the transport experiments. Therefore comparison was made from the data at such a time that the amount of Hg^{II} transported was the largest, but < 100% for each experiment, *i.e.* after 12 h for **1** and 24 h for **3**. Competitive transport experiments of **2** were also performed and a selectivity increase for $Hg^{II} : Ag^{I}$ (6.2 : 1) compared to 5.1 : 1 for carrier **1** was observed as a result of lower transport ability for Ag^{I} (Table 2, run 5).

Table 2 Amount of transition-metal ions competitively transported after 12 or 24 h[a]

Run	Carrier (t/h)	Metal ions transported to the receiving phase/mol%[b] (μmol)				
		Hg^{II}	Ag^{I}	Cu^{II}	Pb^{II}	Selectivity
1	**1** (12)	87 (130)	17 (25)	—	—	Hg/Ag = 5.1
2	**1** (12)	98 (147)	—	7 (11)	—	Hg/Cu = 14
3	**1** (12)	86 (128)	—	—	1.0 (1.5)	Hg/Pb = 86
4	**1** (12)	—	—	34 (51)	12 (18)	Cu/Pb = 2.8
5	**2** (24)	99 (149)	16 (24)	—	—	Hg/Ag = 6.2
6	**2** (24)	92 (138)	—	—	1.2 (1.9)	Hg/Pb = 77
7[c]	**3** (24)	92 (135)	—	16 (24)	—	Hg/Cu = 5.8

[a] Initial transport conditions (25 °C): source phase; 10 mmol dm^{-3} metal acetate AcONa–AcOH buffered solution, pH *ca.* 6.0–6.4, 15 ml. liquid membrane; 0.15 mmol of imide acid in 30 ml of chloroform. Receiving phase; 0.1 mol dm^{-3} HNO_3, 15 ml. Each phase was mechanically stirred at 200 rpm. [b] mol% as in Table 1. [c] Initial conditions are the same except that 0.30 mmol carrier **3** is used.[4]

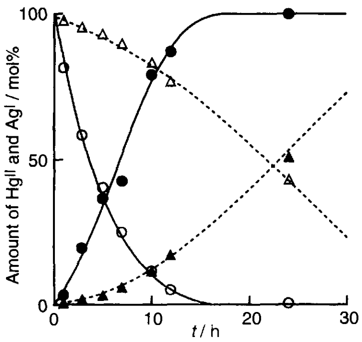

Fig. 1 Time dependence of the amount of Hg^{II} (○,●) and Ag^{I} (△, ▲) in the source (○,△) and receiving (●, ▲) phases of the dual ion competitive transport

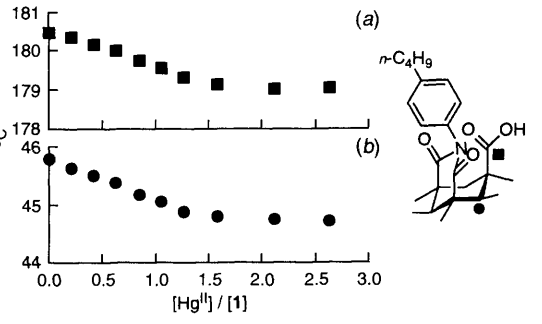

Fig. 2 Hg^{II}-induced chemical shift changes in ^{13}C NMR spectra of Kemp's acid imide **1** (5.04 × 10^{-2} mmol with the same amount of NEt_3 in 450 μl of CD_3CN and 50 ml of $CDCl_3$ containing 0.03% $SiMe_4$ as an internal standard)

To obtain information about the complexation species with a divalent metal ion, ^1H and ^{13}C NMR titration experiments were performed with the combination of a 1 : 1 mixture of **1** and NEt_3, and various amounts of $HgCl_2$ (Varian Gemini 300BB). Hg^{II} was chosen because of its high affinity for the ligand, as expected from the transport data. Fig. 2(*a*) and (*b*) show that both signals move upfield with increasing concentration of $HgCl_2$ and reach the equilibrium asymptote at $[Hg^{II}]/\mathbf{1}$ *ca.* 1.3–1.5. This suggests a complexation ratio of metal : ligand of between 1 : 1 and 2 : 1. These ratios indicate several possible complexes such as 1 : 1 (or 2 : 2), 3 : 2 or 2 : 1 (or 4 : 2) species considering the structures of **1**. The results of ^1H NMR measurements also show similar results for the equatorial protons of a cyclohexane ring. During the NMR titration experiments precipitation of $HgCl_2$ was observed above a metal : ligand ratio of 0.6 : 1. These results meant that complete complexation was impossible even below a ratio of 1.0 : 1. Therefore the 1 : 1 (2 : 2) complex of **1** and Hg^{II} was the major species in the homogeneous acetonitrile solution.

Even though 1 : 1 (2 : 2) complexation was expected in the homogeneous organic solution in the presence of organic base, the form of metal ion species in the organic phase, as a penetrant species, was not clear under the transport experiment conditions. In order to accumulate further information, the aqueous receiving phase was analysed for run 7 in Table 1 by ion chromatography (Dionex 4540i). It was obvious that substantial amounts of acetate ion existed in the receiving phase, which rationalizes that the original counter anion was simultaneously transported with the metal ions. Our data suggests the major transport mechanism involved divalent metal ion chelated and transported by imide acid in a 1 : 1 ratio composition accompanied by one non-ligand counter anion. This form is supported by the X-ray analysis data recently reported[15] for a bis(Kemp's acid imide)–magnesium (2 : 2) complex containing a coordinated nitrate anion.

Footnotes

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