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TWEEZER LIGANDS FOR pH REGULATED SELECTIVE METAL ION TRANSPORT

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Abstract—Tweezer ligands derived from the condensation of 2-hydroxy-5-methyl benzene-1,3-dicarbaldehyde (**1**) or 2,9-diformyl-1,10-phenanthroline (**2**) with *o*-amino benzoic acid were used for the transport of metal ions across liquid membranes. Ligand **1** showed high selectivity for Cu^{2+} ion and transport was completed over a period of 24 h at a pH value of 1.00. Ligand **2** exhibited selective transport of Pb^{2+} ion which was completed over a period of 96 h at a pH value of 4.5.

A number of synthetic macrocyclic polyethers and acyclic carriers have been used for the specific transport of alkali and alkaline earth cations.[1–4] Cation specificity of carriers has been utilized for the removal of toxic and heavy metal ions from effluents and in waste water treatment.[5–7] Often cation transport is facilitated by counter gradient of pH or metal ion concentration or in the presence of a counter gradient of ammonium ions.[8,9] Recently, it has been shown that Schiff base ligands derived from the condensation of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde with substituted anilines are also good carriers for the specific "uphill" transport of copper(II) ions through liquid membranes.[10]

We report here the results of our investigation on the transport of copper(II), cadmium(II) and lead(II) ions by tweezer type ligands. By varying the pH of the receiving phase and increasing the number of coordination sites, cation selectivity changes considerably.

EXPERIMENTAL

2-Hydroxy-5-methyl benzene-1,3-dicarbaldehyde was prepared by a procedure reported earlier.[11] Tweezer ligand **1** was obtained by the reaction of 2 mM of the dialdehyde in dry acetonitrile (30 cm^3) and 4 mM of *o*-aminobenzoic acid in dry acetonitrile (30 cm^3) under reflux for 6 h. The resulting crude product was recrystallized from chloroform to give pink crystals. IR (C=N 1614 cm^{-1}, C=O 1697 cm^{-1}); ^1H NMR (200 MHz; $CDCl_3$) $\delta = 8.3$ (s, 2H, N=CH). Found; C, 68.1; H, 4.3; N, 6.3. Calc.; C, 68.6; H, 4.5; N, 6.9%.

2,9-Diformyl-1,10-phenanthroline was prepared from 2,9-dimethyl-1,10-phenanthroline by SeO_2 oxidation.[12] Ligand **2** was prepared from 2,9-diformyl-1,10-phenanthroline under similar reaction conditions as described for ligand 1. IR (C=N 1620 cm^{-1}, C=O 1697 cm^{-1}); ^1H NMR (200 MHz; $CDCl_3$) $\delta = 8.4$ (s, 2H, N=CH). Found; C, 70.0; H, 3.6; N, 11.5; Calc.; C, 70.8, H, 3.8, N, 11.8%.

Complexes **3** and **4** were prepared by stirring Schiff base **1** or **2** (1 mM) in dichloromethane (20 cm^3) with $Cu(NO_3)_2 \cdot 3H_2O$ (2 mM) or $Pb(NO_3)_2$ (1 mM) in water (10 cm^3) for 3 h. The dichloromethane layer was separated and the complex was obtained by evaporation of dichloromethane; recrystallized from methanol. Complex **3**; Found; C, 47.6; H, 2.3; N, 6.7; Calc.; C, 47.0; H, 2.5; N, 7.1%. Complex **4**, Found; C, 49.3; H, 2.1; N, 8.2; Calc; C, 49.4; H, 2.4; N, 8.2%.

Physical measurements

The electronic spectral measurements were carried out on a JASCO model 7800 UV–vis spectrophotometer. IR spectra were recorded on a

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JASCO FT/IR-5300 spectrophotometer in KBr pellets. The ^{1}H NMR spectrum was recorded with a Bruker MSL-500 NMR spectrometer. Differential pulse stripping voltammetric measurements were done on a Cypress system model CS-1090/model CS-1087 computer controlled electroanalytical system.

Transport experiments were carried out at 25°C in U-shaped glass cells of 10 mm diameter, 50 mm height, with base width of 30 mm as described earlier.[11] At regular intervals of time, 1 cm^3 sample of the aqueous phase (II) was withdrawn and the metal ion concentration was determined by differential pulse stripping voltammetric technique. Anodic stripping voltammetric experiments were conducted using 1 cm^3 of KCl (0.1 M) solution in presence of 0.3 cm^3 solution of $HgCl_2$ (5×10^{-2} M) using glassy carbon working electrode, Ag/Ag^+ reference electrode and Pt wire auxilliary electrode. Unknown metal ion concentrations were determined by the comparison of current (i_p) values with that of the standard samples. The Cu^{2+} ion concentration was also checked by spectrophotometric technique using the carbamate method,[13] the deviation being ~2% in Cu^{2+} ion concentration.

RESULTS AND DISCUSSION

Schiff base ligands **1** and **2** and their complexes were prepared as described in the experimental section and these were characterized by CHN analytical, IR and ^{1}H NMR data. Based on these data, structures of these molecules are proposed as shown in Fig. 1. The arrangement of phases for transport experiments is shown in Fig. 2. Anodic stripping voltammetric measurement of rate of increase of Cu^{2+} ions in single experiment mediated by carrier molecule **1** is shown in Fig. 3 for the nitrate anion and in Fig. 4 for the perchlorate anion. After 24 h, 91% Cu^{2+} was transported to the aqueous phase (II) when $Cu(NO_3) \cdot 3H_2O$ was used in the source phase. With perchlorates, the rate of transport of Cu^{2+} was only 68% after 72 h. The decreased transport for perchlorate salts is in accordance with the known results which have shown variation in transport by several orders of magnitude by altering the anion present in the original salt solution. The time dependent rate of increase in Cu^{2+} content in the aqueous phase (II) and the transport velocity are tabulated in Table 1 for nitrate and perchlorate salts. It also should be mentioned that transport is

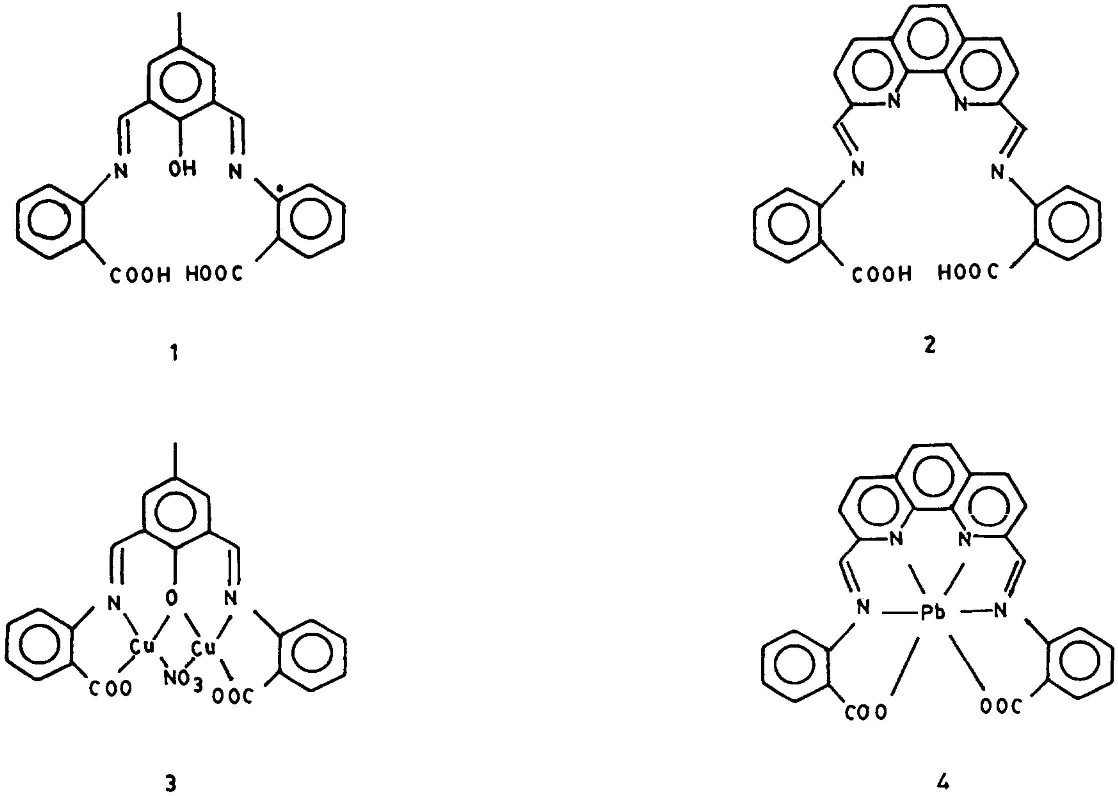
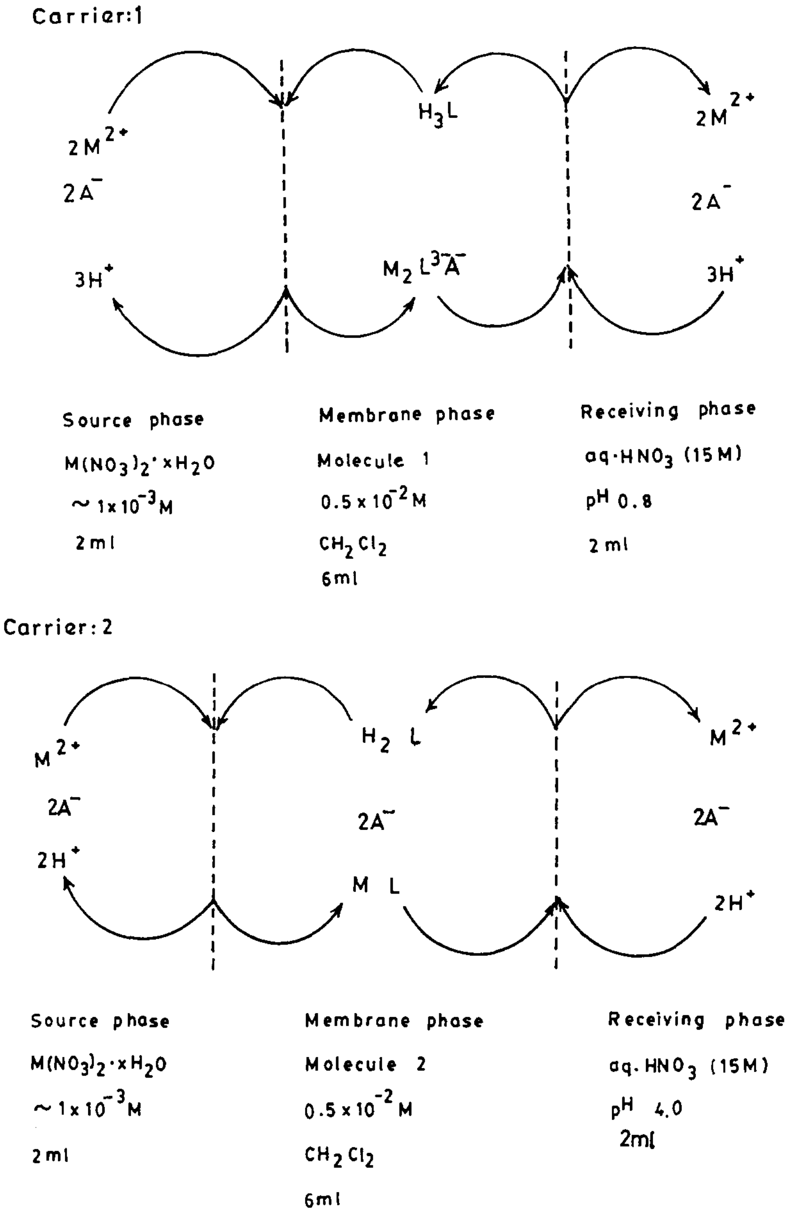


Fig. 1. Proposed structures of carrier molecules **1** and **2** and their Cu^{2+} and Pb^{2+} complexes formed in the membrane phase.



Carrier:1

Source phase	Membrane phase	Receiving phase
M(NO$_3$)$_2$·xH$_2$O	Molecule 1	aq·HNO$_3$ (15M)
~ 1x10^{-3}M	0.5x10^{-2}M	pH 0.8
2ml	CH$_2$Cl$_2$	2ml
	6ml	

Carrier:2

Source phase	Membrane phase	Receiving phase
M(NO$_3$)$_2$·xH$_2$O	Molecule 2	aq. HNO$_3$ (15M)
~ 1x10^{-3}M	0.5x10^{-2}M	pH 4.0
2ml	CH$_2$Cl$_2$	2ml
	6ml	

Fig. 2. Arrangement of phases and proposed proton coupled carrier mediated transport mechanism for molecules **1** and **2**.

observed at an optimum pH value of 1.0 in the aqueous phase (II). In the absence of carrier molecules **1** and **2**, no transport was observed. Precipitation of ligands at the interface of membrane and receiving phases was not observed under the experimental pH conditions. When conc. HNO$_3$ (15 M) was used without dilution transport was not observed.

Competitive transport of Cu^{2+} ions in the presence of Cd^{2+} and Pb^{2+} nitrates was also examined and the results are shown in Fig. 5. The Cu^{2+} was found to be transported selectively to the extent of 77% after 24 h, followed by Pb^{2+} at 11% with no transport of Cd^{2+}. Thus the Cu^{2+}/Pb^{2+} selectivity in single experiments is calculated to be 7.6 and Cu^{2+}/Cd^{2+} selectivity to be nearly 100. In competitive experiments also, the values were the same as observed in single experiments. At higher pH values of around 4.5 or 7.0 Cu^{2+} ion transport decreased to about 6.5% but Pb^{2+} transport increased to about 51%. The transport rate of Cu^{2+} at pH 1.00 was found to be 5.00 x 10^{-4} mol h^{-1} and that of Pb^{2+} was 4.68 x 10^{-5} mol h^{-1}. These results suggest a proton coupled mechanism for the transport and are shown in Fig. 2. In this, the carrier molecule **1** which can be written as H$_3$L, incorporates two copper ions releasing three protons into the source phase (SP). The complex diffuses to the

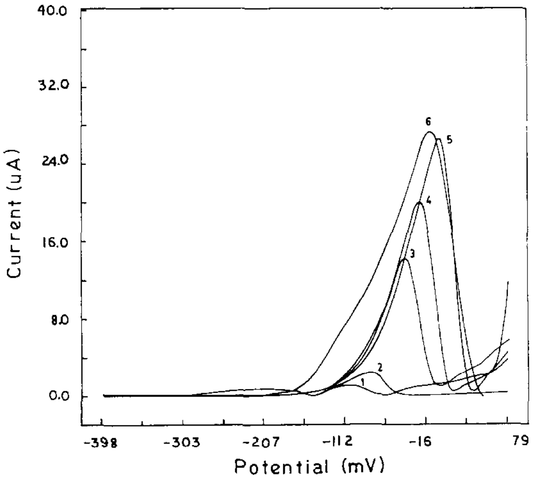


Fig. 3. Rate of transport of Cu^{2+} ions in single experiments mediated by carrier molecule **1** (nitrate as the counter ion). 1: RP after 2 h; 2: RP after 4 h; 3: RP after 18 h; 4: RP after 20 h; 5: RP after 24 h; 6: SP before transport.

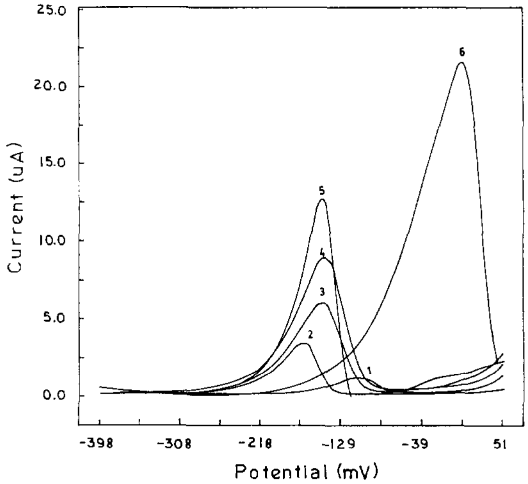


Fig. 4. Rate of transport of Cu^{2+} ions in single experiments mediated by carrier molecule **1** (perchlorate as the counter ion). 1: RP at 0 h; 2: RP after 6 h; 3: RP after 24 h: 4: RP after 36 h; 5: RP after 72 h; 6: SP before transport.

receiving phase (RP) where on deprotonation of the carrier molecule releases Cu^{2+} ion into the acidic aqueous phase. On the whole, Cu^{2+} ions move from SP to RP, and H^+ ions move in the opposite direction in a 2:3 molar ratio, the Schiff base operating as a shuttle. From the experimental data it appears that the transport of Pb^{2+} is kinetically controlled and the transport of Cd^{2+} is thermodynamically controlled. Selective transport of Cu^{2+} was found in competitive systems when carrier molecule **1** was used. This selectivity can be controlled by proper adjustment of aqueous phase (II) pH values.

To characterize the type of Cu^{2+} complex involved in the transport of metal ions, this was isolated from the membrane phase. This is shown to be dinuclear in nature with a bridging nitrate group and the structure is supported by CHN analytical data, IR and conductance data. IR spectra showed a sharp peak around 1529 cm^{-1} of N=O stretching and bands at 1238 and 1070 cm^{-1} all characteristic of a bridging nitrate group.[14] The very low conductance value, namely 30 mho cm^2 mol^{-1}, of this complex shows its nonelectrolytic nature. The room temperature μ_{eff} value per copper atom for this complex is 1.62 BM, slightly lower than that normally observed for mononuclear copper complexes. Room temperature ESR shows a four-line pattern in methanol indicating the absence of

Table 1. Time dependent transport of Cu^{2+} ions across the dichloromethane membrane for nitrate and perchlorate anions

Nitrate			Perchlorate		
Time (h)	%Cu in aq. phase(II)	v^a (10^{-4} mol h^{-1})	Time (h)	%Cu in aq. phase(II)	v (10^{-4} mol h^{-1})
2	0.87	2.05			
4	8.62	2.75			
			6	17.71	2.65
18	48.34	3.55			
20	69.28	4.60			
24	90.66	5.00	24	30.71	1.15
			36	45.57	1.14
48	95.76	0.73			
			72	68.17	0.85

[a] v = Transport velocity.

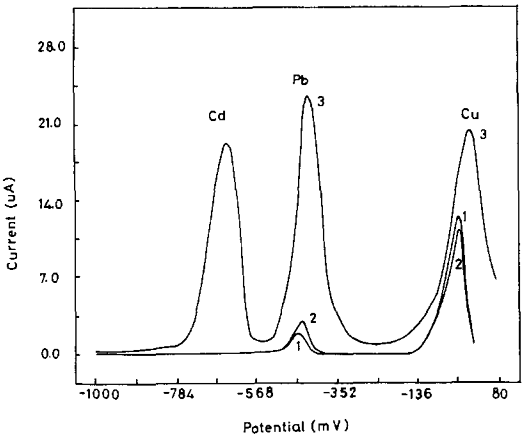


Fig. 5. Competitive transport of Cu^{2+} ions by carrier molecule **1** in presence of Cd^{2+} and Pb^{2+} nitrates. 1 : RP after 24 h ; 2 : RP after 48 h ; 3 : SP before transport.

any significant antiferromagnetic interaction between the two copper centres. The proposed structure of the dicopper complex is shown in Fig. 1.

Table 2. Comparison of single competitive Cu^{2+} and Pb^{2+} transport rates in liquid membrane systems containing carriers **1** and **2**

Single					
System	Carrier	pH (RP)	Time (h)	v^a (10^{-7}mol s^{-1})	% $(M^{2+})^b$
Cu^{2+}	1	0.8	24	1.38	91
	2	4.5	96	0.03	9
Pb^{2+}	1	0.8	24	0.15	12
	2	4.5	96	0.26	83
Competitive					
System	Carrier	pH (RP)	Time (h)	v^a (10^{-8}mol s^{-1})	% $(M^{2+})^b$
Cu^{2+}	1	0.8	24	2.83	77
	2	4.5	96	0.08	11
Pb^{2+}	1	0.8	24	0.33	9
	2	4.5	96	0.6	78

[a] Transport velocity.

[b] Percentage of metal ion in the receiving phase (determined by differential pulse stripping voltammetric technique).

Schiff base system **2**, analogous to molecule **1**, was found to decompose at low pH values in the aqueous phase (II), but at higher pH values namely 4.5, selective transport of Pb^{2+} was observed. The transport of Pb^{2+} found to be complete after 96 h. Aqueous phase (II) contained 83% Pb^{2+} in single experiments and 78% in competitive experiments after 96 h. Pb^{2+}/Cu^{2+} selectivity under the present set of conditions was 9.2 and Pb^{2+}/Cd^{2+} selectivity was nearly 100 in single experiments. In competitive experiments, Pb^{2+}/Cu^{2+} selectivity was 8.6 and Pb^{2+}/Cd^{2+} was 100. Cu^{2+} and Pb^{2+} contents in the receiving phase at the end of transport experiments in single and competitive systems by the two types of carriers are presented in the Table 2. The decreased value of transport flux of Pb^{2+} by carrier **2** may be correlated with the stability of the complex formed in the membrane phase and the rate of diffusion of the complex. Transport of Pb^{2+} ions by the carrier molecule **2** to the weakly acidic receiving phase suggests a proton coupled mechanism similar to the one suggested for carrier molecule **1**, and is shown in Fig. 2. The metal complex involved in the transport of Pb^{2+} ions by carrier molecule **2** was isolated from the membrane phase and characterized by CHN analytical and IR data. The complex was found to be mononuclear and the proposed structure is shown in Fig. 1.

These results demonstrate that the tweezer ligand **1** is a good carrier for the selective transport of Cu^{2+} ions and ligand **2** for Pb^{2+} ions. The selectivity can be controlled by proper adjustment of pH values between the source and receiving phases.

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