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Specific Transport of Copper(II) Ions Across Liquid Membrane by Schiff Base Ligands

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Synopsis. Schiff base ligands derived from the condensation of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde with substituted anilines are found to be excellent carriers for the specific transport of copper(II) ions through a liquid membrane.

Crowns, azacrowns, and a number of acyclic carriers have been found to be very efficient for the specific transport of alkali and alkaline earth cations.[1,2] Macrocycles containing phenolic groups, armed macrocycles and polyaza macrocycles that form neutral 1 : 1 complexes with transition metal ions show good transport activity for the aforesaid metal ions.[3—5] Recently proton ionizable acyclic diamides like substituted glutaramides and tetradentate hydroxamate have been reported to exhibit highly selective and uphill transport of heavy metal ions.[6,7] Anionic transport has also been made possible using protonated sapphyrin and vitamin B_{12} derivatives as carriers.[8—10] Systems with bipyridine and azacrowns need supporting groups as backbones to be hydrophobic to act as efficient carriers.[11—13]

Naturally occurring biological ionophores, synthetic carriers like macrocycles, crowns and azacrowns involve difficult synthetic procedures. Schiff base ligands can be more easily synthesised than these ligands and some of these show high selectivity for Cu^{2+} transport.

Here we wish to report the cation binding and specific uphill transport properties of a few Schiff base ligands obtained from the condensation of a bidentate ligand 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde with substituted anilines.

Experimental

General. The electronic spectral measurements were carried out on a JASCO model 7800 UV-vis spectrophotometer. Metal estimations were carried out using an inductively coupled plasma spectrometer (ICP), Labtem, Australia. The proton NMR spectra were recorded with a Bruker MSL-500 NMR spectrometer. Analytical grade $CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$ were used for the preparation of complexes. 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde was prepared by a procedure reported elsewhere.[14] Aniline, *o*-anisidine, and *o*-toluidine were redistilled under vacuum prior to use. All the solvents were of extra pure grade and were used without any further purification.

Preparation of Schiff Base Carriers. The Schiff base ligands L^1, L^2, and L^3 were obtained by the condensation of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and respective substituted anilines. In a typical experiment, 0.328 g (2 mM, M=mol dm^{-3}) of the dialdehyde was dissolved in methanol (50 cm^3) and a methanolic solution of amine (9 mM) was added and solution was refluxed for 6—8 h. The resulting crude products were recrystallised from methanol to give orange-red needles.

Data for Ligand L^1: Mp (99—100 °C); IR (C=N 1640 cm^{-1}, O–H 3200 cm^{-1}); ^{1}H NMR (200 MHz, $CDCl_3$) δ=2.5 (s, 3H), 7.7 (s, 2H), 8.7 (s, 2H), 6.8 (m, 10H). CHN analysis. Found: C, 79.82; H, 5.80; N, 8.92%. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.90%.

Ligand L^2: Mp (119—120 °C); IR (C=N 1640 cm^{-1}, O–H 3200 cm^{-1}); ^{1}H NMR (200 MHz, $CDCl_3$) δ=2.5 (s, 3H), 7.7 (s, 2H), 8.7 (s, 2H), 2.1 (s, 6H), 6.75 (d, 2H), 7.0 (t, 4H), 7.25 (d, 2H). CHN analysis. Found: C, 81.00; H, 6.49; N, 8.02%. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.47; N, 8.18%.

Ligand L^3: Mp (107—108 °C); IR (C=N 1640 cm^{-1}, O–H 3200); ^{1}H NMR (200 MHz, $CDCl_3$) δ=2.5 (s, 3H), 7.85 (s, 2H), 8.7 (s, 2H), 3.8 (s, 6H), 6.75 (d, 2H), 7.0 (t, 4H), 7.25 (d, 2H). CHN analysis. Found: C, 73.55; H, 5.69; N, 7.42%. Calcd for $C_{23}H_{22}N_2O_3$: C, 73.79; H, 5.88; N, 7.48%.

Preparation of $M(L^n)_2$ Complexes (n=1,2,3). To an acetone solution of the ligand L^1 (0.628 g; 2 mM), an aqueous solution of cupric chloride dihydrate (0.170 g; 1 mM) was added and stirred for 2 h. The resulting dark brown solids were filtered, washed with water and recrystallised from chloroform. A similar procedure was adopted for the preparations with ligands L^2 and L^3. (CHN analysis: $M(L^1)_2$: Found: C, 70.50; H, 4.62; N, 7.76%. Calcd for $C_{42}H_{34}N_4O_2Cu\cdot H_2O$: C, 71.23; H, 4.80 ; N, 7.91%.

Metal Ion Transport. The transport experiments were carried out at 25 °C in a U-shaped glass cell of 10 mm diameter, 50 mm height and the base width being 30 mm. It has been observed that with a cell of larger size with larger volume of membrane phase, transport of Cu^{2+} ions was not so efficient as the present setup. The cells (Fig. 1b) consisted of a 6.0 ml membrane phase interface to 2.0 ml source phase (aq phase I) and 2.0 ml receiving phase (aq phase II). The aq phase I consisted of analytical grade $CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$, membrane phase of reagent grade dichloromethane and the aq phase II of aqueous HCl solution of pH 1.00. All the experiments were performed in specially made thermostated flasks at 27 °C. Blank experiments were carried out to determine the membrane phase leakage. After a period of 24 h a 1 mL sample of the aqueous phase II was withdrawn and the metal ion concentration was determined by spectrophotometry using carbamate method[15] and by inductively coupled plasma spectrophotometric techniques.

Results and Discussion

The complexing abilities of the closely related ligands have been studied[16] and the complexes are shown to be essentially mononuclear at higher carrier concentra-

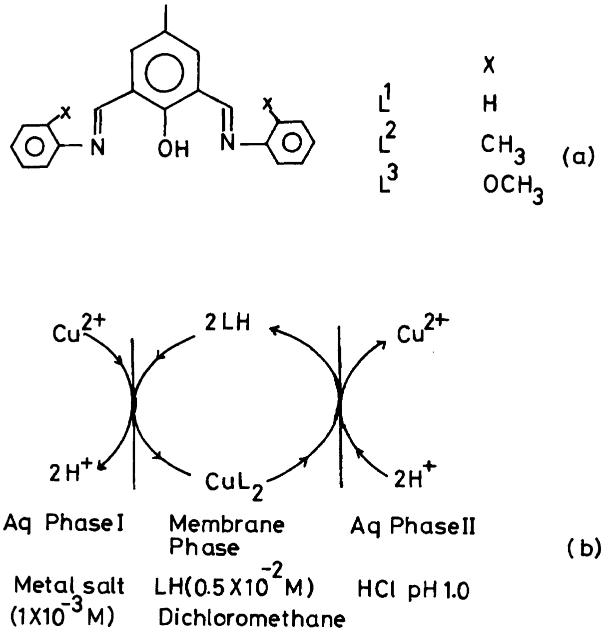

Fig. 1. Structure of the ligands. (b) Model cell for the transport of d-metal ions across an organic membrane.

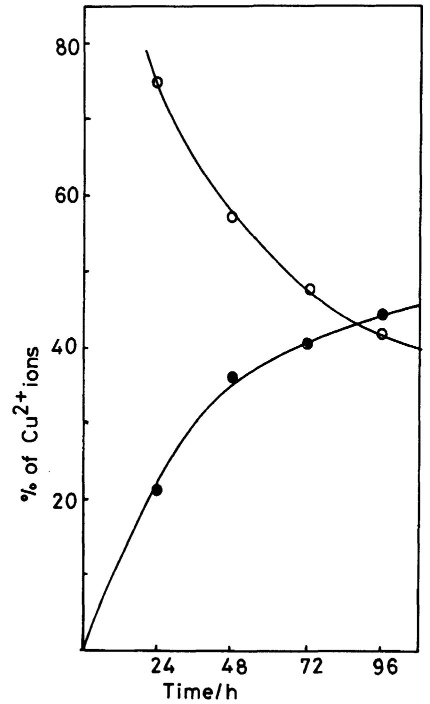

Fig. 2. Amount of Cu^{2+} ions in Aq I and Aq II as function of time for the transport with L^1. ○ shows amount of Cu^{2+} ions in Aq I and ● in Aq. II.

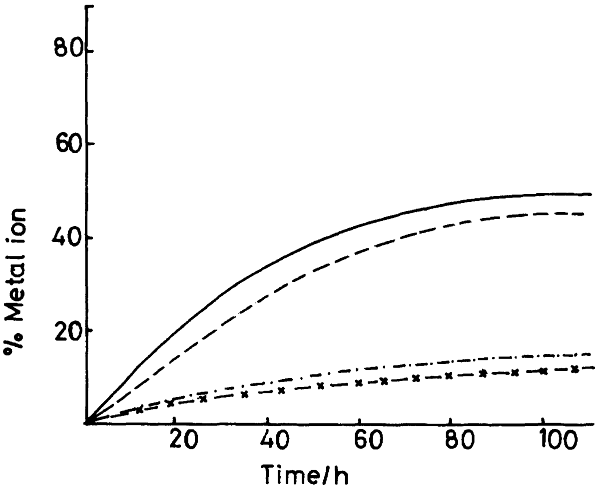

Fig. 3. Rate of transport of metal ions across liquid membrane with L^3. Cu^{2+} (—); Ni^{2+} (-x-x-); Co^{2+} (-•-) and Cu^{2+} in mixture (---).

tions. Electrochemical reduction of the copper(II) complexes indicates the stabilization of Cu(I) species by the carrier ligands under study. Complexes formed in the membrane phase have 1 : 2 metal to ligand composition. The metal moves from the aq phase I to dichloromethane membrane which contains the Schiff base carrier, forming a stable neutral complex of 1 : 2 metal to ligand composition. This neutral complex moves towards the interface of membrane and aq phase II and the availability of protons in the aqueous phase II effects the release of free metal ion into the aqueous phase II by protonation of the Schiff base carrier. As a consequence, the proton abundance in aqueous phase I increases and that in aqueous phase II decreases. This is confirmed by measuring pH of both source and receiving phases intermittantly. A typical experiment with the ligand L^1 is illustrated in Fig. 2, wherein the concentration of the Cu^{2+} in aqueous phase II increased proportionally with time. Transport was complete after 96 h; maximum transport attained being 49% for Cu^{2+}. Lower transport rate ca. 10% for Ni^{2+}, Co^{2+} after 96 h shows that the complexes of Ni^{2+} and Co^{2+} are more stable than the corresponding Cu^{2+} complexes thereby not decomplexed into the receiving phase. Figure 3 shows the rates of transport of Cu^{2+}, Ni^{2+}, and Co^{2+} ions. Transport experiment with a mixture of 1 mM each of Cu^{2+}, Ni^{2+}, and Co^{2+} in the aq phase I was done. ICP analysis of the aq phase II intermittantly showed increase in the concentration of Cu^{2+} whereas no transport of Ni^{2+} and Co^{2+} ions was observed during the same period. In a mixture, Cu^{2+} ion competes in complexation with the described carrier ligand over Ni^{2+} and Co^{2+} ions. Moreover lower stability of Cu^{2+} complex helps the decomplexation at the inter phase of membrane and aq phase II. The amount of Cu^{2+} transported from the mixture is 45% whereas that for Ni^{2+} and Co^{2+} being nil. This shows that the present set of ligands are very specific in the extraction of Cu^{2+} from a mixture. Blank experiments were carried out for each aq phase I salt solutions to determine the cation leakage. It was found to be less than 3×10^{-5} m/24 h.

The percentages of Cu^{2+} ions transported during the experiments measured by carbamate method are listed in Table 1. Table 2 gives the percentages of Cu^{2+}, Ni^{2+}, and Co^{2+} ions transported individually and in a mixture with ligand L^3 as the carrier. Metal ions were estimated after 96 h by ICP technique. No precipitation of copper (II) hydroxide was observed in the receiving phase. The Schiff base in the membrane is not decomposed, confirmed by isolation of ligand intact from the membrane phase after 96 h using blank aq phase I. Once the equilibrium has been attained between the two aqueous phases, no further transport is observed even with increased time ca., after 96 h. From Table 1, it is clear that substitution on the phenyl azomethine ring of the ligands L^1—L^3 showed marginal effect on the rate of transport of the metal ions. Experiments with a conventional ligand viz., 2-hydroxy-5-methylbenzene -1,3-dicarbaldehyde showed transport rate less than ca. 8% even after 96 h. These experiments demonstrate that the present set of Schiff base ligands are excellent carriers for the selective transport of Cu^{2+} through liquid membranes from a mixture of Cu^{2+}, Ni^{2+}, and Co^{2+} ions.

Table 1. Time Dependent Transport of Copper(II) Ions across the Membrane[a)]

Ligand	Time	% of Cu in		
	h	Aq I	Aq II	Organic phase
L^1	24	75	21	4
	48	57	36	7
	72	48	40	12
	96	42	44	14
L^2	24	72	22	6
	48	55	39	6
	72	47	43	10
	96	41	48	11
L^3	24	70	23	7
	48	54	38	8
	72	44	46	10
	96	39	49	12

a) Initial conditions: Aq I aqueous solution (pH 7.0) containing metal ion 1×10^{-3} M; Aq II HCl acid aqueous solution of pH 1.0 and organic phase dichloro methane solution containing Schiff base ligand 0.5×10^{-2} M; reproducibility is within 2%.

Table 2. Transport of Metal Ions by the Ligand L^3 after 96 h[a)]

Metal ion(s)	% of Metal ion(s) in		
	Aq I	Aq II	Organic phase
Cu	39	49	12
Ni	67	10	23
Co	80	12	8
Mixture			
Cu	24	45	31
Ni	95	0	5
Co	98	0	2

a) Initial conditions: same as given for Table 1.

It is to be noted that in the absence of HCl in the receiving phase no transport was observed. When the aq HCl in phase II was replaced by a buffer solution of pH 3.0—4.0 or when the pH was increased from 1.00—6.00 the transport rate decreased drastically the value being less than 5% for Cu^{2+}. So, transport by the present set of carriers is pH driven and occurs when a pH gradient is applied between the two aq phases. The fact that the transport of Cu^{2+} ion has taken place with the counter flow of protons from aqueous phase II to aqueous phase I is confirmed by the decrease in the pH value of the aqueous phase I. The counter flow of the protons is expected because of the presence of labile protons in the carrier.

These results demonstrate that the present set of bidentate Schiff base ligands are lipophilic in nature and good carriers for the selective transport of copper(II) ions through liquid membranes.

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