The Specific and Uphill Transport of Copper(II) Ions by a 6,6′-Diamino-2,2′-bipyridine Derivative

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6-Amino-6′-dodecylamino-2,2′-bipyridine is an excellent synthetic carrier for the specific transport of Cu^{II} ions through a liquid membrane, and has the ability to transport Cu^{II} ions uphill when a proton gradient is available.

The specific transport of a metal ion through a membrane is widely known to play an essential role in biological processes.[1] Many artificial ligands, especially crown ethers, have been shown to mimic the function of natural carriers in transporting alkali metal ions or organic ammonium cations.[2] However, only a few synthetic carriers have been reported for the transport of transition or heavy metal ions.[3] We have found that the complexing abilities of 6,6′-diamino-2,2′-bipyridine (DABP) are sensitive to the pH of the solution and that DABP binds strongly to Cu^{II} ions.[4] Here, we report that a lipophilic derivative of DABP, 6-amino-6′-dodecylamino-2,2′-bipyridine (ADBP) is an excellent carrier for the specific and uphill transport of Cu^{II} ions through a liquid membrane.

DABP was allowed to react with a large excess of n-dodecyl bromide in dioxane for 10 h in the presence of sodium hydroxide and a catalytic amount of tetra-n-butylammonium bromide. Pure ADBP was obtained after chromatographic separation (yield 66%),[†] and it was found to be soluble in organic solvents but not in water or hydrochloric acid.

The transport experiments were carried out at 20 °C in a cylindrical glass cell,[‡] where aqueous phase I (Aq.I) and aqueous phase II (Aq.II) were separated by a ADBP–chloroform phase. Metal ions were dissolved initially in Aq. I. The changes in the amounts of metal ions in Aq.I and Aq.II were followed by atomic absorption spectrophotometry.

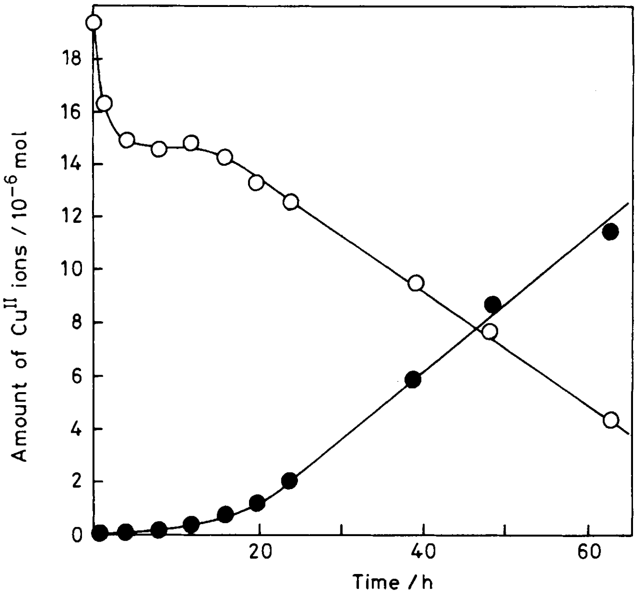

Figure 1. A plot of Cu^{II} ion transport by ADBP *vs.* time. ○ shows amount of Cu^{II} ions in Aq.I and ● in Aq.II. Initial conditions: Aq.I ammonium acetate buffer (pH 7.0) with Cu^{II} (1.9×10^{-5} mol); Aq.II HCl–KCl buffer (pH 1.0); and organic phase $CHCl_3$ containing ADBP (5.0×10^{-6} mol).

It was found that Cu^{II} ions were transported from Aq.I to Aq.II through the chloroform phase, mediated by ADBP complex formation, when Aq.I was neutral and Aq. II acidic.

[†] M.p. 72—74 °C; a satisfactory elemental analysis was obtained; M^+ 354.2693, $C_{22}H_{34}N_4$ requires 354.2786; ^{1}H n.m.r. δ (100 MHz, $CDCl_3$, Me_3Si) 7.63—7.52 (4H, m, 3,3′ and 4,4′-H pyridine), 6.55—6.41 (2H, m, 5,5′-H pyridine), 4.54 (3H, br. s, NH and NH_2), 3.34 (2H, t, N-CH_2-), 1.22 (20H, s, -CH_2-), and 0.84 (3H, t, Me).

[‡] A cylindrical glass cell of 4 cm diameter and 6 cm height was divided into two vertical parts by a glass plate except for the bottom portion (1 cm). Thus, the two aqueous phases were separated from each other by the glass plate and the chloroform layer was placed at the bottom. Initial conditions: Aq.I 10 cm³ of 0.2 mol dm⁻³ ammonium acetate buffer (pH 7.0) containing 1×10^{-6} mol of $CuCl_2$, $NiCl_2$, and/or $CoCl_2$; Aq.II 10 cm³ of 0.1 M HCl–KCl buffer (pH 1.0) without metal ion; and organic phase 25 cm³ of $CHCl_3$ containing ADBP (2.5×10^{-7}—1×10^{-6} mol). The cell was thermostated at 20 °C.

Table 1. Distribution of the metal ions after 20 h at 20 °C [relative to the initial amount of metal ions present (%)].[a]

	Aq.I	Organic phase	Aq.II
Individual			
Cu^{II}	25	21	54
Ni^{II}	95	3	2
Co^{II}	89	7	4
Mixture			
Cu^{II}	27	20	53
Ni^{II}	94	2	4
Co^{II}	95	3	2

[a] Initial conditions: Aq.I ammonium acetate buffer (pH 7.0) solution containing a metal ion (1×10^{-6} mol), or a mixture of metal ions (1×10^{-6} mol for each metal); Aq.II pH 1.0 buffer solution; and organic phase $CHCl_3$ containing ADBP (2.5×10^{-7} mol).

When Aq.I and Aq.II were at the same pH or in the absence of ADBP, only a trace or no Cu^{II} ions were transported. Figure 1 shows a plot of Cu^{II} ion transport from Aq.I (pH 7.0) to Aq.II (pH 1.0) *vs.* time. After an initial induction period, the amount of Cu^{II} ions travelling from Aq.I to Aq.II was constant (2.3×10^{-7} mol h^{-1}). As shown in Figure 1, transport of Cu^{II} ions continued even when the Cu^{II} ion concentration in Aq.I became lower than that in Aq.II. Thus, ADBP is shown to transport Cu^{II} ions uphill when a proton gradient is available. Since protons were found to be transported by ADBP from acidic Aq.II to neutral Aq.I in the absence of metal ions, it is possible that the uphill transport of Cu^{II} ions by ADBP against its reverse concentration gradient is coupled with a counterflow of protons from Aq.II to Aq.I. In addition, it is worth noting that the amount of Cu^{II} ions transported from Aq.I to Aq.II was more than the amount of ADBP in the organic phase, indicating that ADBP acts as a mediator.

The transport of Ni^{II} and Co^{II} ions by ADBP was also studied. Table 1 shows the final distribution of metal ions in the two aqueous phases after 20 h. Although a considerable number of Cu^{II} ions were transported from Aq.I to Aq.II, Ni^{II} and Co^{II} ions were not transported under the same conditions. Moreover, Cu^{II} ions were preferentially transported and concentrated into Aq.II from a mixture of these metal ions, demonstrating the high specificity of ADBP for Cu^{II} ions.

These results demonstrate that ADBP has the ability to transport Cu^{II} ions selectively between two aqueous phases in the presence of a proton gradient.

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