A Proton-driven Copper(II) Ion Pump with a Macrocyclic Dioxotetra-amine. A New Type of Carrier for Solvent Extraction of Copper

Eiichi Kimura,* Chairul Azhar Dalimunte, Aiko Yamashita, and Ryosuke Machida

Department of Medicinal Chemistry, Hiroshima University School of Medicine, Kasumi, Minami-ku, Hiroshima 734, Japan

The macrocyclic dioxotetra-amine (2) acts as a carrier for the membrane transport of copper(II) ions against the concentration gradient by the coupled counter-transport of protons and is potentially useful for solvent extraction of copper.

The membrane transport of cations, effected by ionophore antibiotics[1] and synthetic carriers,[2] is well established. Of particular interest is transport coupled to free-energy gradients which drive the flux of cations against the cation concentration gradient. Potential applications of this technology include the separation and concentration of chemical species. While there are a number of ion pumps available for alkali and alkaline earth metals,[3] only a few devices have been developed for heavy and transition metals, which derive the free-energy from either amino acid complexation[4] or redox potential.[5] A liquid membrane system with simultaneous proton counter-transport was developed for selective solvent extraction of Cu^{II} over Ni^{II} and Co^{II} using benzoylacetone as a mobile carrier,[6] but its selectivity has been questioned.[4] Improved solvent extraction reagents are in great demand to produce copper continuously from ores.[7]

We report here the use of a new class of liquid membrane system containing a lipophilic dioxocyclam derivative (2) (see Figure 1) (cyclam = 1,4,8,11-tetra-azacyclotetradecane) to cause selective and efficient transport and extraction of Cu^{II} with simultaneous counter-transport of protons. Our system is similar in character to biological Cu^{II} transport by peptides such as Gly-His-Lys[8] and Asp-Ala-His.[9] The underlying principle is the unique chelating behaviour of the dioxocyclam (1) which was earlier discovered to possess the dual ligand functions of macrocyclic tetra-amine (cyclam) and peptides.[10] That is, it encloses metal ions (like cyclam) with simultaneous deprotonation of the two amides (like peptides) to yield stable

1:1 complexes with only Cu^{II}, Ni^{II}, Co^{II}, or Pd^{II} in neutral to alkaline pH. These complexes, like peptides, undergo immediate dissociation when exposed to strong acid.[11]

The carrier (2) was prepared by refluxing the alkylated malonate and 1,9-diamino-3,7-diazanonane in MeOH (25% yield, m.p. 113 °C from MeOH–benzene). The pK_a values of
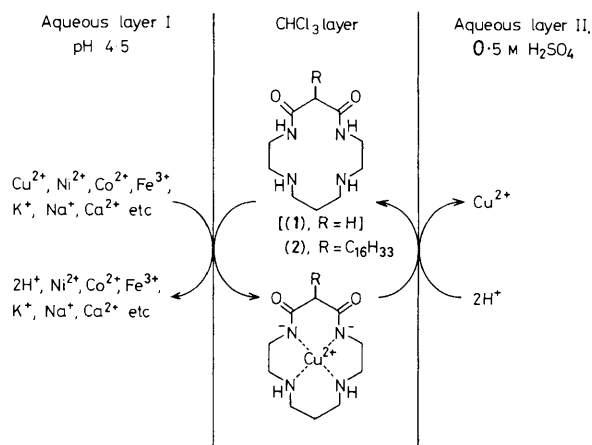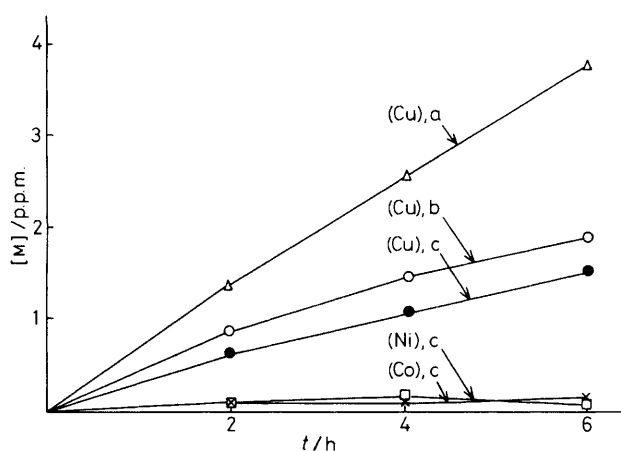

Figure 1. Transport of Cu^{2+} ions through a liquid membrane system mediated by the dioxocyclam carrier (2).

Table 1. Carrier-mediated extraction of metal ions in shakeout tests with a CH_2Cl_2 liquid membrane for 1 h periods in an automatic shaker (325 strokes min^{-1}).

Run	Metal ion	Aqueous layer I Concentration/mM	Initial pH	Concentration of (2) in CH_2Cl_2/mM	Number of CH_2Cl_2 extractions	% Metal remaining in layer I	% Metal extracted into layer II
1	Cu^{2+}	0.1	4.6	0.1	1	98	1
2	Cu^{2+}	0.1	5.7	0.1	1	67	20
3	Cu^{2+}	0.1	5.7	0.5	3	4	93
4	Cu^{2+}	0.1	7.5	0.1	1	17	79
5	Cu^{2+}	0.1	7.5	0.1	3	~ 0	95
6	Cu^{2+}	0.1	7.5	0.1	3	~ 0	94
	Ni^{2+}	0.1				95	2
	Co^{2+}	0.1				98	1
	Fe^{3+}	0.1				100	0
7	Cu^{2+}	0.1	7.5	0.1	3	10	86
	Ni^{2+}	1.0				95	< 5
	Co^{2+}	1.0				95	< 5
8	Cu^{2+}	0.1	8.6	0.1	3	3	96

Figure 2. The concentration of metal ion in aqueous layer II as a function of time. Details of the liquid membrane system are the same as those given in the text unless otherwise stated. The metal ion used (10 mM) in aqueous layer I and the carrier concentration in the liquid membrane were varied: (a) $CuSO_4$, 2mM of (2); (b) $CuSO_4$, 1 mM (2); (c) $CuSO_4$, $NiSO_4$, and $CoSO_4$, initial pH 4.2, 1mM (2).

9.6 and 6.0 for (2) are deduced from those for (1).[10] The transport of Cu^{II} ions across a $CHCl_3$ membrane was studied using a cell similar to that previously reported.[12] The cell consisted of a 20 ml membrane phase ($CHCl_3$ containing 1 mM carrier, stirred at 300 r.p.m. by a magnetic stirrer at 35.0 °C), interfaced to both a 20 ml source phase, aqueous layer I (metal salt solution, unbuffered at initial pH 4.5) and a 5 ml receiving phase, aqueous layer II (0.5 M H_2SO_4 aqueous solution). At certain intervals, a 1 ml sample of the receiving phase was withdrawn and the concentration of metal cations was determined by atomic absorption spectroscopy. Blank experiments (no carrier present) were performed to demonstrate the absence of membrane leakage. The carrier (2) resides in the $CHCl_3$ layer with no sign (by t.l.c.) of decomposition or migration into the aqueous layers. Cu^{II} was effectively and selectively transported from layer I to the acidic layer II of the membrane thereby creating a Cu^{II} ion gradient, as shown by a typical curve (a) (Figure 2) depicting the increasing Cu^{II} concentration in layer II as a function of time. An interesting feature of the data is the transport selectivity for Cu^{II} over Ni^{II}

and Co^{II}, Figure 2, curves c. This selectivity corresponds to the known thermodynamic selectivity of dioxocyclam (1) for Cu^{II}, as reflected in log K (= $[M(H_{-2}L)][H^+]^2/[M][L]$) values measured in water: 1.0 (Cu),[7] −5.5 (Ni),[13] and −11.4 (Co)[14] at 35 °C. The chelation of Cu^{II} by (1) occurs more rapidly than that of Ni^{II} and Co^{II} and this kinetic effect may also contribute to the Cu^{II} selectivity. The slope of curve b is half that of curve a and thus indicates that the rate of Cu^{II} transport is proportional to the carrier concentration in the liquid membrane. The presence of a large excess of alkali metal ions or alkaline earth metal ions does not hinder the Cu^{II} transport at all.

The occurrence of counter-transport of Cu^{II} ions and protons can be shown by measurement of initial (4.50) and final (after 6 h) pH (4.27) values of the aqueous solution I. The observed pH change corresponds to the transfer of ca. 4.4 × 10^{-7} mol of protons from II to I. The Cu^{II} concentration change indicates the transfer of ca. 1.7 × 10^{-7} mol of Cu^{II} from I to II. Thus $2H^+–Cu^{2+}$ counter-transport depicted in Figure 1 has been observed. Under identical conditions the previously reported counter-transport carrier benzoylacetone[4] did not transport Cu^{II} at all.

The high degree of transport selectivity demonstrated by the macrocyclic ligand led us to perform Cu^{II} extraction experiments. In a typical extraction experiment aqueous solution I (30 ml; pH 7.5, unbuffered) containing 0.1 mM of each of the ions Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} was shaken for 1 h by an automatic shaker (325 strokes/min) 1—3 times each with 30 ml of CH_2Cl_2 solution containing 0.1 mM of (2). After careful phase separation, the aqueous solution I was analysed for the metal ion(s) remaining unextracted. The CH_2Cl_2 layer was then shaken for 1 h using the same automatic shaker with 30 ml of 0.05 M H_2SO_4 aqueous solution II. The aqueous solution II was analysed for the metal ions extracted, see Table 1. The sum of the unextracted and extracted metal ions roughly accounts for the total metal ions, which proves rapid transport through the CH_2Cl_2 layer.

It is evident from Table 1 that the copper(II) ion can be selectively and effectively extracted from a mixture of Cu^{II}, Ni^{II}, Co^{II}, Fe^{III} by our transport system. This contrasts with the unselective[4] or Fe^{3+}-poisoned[6] Cu^{II} transport by the benzoylacetone system and with the lower Cu^{II} selectively by the urea system.[4]

The efficiency and selectivity of (2) for Cu^{II} demonstrates the potential use of macrocyclic oxopolyamines in removing,

concentrating, and purifying Cu^{II} or other metallic elements from mixtures.

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