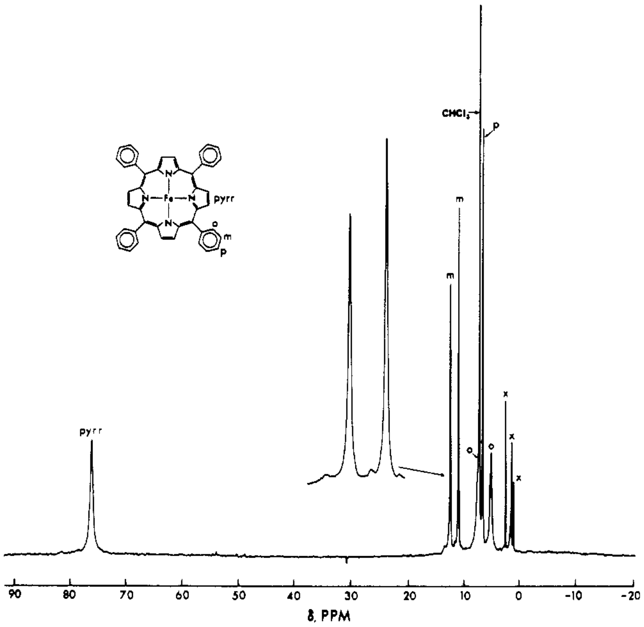

Figure 1. Proton NMR spectrum at 360 MHz of the μ-chromato dimer complex ($CDCl_3$ solvent, 25 °C, referenced to $(CH_3)_4Si$).

0.02. Chromate ion was quantitatively extracted into aqueous sodium hydroxide solution from a CH_2Cl_2 solution of the iron porphyrin complex, and the ion was identified by the UV spectrum. A molecular weight determination (vapor pressure osmometry, toluene solvent; Galbraith Laboratories) revealed a value of 1445 for $(C_{44}H_{28}N_4Fe)_2CrO_4 \cdot 0.71C_7H_{16}$) as compared with the expected value for the unsolvated dimer of 1453. The optical spectrum (CH_2Cl_2 solvent) revealed bands at 380 (shoulder), 415 (Soret), 512, 575, 655, and 687 nm much as is the case for other high-spin iron(III) porphyrin complexes. Infrared spectra (KBr pellet) revealed bands at 473 and 754 cm^{-1} that are distinctive for $[(TPP)Fe]_2CrO_4$ as compared with the μ-oxo dimeric and chloride complexes of the iron(III) porphyrin (proton NMR of the porphyrin complex, which was extracted from the KBr pellet with $CDCl_3$, verified that it was still the μ-chromato dimeric complex). Room-temperature magnetic moments on a per iron basis of 5.9 ± 0.1 and 6.0 ± 0.1 μ_B were measured respectively in the solid state and in $CDCl_3$ solution. Electron spin resonance signals for the dimer were not detected at −180 °C, analogous to the case for $[(TPP)Fe]_2SO_4$.[2,3]

Proton NMR spectroscopy has been of utility for monitoring conversion from the chloro to the chromato complex, and for structural elucidation of the final product. The 360-MHz proton NMR spectrum of $[(TPP)Fe]_2CrO_4$ is shown in Figure 1. A pyrrole proton signal at 74.9 ppm is indicative of a high-spin iron(III) porphyrin configuration and compares closely with the value of 72.9 ppm ($CDCl_3$) for the analogous sulfato dimeric complex.[2,3] The chemical shift pattern shows no evidence for partial iron(III) porphyrin oxidation by the chromate ligand. The ortho and meta phenyl signals of $[(TPP)Fe]_2CrO_4$ are split as a consequence of an out-of-plane iron atom and orthogonality of phenyl groups with respect to the porphyrin plane. Significant line width differences are noted for meta phenyl signals, and the 1.48 ppm separation of the doublet is to be compared with a value of only 1.10 ppm observed for the (TPP)FeCl complex. The larger splitting and line width differences are fully consistent with a dimeric structure in which chemical shift and relaxation parameters of half the ortho and meta phenyl protons are partially modulated by the neighboring iron atom. Variable-temperature NMR spectra reveal deviations from the Curie law that are no larger than those for the monomeric (TPP)FeCl species. This observation and the measured spin-only magnetic moment (at ambient temperature) indicate that magnetic interactions between iron centers must be relatively small.

The carbon-13 NMR spectrum of $[(TPP)Fe]_2CrO_4$[15] is also revealing in terms of empirical correlations possible for other high-spin iron(III) porphyrin complexes.[16] A far-downfield methine carbon signal at 434 ppm is fully consistent with five-coordinate rather than six-coordinate geometry. Chemical shift values for this and other carbon atoms of $[(TPP)Fe]_2CrO_4$ indicate that the ligand field strength for bridging CrO_4^{2-} is slightly greater than for SO_4^{2-}.

Additional new oxyanion iron(III) tetraphenylporphyrin complexes have been prepared by metathesis reactions or an acid cleavage route. Preliminary characterization of the species has relied largely on unique pyrrole proton chemical shift values. The following chemical shift values and synthetic routes are noted for the new, presumably monomeric, derivatives: iodate, 76.2 ppm (acid cleavage); perrhenate, 60.6 ppm (silver ion metathesis); vanadate, 73.0 ppm (silver ion metathesis). Two species with signals at 66.9 and 73.4 ppm are obtained from silver tungstate metathesis. One component is thought to be the dimeric complex, and the other may be the monomeric tungstate complex in which a single silver ion is retained. On the basis of chemical shift patterns, all these compounds appear to be in the iron(III) oxidation state with a predominant high-spin $S = {}^5/_2$ configuration. Minor admixture of the $S = {}^3/_2$ state is possible for the ReO_4^- adduct in view of the upfield bias of the pyrrole proton signal.

Investigation of a variety of organic substrate oxidations by oxyanion metalloporphyrin complexes is in progress.

Acknowledgment. Support from National Science Foundation Grant CHE 83-17451 is gratefully acknowledged. The Bruker WM-360 NMR spectrometer was purchased in part with National Science Foundation Grant CHE 82-01836.

Registry No. (TPP)FeCl, 16456-81-8; $[(TPP)Fe]_2CrO_4$, 95978-30-6; $[(TPP)Fe]_2O$, 12582-61-5; $(TPP)Fe(IO_3)$, 95978-31-7; $(TPP)Fe(ReO_4)$, 95978-32-8; $(TPP)Fe(VO_4)$, 95978-33-9; $[(TPP)Fe]_2WO_4$, 95978-34-0; $[(TPP)Fe]WO_4Ag$, 95978-35-1.

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(14) Anal. Calcd for $(C_{44}H_{28}N_4Fe)_2CrO_4 \cdot 0.71C_7H_{16}$: C, 73.23; H, 4.45; N, 7.38; Fe, 7.33; Cr, 3.41. Found: C, 72.47; H, 4.23; N, 7.29; Fe, 7.16; Cr, 3.28.

(15) Carbon-13 NMR assignments (ppm, $CDCl_3$ solvent, 25 °C, Me_4Si reference): pyrroles, 1243; methine, 434; quaternary phenyl, −30.6; ortho phenyl, 361.5, 354.3; meta phenyl, 148.9, 145.8; para phenyl, 140.8.

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Received August 30, 1984

Specific Transport of Copper(II) Ions across a Liquid Membrane Mediated by a Lipophilic Tetraaza Macrocycle

Sir:

We report the specific and uphill transport of Cu(II) ions across a liquid CH_2Cl_2 membrane, mediated by a polyaza macrocycle and driven by a pH gradient, between two aqueous phases.

The experiment of transport of metal ions through liquid membranes mediated by appropriate ligands has recently attracted much attention for both biological (as a model for the transport across natural membranes)[1] and practical implications (waste water treatment, recovery of metals from effluents).[2]

Crown ethers and related ligands have been found to be very efficient and specific in the transport of alkaline and alkaline-earth

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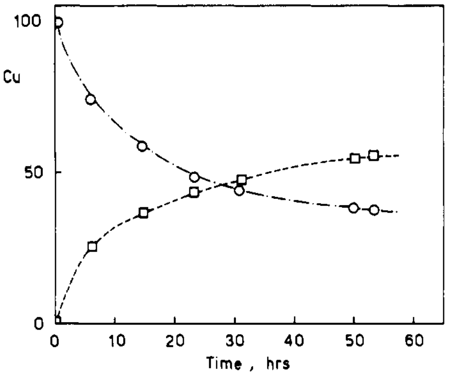
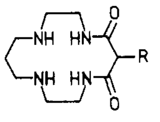


Figure 1. Plot of the concentration of Cu^{2+} in the source phase (○) and receiving phase (□), during a transport experiment. Initial conditions: source phase 10 cm^3, 10^{-2} M in Cu^{2+}, 0.1 M in Tris, pH 6.7; CH_2Cl_2 membrane 35 cm^3, 10^{-3} M in **2**; receiving phase 10 cm^3, 0.1 M phthalate buffer, pH 3. The percentage of metal transported at the end of the experiment (53.5 h) was 56 ± 5%, based on two separate transport experiments, performed under identical conditions.

cations, the transfer through the membrane being driven solely by the metal concentration gradient.[3] Very recently, macrocycles containing phenolic groups were used as carriers,[4] and the cation transfer has been coupled by a counterflow of protons (the transport of block s cations being thus controlled also by a pH gradient). On the other hand, the transport of block d metal ions through liquid membranes has been considered to a much lesser extent. We thought that nitrogen analogues of crown ethers, i.e. polyaza macrocycles, that form stable 1:1 complexes with transition-metal ions according to an uncomplicated step, could be good candidates to the d metal transport. Among the macrocyclic polyaza ligands that have been developed in the past 2 decades, we have chosen the dioxocyclam ring **1**, which is able to incorporate a divalent metal cation (Cu^{II}, Ni^{II}) with simultaneous extrusion of two protons ($M^{2+} + H_2L \leftarrow [ML]^0 + 2H^+$).[5,6]



1 R = H

2 R = $C_{16}H_{33}$

For transport purposes, we have synthesized the functionalized ligand **2**, in which a lipophilic group has been inserted into the ligand's aliphatic backbone.[7] **2** is soluble in the most common organic solvents and insoluble in water. In a typical transport experiment,[9] an aqueous solution 10^{-2} M in Cu^{2+}, adjusted to pH 6.7 by a 0.1 M Tris buffer (source phase, SP), and an aqueous solution buffered to pH 3 by phthalate buffer (receiving phase, RP) were interfaced by a dichloromethane layer, which was 10^{-3} M in **2**. The concentration of Cu^{2+} in SP, monitored by atomic absorption spectrometry, was found to decrease progressively, whereas Cu^{2+} ions appeared in RP and their concentration increased with time (see Figure 1).

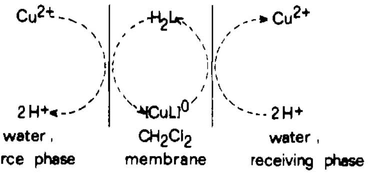


Figure 2. Cu^{2+} transport across a CH_2Cl_2 membrane containing the lipophilic macrocycle **2** (H_2L). Interactions of Cu^{2+} with buffer in the two aqueous phases have been omitted.

The Cu^{2+}-transfer process can be interpreted according to the scheme depicted in Figure 2: the macrocycle H_2L, at the interface SP/membrane, incorporates a Cu^{2+} cation, simultaneously releasing two protons into the aqueous layer; the neutral $Cu^{II}L$ complex diffuses to the membrane/RP interface, where the two deprotonated amido groups bind two hydrogen ions and Cu^{2+} is released into the acidic aqueous layer. On the whole, Cu^{2+} ions move from SP to RP, and H^+ ions, in a 2:1 molar ratio, move in the opposite direction, the lipophilic macrocycle **2** operating as a shuttle. A few minutes after the beginning of the experiment, the CH_2Cl_2 membrane becomes pale pink-violet in color, confirming the presence of the Cu(II) dioxocyclamato (2−) complex.

It should be noted that Cu^{2+} in SP is present as a 1:2 complex[11] with Tris rather than as the simple aqua ion (Tris was deliberately used as a complexing agent to avoid copper hydroxide precipitation). Transport of Cu^{2+} does not occur (i) when the membrane layer does not contain **2** as a carrier and (ii) when a pH gradient between SP and RP is not available.[12]

The system outlined is totally specific for copper(II), since other block d and p cations (Co^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+}) are not complexed by **2** at the interface CH_2Cl_2/aqueous Tris buffer; thus, their transport does not take place.

Separate experiments have shown that Ni^{2+} is extracted very slowly (in term of days) from aqueous alkaline solutions by a CH_2Cl_2 solution containing **2** (whereas the extraction of copper is in a matter of minutes). This could be ascribed to the inertness of nickel(II) ion toward the incorporation by tetraaza macrocycles, as documented by previous solution studies.[13]

Transport experiments using a source phase 10^{-2} M in both Ni^{2+} and Cu^{2+} have shown that Ni^{2+} is not transported in the typical time scale of the experiment and the transport of Cu^{2+} proceeds regularly at the same rate. Therefore, it appears that the selectivity of the Cu^{2+} transport with respect to Ni^{2+} is kinetically rather than thermodynamically controlled.

Recently, the pH-driven quasi-specific transport of Cu^{2+}, through a CH_2Cl_2 membrane, mediated by a lipophilic ligand derived from 2,2′-bipyridine was reported.[10] Due to the neutral nature of the carrier, the Cu^{2+} transport also involves the simultaneous transfer of counterions (e.g., Cl^-). On the contrary, the transport mechanism outlined here does not involve participation of anions.

Acknowledgment. This work was supported by the CNR, Rome (Progetto Finalizzato Chimica Fine e Secondaria).

Registry No. **2**, 66178-58-3; CH_2Cl_2, 75-09-2; Cu, 7440-50-8.

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(7) The synthesis of **2**, which is based on the method reported by Tabushi,[8] involves the condensation of diethyl 2-cetylmalonate and 1,4,8,11-tetraazaundecane in refluxing absolute ethanol (5 × 10^{-2} M scale, 3 days). The crude product obtained on concentration of the ethanolic solution was purified by column chromatography on alumina, using a 95:5 chloroform/ethanol mixture as eluent.

(8) Tabushi, I. British Patent, 1 529 150, 1979; *Chem. Abstr.* **1979**, *91*, 123 761*R*.

(9) In the experiments, we used a beaker (4-cm diameter × 8-cm height) divided in two parts by a glass plate, except for the bottom portion (1 cm), as described elsewhere.[10] The dichloromethane layer, placed in the bottom up to a height of 2.5 cm, interfaced the two aqueous portions separated by the glass plate and was magnetically stirred. Experiments were performed at 20 ± 1 °C.

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(12) Some experiments were performed using 0.1 M HCl as receiving phase; however, after a few hours a white turbidity appeared in the CH_2Cl_2 layer, possibly due to the precipitation of the dihydrochloride of **2**. In any case the Cu^{2+}-transport efficiency decreased drastically.

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Received December 5, 1984