# A Lipophilic Copper Complex as a New Class of Anion Transport Carrier

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*Summary* A new type of carrier, a lipophilic copper complex, has been shown to transport a variety of anionic substrates such as phenolate, phosphate, carboxylate, and sulphonate with high efficiency and unique selectivity.

RECENTLY much research into transport phenomena has been carried out, both in chemistry and in biology, and many synthetic and naturally derived carriers for transporting electrons[1] and cations[2] have been discovered. In marked contrast, only a few synthetic carriers for the transport of anionic substrates have been reported,[3] mostly 'lipophilic ammonium cation'-type compounds capable of forming lipophilic ion-pair complexes with anions.

Here we report that a novel type of carrier, a 'lipophilic metal complex,' can transport anionic substrates through a liquid membrane effectively and specifically. Recently several model studies on metalloenzymes[4] have revealed that some simple metal complexes can recognise and carry anionic substrates *via* the formation of an 'anion–metal ion–ligand' ternary complex. Therefore, it was possible that such metal complexes might be used in the design of a new class of specific carriers for anion transport. We have examined a lipophilic copper complex (**1**) composed of a neutral ligand $[CH_2CH_2N(CSNHPh)]_n$ ($n = 8$) (L) and copper(II) chloride as a carrier for transporting anionic substrates.

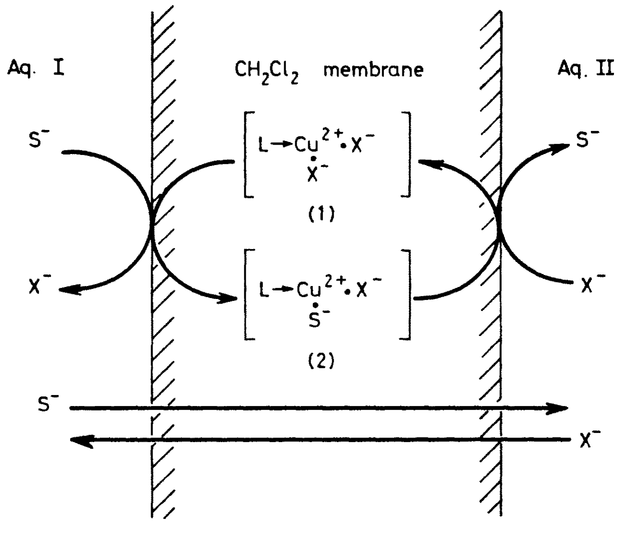

FIGURE. Liquid membrane system. $S^-$: anionic substrate, $X^-$: antiport anion, L: neutral ligand $[CH_2CH_2N(CSNHPh)]_{n=8}$ (4 mol. equiv. to $Cu^{2+}$ ion), (**1**): lipophilic copper complex carrier, (**2**): transient ternary complex.

The 'liquid membrane' system used here is shown schematically in the Figure.† The lipophilic copper complex (**1**) is much less soluble in the aqueous phases I and II than in the methylene chloride membrane. The leakage of copper ion into the aqueous phases is undoubtedly negligible under the conditions employed (see the Table). When (**1**) was added to the membrane, the anionic substrate($S^-$) and antiport anion($X^-$) were taken up and exchanged across the interfaces, so that $S^-$ and $X^-$ appeared simultaneously in the aqueous phases II and I, respectively. In the absence of carrier there was little transport of $S^-$. Therefore, this transport process can be described as 'antiport transport' mediated by the copper complex (**1**).

TABLE. Carrier-mediated anion transport.[a]

| | | Transport rate × $10^6$/mol $h^{-1}$ [b] | |
|---|---|---|---|
| $S^-$ | $X^-$ | (**1**) | (**3**) |
| *p*-Nitrophenolate | $OH^-$ [c] | 0·35 | 0·13 |
| | $Cl^-$ | 8·12 | 2·42 |
| | $ClO_4^-$ | 26·57 | 13·20 |
| | $SCN^-$ | 15·94 | 30·41 |
| *m*-Nitrophenolate | $Cl^-$ | 4·62 | 3·98 |
| *o*-Nitrophenolate | $Cl^-$ | 3·55 | 5·00 |
| *oo'*-$(O_2N)_2C_6H_3O^-$ | $Cl^-$ | 5·95 | 0·42 |
| Picrate | $Cl^-$ | 2·65 | 0·05 |
| *p*-$O_2NC_6H_4CO_2^-$ | $Cl^-$ | 26·50 | 9·40 |
| *m*-$O_2NC_6H_4CO_2^-$ | $Cl^-$ | 22·22 | 12·65 |
| *o*-$O_2NC_6H_4CO_2^-$ | $Cl^-$ | 28·33 | 16·25 |
| *p*-$O_2NC_6H_4OPO_3^{2-}$ | $Cl^-$ | 21·40 | 15·82 |
| *m*-$O_2NC_6H_4SO_3^-$ | $Cl^-$ | 23·57 | 2·57 |

[a] Initial concentration: aqueous phase I, sodium salt of substrate, 0·4 mmol/$H_2O$, 4 ml; (pH 7—10). Aqueous phase II, sodium or potassium salt of antiport anion, 5 mmol/$H_2O$, 10 ml. Organic phase, carrier, 0·037 mmol/methylene chloride, 8 ml. The organic phase was constantly stirred by a magnetic stirrer. [b] Transport rate was obtained from the rate of appearance of substrate anion in aqueous phase II; reproducibility, ± 10% or better. [c] No antiport anion salt was added to aqueous phase II.

The ligand (L) was prepared by ring-opening oligomerization of 1-(*N*-phenylthiocarbamoyl)aziridine with diethyl sulphate in good yield (90%).[5] This is a linear octamer having a regular recurrence of metal co-ordinating groups (>NCSNH–) and hydrophobic units(–Ph) in a single chain, and acts as a lipophilic multidentate ligand.[6] The copper complex carrier (**1**)‡ was obtained by mixing the ligand (L) (0·15 unit mmol) and copper(II) chloride (0·037 mmol) in 20 ml of methanol–methylene chloride solution (1 : 1, v/v) at room temperature for 30 min. After removal of the solvent, the remaining green complex was dissolved in 8 ml of methylene chloride($\lambda_{max}$ 710 nm) and used *in situ*. For comparison, trioctylmethylammonium chloride (**3**), a similar

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† The cell used was similar to the one described in ref. 2b.

‡ Under the conditions stated in the text, (**1**) acts as an uncharged ligand, and forms an essentially square planar copper complex with the chloride anions as counteranions. Further properties of this type of complex have been reported previously (ref. 6).

$\{(Me[CH_2]_7)_3NMe\}^+Cl^-$

**(3)**

phase transfer catalyst which is effective for transporting anions, was also examined.[3a] The concentrations of anionic substrates in the aqueous phase II were monitored spectroscopically and the initial transport rates obtained are listed in the Table.

Our carrier (**1**) showed a higher transport efficiency than the conventional carrier (**3**) for a variety of anionic substrates: phenolate, phosphate, carboxylate, and sulphonate anions. For example, the carrier (**1**) transported simultaneously the *p*-nitrophenolate anion in an amount equal to 22% of the total after 12 h and the chloride anion in the opposite direction. The u.v. spectrum of the methylene chloride membrane phase during the transport clearly demonstrated the formation of a ternary complex $[L–Cu^{II}–S^-]\ Cl^-$ (**2**) as a transient species as shown in the Figure; $\lambda_{max}$ 394 nm (new band due to co-ordinated *p*-nitrophenolate anion), $\lambda_{max}$ 650 nm (shifted d–d transition band of the copper complex).

The rates of this transport system were increased by using perchlorate or thiocyanate anion as an antiport anion($X^-$). They may readily release bound anionic substrate($S^-$) to the copper complex as reported in the related system.[3b]

The new carrier (**1**) exhibited an interesting and unique transport selectivity sequence: phenolate anion $<<$ phosphate dianion§ $<$ carboxylate anion $\sim$ sulphonate anion. This was quite different from that displayed by the ammonium cation type carrier (**3**): sulphonate anion $\sim$ phenolate anion $<$ carboxylate anion $<$ phosphate dianion. In particular, our carrier (**1**) had great advantages in the transport of 2,6-dinitrophenolate, picrate, and nitrobenzenesulphonate anions, which are transported slowly by the carrier (**3**). These results clearly indicate that copper co-ordination chemistry is an essential factor in the control of the transport phenomena in our system, and suggest that such a metal complex-type carrier should have great advantages over previously reported systems, although the origin of the substrate–carrier interactions in a ternary complex system is very complicated and unclear at this stage.[7]

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§ The phosphate dianion is predominant under the conditions employed (pH 8—9).

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