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Metal-ion recognition. Competitive bulk membrane transport of transition and post transition metal ions using oxygen–nitrogen donor macrocycles as ionophores

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A series of competitive metal ion transport experiments have been performed. Each involved transport from an aqueous source phase across a chloroform membrane phase into an aqueous receiving phase. The source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) while the membrane phase incorporated an ionophore chosen from a series of single-ring and double-ring macrocyclic ligands (incorporating mixed oxygen–nitrogen donor sets) together with hexadecanoic acid. The transport process was 'driven' by a back flux of protons, maintained by buffering the source and receiving phases at pH 4.9 and 3.0, respectively. Transport selectivity for copper(II) was observed in all cases. The results confirm that consideration of the mass balance of the metal ions present across all three transport phases is important for a fuller understanding of the nature of the discrimination process for the present systems.

There have now been many reports of the transport of transition and post-transition metal cations through bulk liquid membranes using synthetic ionophores. The latter have included a wide range of crown and azacrown derivatives as well as macrocycles incorporating other donor-atom set combinations.[1] It is clear from numerous studies that transport fluxes can be influenced by a range of factors,[2,3] with the transport limiting step differing from one system to the next (for many systems, and especially when the organic phase is stirred,[4] the limiting step appears frequently to correspond to diffusion across one of the interfacial layers although, for other systems, rates of complexation/decomplexation have been found to dominate the process).

The most common configuration encountered in these systems involves a three phase arrangement consisting of two aqueous phases (source and receiving phases) separated by an immiscible organic membrane phase incorporating the ionophore.[1,5] When the source and receiving phases are similar, the presence of the ionophore in the organic phase will promote the transport of a metal ion until the concentrations in both aqueous phases are equal and the system reaches equilibrium. However, under appropriate conditions transport can be driven past the 50 percent mark by means of the back transport of a species (commonly protons) from the receiving phase to the source phase. For the case where there is back transport of protons, typically both aqueous phases are buffered appropriately to maintain the required pH gradient.

In previous studies we have synthesized a range of mixed oxygen–nitrogen donor macrocycles that include single ring and double ring systems of types **1**–**8**.[6–8] The interaction of many of these ligands with particular transition and post-transition metal ions has also been investigated.[9] An aim of these studies was to document structure–function relationships underlying the observed respective thermodynamic stabilities of the resulting complexes. More specifically, we have employed systematic variation of the macrocyclic ring size, the donor set present and/or the degree of substitution of the parent ring structure to 'tune' the affinity of a given ring type for metal ions of interest.[10] The investigation now reported is an extension of these studies and has involved the use of competitive membrane transport experiments to probe (possible) metal ion discrimination behaviour using **1**–**8** as ionophores. These systems appeared suitable for the planned studies since, in particular cases, the mixed donor sets present have been demonstrated (see later) to result in complexes showing only moderate thermodynamic and kinetic stabilities with the present metals (in contrast to the behaviour of corresponding complexes of many all-nitrogen donor macrocycles).[11] Possible exceptions to the above are the present nickel(II) complexes; the dissociation kinetics of particular single ring derivatives of this ion has been shown previously by us to be somewhat sluggish.[12,13] Slow kinetics and/or thermodynamic stabilities that are either too low to permit uptake of metal into the organic phase, or too high to allow its loss to the receiving phase, will all inhibit transport efficiency.

The metal ion transport arrangement used in the present investigation is represented schematically in Fig. 1. The study involved metal ion transport from an aqueous source phase containing an equimolar mixture of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) across a bulk chloroform membrane (incorporating an ionophore chosen from **1**–**8** plus hexadecanoic acid) into an aqueous receiving phase against a back gradient of protons.

Experimental

All reagents were of analytical grade and used without further purification. The macrocyclic ligands of type **1**(R = H),[6] **2**,[8] **3**,[8] **4**(R = H),[7] **4**(R = *t*-Bu)[8] and **5**–**8**[8] were prepared and characterised as described previously. Macrocycle **1**(R = *t*-Bu) was synthesized by an identical procedure to that employed for

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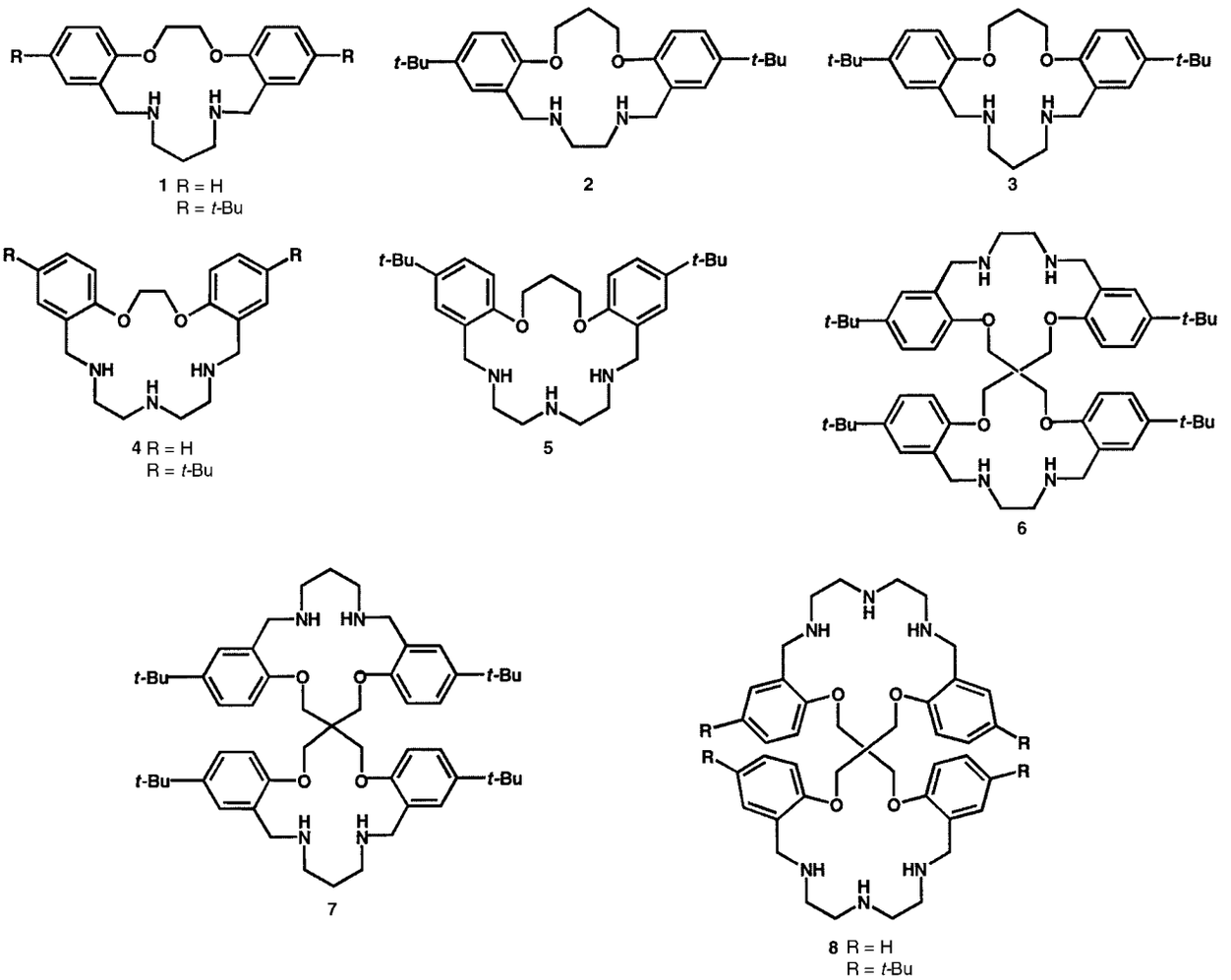

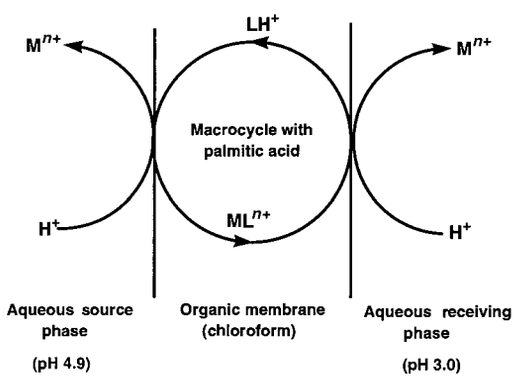

Fig. 1 The arrangement used in the present studies for the transport of a metal ion across a chloroform membrane phase.

1(R = H) except that 5-*t*-butylsalicylaldehyde was substituted for salicylaldehyde.[14] All aqueous solutions were prepared using deionised water. Chloroform used for the membrane phase was presaturated with water by shaking a two phase water–chloroform mixture then removing the aqueous phase.

Potentiometric titrations

Potentiometric titrations were carried out in a water-jacketed titration vessel and a water-jacketed calomel reference electrode, connected by a salt bridge. A Philips glass electrode (GA-110) was used for all pH measurements. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the background electrolyte. Methanol-saturated nitrogen was bubbled through the solution in the measuring cell; tetraethylammonium hydroxide solution (0.1 mol dm^{-3}) was introduced into the cell using a Metrohm Dosimat 655 automatic titrator. A Corning model 130 Research pH meter was employed for the pH determinations. The data were processed using a local version of MINIQUAD[15] with selected data also being processed with SUPERQUAD;[16] the two programs yielded near identical log *K* values in each case. All quoted log *K* values represent the mean of data from at least two (and up to five) titrations performed at different metal to ligand ratios. All measurements were fully automated under personal computer control. Titrations were performed at 25.0 ± 0.05 °C at constant ionic strength (I = 0.1 mol dm^{-3}, Et_4NClO_4) in 95 percent methanol solution under purified nitrogen. Analytical grade methanol was fractionated and distilled over magnesium before use.

Under the conditions employed, low solubilities of the spiral-linked systems of type **6**–**8** and/or their metal-containing species lead to precipitation during the course of the respective tirations; because of this it proved not possible to obtain usable titration data for these systems.

Membrane transport

The transport experiments employed standardised 'concentric cells' in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) were separated by a chloroform phase (50 cm^3). Details of the cell design have been reported elsewhere.[17] For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 rpm using stirring paddles for the receiving phase and propellers for the source and organic phases each coupled to a single (geared) synchronous motor; the cell was enclosed by a water jacket and thermostatted at 25 °C. The aqueous source phase consisted of a buffer solution at pH 4.9 ± 0.1 (6.95 cm^3 of 2 mol dm^{-3} sodium acetate solution and 3.05 cm^3 of 2 mol dm^{-3} acetic acid made

Table 1 Stability constant data for the ML^{2+} complexes of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) complexes of the single-ring macrocycles **1**–**5**[a]

Ligand	Donor set	Protonation constants			Log stability constants						
		log K_1	log K_2	log K_3	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	Ag^{I}	Pb^{II}
1 (R = H)	O_2N_2	9.85[b]	6.78[b]		<3.6[b]	4.8[b]	7.3[b]	<4.5[c]	<4[c]	[d]	[d]
1 (R = *t*-Bu)	O_2N_2	9.63	6.98		<4	4.67	7.19	<4	<4	[d]	[d]
		(0.03)	(0.02)			(0.21)	(0.02)				
2	O_2N_2	9.22	5.33		<4	4.69	8.83	4.30	4.07	6.00	4.81
		(0.03)	(0.06)			(0.17)	(0.05)	(0.16)	(0.21)	(0.05)	(0.10)
3	O_2N_2	10.07	7.09		<4	4.92	7.39	<4.5	<4	[d]	5.38
		(0.01)	(0.01)			(0.11)	(0.04)				(0.05)
4 (R = H)	O_2N_3	9.69[e]	8.45[e]	≈2.0[e]	7.7[e]	10.0[e]	14.2[e]	7.5[f]	8.7[f]	8.7[g]	8.1[g]
4 (R = *t*-Bu)[h]	O_2N_3	9.65	8.33		7.41	[d]	14.00	7.48	8.81	8.63	7.92
		(0.03)	(0.04)		(0.12)		(0.08)	(0.07)	(0.05)	(0.05)	(0.06)
5	O_2N_3	9.85	8.48	≈2.3	7.37	10.10	14.55	7.91	7.66	7.49	7.92
		(0.04)	(0.07)		(0.03)	(0.13)	(0.06)	(0.01)	(0.03)	(0.16)	(0.03)

[a] In 95% MeOH; $I = 0.1$ mol dm^{-3}, Et_4NClO_4 at 25.0 °C. Each value is the mean of between two (and up to five) determinations at different metal : ligand ratios; standard deviations for values obtained in the present study are given in parentheses. [b] From ref. 23. [c] From ref. 25. [d] Precipitation, slow approach to equilibrium or competing hydrolysis prevented log *K* determinations. [e] From refs. 24 and 26. [f] From ref. 26. [g] From ref. 9. [h] The corresponding log *K* values for the derivative **4** (R = C_9H_{19}) are: ligand log K_1, 9.65; log K_2, 8.32; complexes (log K_{ML} values) cobalt(II), 7.7; nickel(II), precipitation; copper(II), 14.1; zinc(II), 7.4; cadmium(II), 8.6; silver(I), 8.5; lead(II), 8.0.

up to 100 cm^3)[18] containing an equimolar mixture of the metal ions (see Results and discussion section), each at a concentration of 1.0×10^{-2} mol dm^{-3}; the total 'all-metal' concentration was 7.0×10^{-2} mol dm^{-3}. The chloroform phase contained the macrocycle at 2×10^{-3} (for the single ring macrocycles, **1**–**5**) or 1.0×10^{-3} mol dm^{-3} (for the double ring species, **6**–**8**) as well as hexadecanoic acid (4.0×10^{-3} mol dm^{-3}). The receiving phase consisted of a buffer solution at pH 3.0 ± 0.1 (56.6 cm^3 of 1 mol dm^{-3} formic acid and 10.0 cm^3 of 1 mol dm^{-3} sodium hydroxide made up to 100 cm^3).[18] All transport runs were terminated after 24 hours and atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period; both the source and the receiving phases were analysed (using a Varian Spectra AA-800 spectrometer) after each transport run. This also enabled the amount of metal remaining in the membrane phase to be calculated. The transport results are quoted as the average values obtained from duplicate runs carried out in parallel using different cells that had previously been shown to yield identical results (within experimental error); the values from each run did not differ by more than 5 percent. The use of the present cell design coupled with precise stirring and temperature control has resulted in better reproducibility than often reported previously[1] for related bulk membrane experiments where variability of up to ±25 percent has been reported.[19] Transport rates (*J* values) are in mol per 24 h and represent mean values measured over 24 h. *J* values equal to or less than 0.22×10^{-7} mol per 24 h are within experimental error of zero and have been ignored in the analysis of the transport results.

Under the conditions employed in the present study, no metal ion transport was observed when only hexadecanoic acid (4×10^{-2} mol dm^{-3}) was present in the membrane phase.

Results and discussion

The competitive mixed metal transport experiments (water–chloroform–water) employed an organic phase containing known concentrations of the ionophore (chosen from **1**–**8**) and hexadecanoic acid. 'Equivalent' concentrations of the single ring (2×10^{-3} mol dm^{-3}) and double ring species (1×10^{-3} mol dm^{-3}) were employed. A major role of the hexadecanoic acid (4×10^{-3} mol dm^{-3}) was to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralisation of the metal cation being transported through ion pairing or adduct formation.[20,21] In this manner the uptake of lipophobic nitrate anions into the organic phase is avoided. An additional benefit of adding lipophilicity in the form of the long-chain acid has been documented for systems of the above type.[20,22] Namely, ion pair/adduct formation serves to inhibit any 'bleeding' of 'partially' hydrophilic species (such as the protonated ionophore and/or its corresponding charged metal complex) from the organic membrane phase into either of the aqueous phases.

The aqueous source phase contained equimolar concentrations of the nitrate salts of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II), with the individual metal ion concentrations being 10^{-2} mol dm^{-3}. As mentioned in the Experimental section, transport was performed against a back gradient of protons, maintained by buffering the source and receiving phases at pH 4.9 and 3.0, respectively.

A feature of the present study (that differs from the majority of prior investigations) is the determination of the metal concentrations in both the aqueous source and receiving phases on termination of each experiment after 24 hours. The latter procedure yielded (by difference) a measure of the metal present in the respective organic phases.

A common feature of all the transport studies based on compounds **1**–**8** was their clear selectivity for copper(II) relative to the other six metals present in each source phase.

Table 2 Data for seven-metal competitive transport across a bulk chloroform membrane employing macrocycles of type **1**–**8** as ionophores (25 °C)[a]

Ionophore		Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	Ag^{I}	Pb^{II}
1 (R = H)	J[b]/mol per 24 h	—	—	2.78	—	—	—	—
	% (receiving)[c]	—	—	2.8	—	—	—	—
	% (membrane)[d]	—	16	—	—	—	—	—
1 (R = *t*-Bu)	J/mol per 24 h	—	—	5.28	—	—	—	—
	% (receiving)	—	—	5.3	—	—	—	—
	% (membrane)	—	20	—	—	—	—	—
2	J/mol per 24 h	—	—	9.38	—	—	—	0.38
	% (receiving)	—	—	9.4	—	—	—	0.4
	% (membrane)	—	19	46	—	—	—	—
3	J/mol per 24 h	—	—	7.97	—	—	0.26	—
	% (receiving)	—	—	8.0	—	—	0.3	—
	% (membrane)	—	17	—	—	—	—	—
4 (R = H)	J/mol per 24 h	—	—	18.8	—	—	—	—
	% (receiving)	—	—	19	—	—	—	—
	% (membrane)	—	17	—	—	—	—	—
4 (R = *t*-Bu)	J/mol per 24 h	—	—	19.1	—	0.91	0.43	0.50
	% (receiving)	—	—	19	—	0.8	0.4	0.5
	% (membrane)	—	12	31	—	—	2.8	—
5	J/mol per 24 h	—	—	9.48	—	—	—	1.12
	% (receiving)	—	—	9.5	—	—	—	1.1
	% (membrane)	—	14	26	—	—	5	—
6	J/mol per 24 h	—	—	32.9	—	—	—	—
	% (receiving)	—	—	33	—	—	—	—
	% (membrane)	—	20	1	—	—	5	—
7	J/mol per 24 h	—	—	5.35	—	—	—	0.50
	% (receiving)	—	—	5.4	—	—	—	0.5
	% (membrane)	—	14	—	—	—	—	—
8 (R = H)	J/mol per 24 h	—	—	18.8	—	—	—	—
	% (receiving)	—	—	19	—	—	—	—
	% (membrane)	—	13	—	—	—	20	—
8 (R = *t*-Bu)	J/mol per 24 h	—	—	10.7	—	—	—	—
	% (receiving)	—	—	11	—	—	—	—
	% (membrane)	—	18	33	—	—	5	—

[a] All values represent the means obtained from duplicate experiments. [b] All J values are $\times 10^{-6}$. [c] Percent of total metal in the receiving phase after 24 hours. [d] Percent of total metal in the membrane phase after 24 hours.

Studies employing the single ring macrocycles 1–5

The results of our prior potentiometric, spectrophotometric and X-ray studies of metal complex formation involving metal ions from the above series and the O_2N_2 macrocycle **1** (R = H) or its larger O_2N_3 ring analogue **4** (R = H) show that 1 : 1 (metal : ligand) complexes readily form in both solution and the solid state.[9,10] In the present study we have extended the solution investigations to include rings of type **1** (R = *t*-Bu), **2**, **3**, **4** (R = *t*-Bu) and **5**. log K determinations were performed under identical conditions (I = 0.1 mol dm^{-3}, Et_4NClO_4, 95 percent methanol, 25 °C) to those used in the earlier studies.[9] The results are presented in Table 1 together with the previously determined values for the complexes of **1** (R = H) and **4** (R = H).[9,23–26] The respective values for the cobalt(II), nickel(II), copper(II) and zinc(II) complexes of all seven ligands given by **1**–**5** indicate that the normal Irving–Williams stability order of cobalt(II) < nickel(II) < copper(II) > zinc(II) is maintained in each case.[27]

It is instructive to compare the transport behaviour for the systems containing the single ring, O_2N_2-donor macrocycles of type **1**–**4** (Table 2). As mentioned above, all six rings strongly favour transport of copper(II): exclusively for **1** (R =H or *t*-Bu) and for **4** (R = H). Very minor amounts of particular other ions were co-transported in the remaining cases: lead for **2**; silver for **3**; and cadmium, silver and lead for **4** (R = *t*-Bu).

Based on the observed J values for copper(II), lowest transport occurs for the system incorporating compound **1** (R = H). Adding lipophilicity in the form of *t*-butyl groups to the benzo rings of this ligand to yield **1** (R = *t*-Bu) results in a clear enhancement of transport efficiency, albeit from a low base. Similarly, enlarging the size of the macrocyclic ring from 15- to 16-membered by increasing the bridge between the ether oxygen donors from two methylene groups to three (to yield **3**) also leads to further enhanced transport of copper(II).

Comparison of the log K values (in 95 percent methanol) for the copper complexes of compound **1** (R = *t*Bu) with that for the complex of **3** (Table 1) indicates that, in the latter case, the presence of an extra methylene group in the ring has only a minor effect on the thermodynamic stability of this complex (log K = 7.4) relative to that observed for **1** (R = *t*-Bu) (log K = 7.2). This result is not unexpected as a prior investigation of the copper complexes of **1** (R = H) and its 14-, 16-, and 17-membered macrocyclic analogues indicated that the copper in these complexes shows a tendency to adopt a 5-co-ordinate geometry.[13] In this, the metal lies out of the macrocyclic cavity (with the latter adopting a non-planar configuration); there is also evidence that the ring-oxygen donors bind quite weakly to the central metal. As a consequence, there is an absence of a well defined macrocyclic ring-size effect on thermodynamic stability across the copper complexes of this 14- to 17-membered ligand series. Indeed, the overall stabilities of the respective complexes appear to be more influenced by the nature of the chelate ring incorporating the two amine donors (with a 5-membered ring contributing more than a 6-membered ring).

In view of the above, the steady increase in copper(II) transport efficiency on passing from compounds **1** (R = H) to **1**(R = *t*-Bu) to **3** appears most likely to be largely a reflection of the increasing lipophilicity along this ligand series rather than any marked change in the inherent metal–donor binding abilities of the respective rings (all form similar 6-membered chelate rings incorporating the amine donors).

Comparison of the transport ability of compounds **2** with that of **1** (R = *t*-Bu) indicates that the former is the more efficient ionophore for copper even though both the macro-

cyclic ring size and the degree of lipophilic substitution is similar for both ligands. The different behaviour apparently reflects the ability of **2** to form a more stable 5-membered chellate ring involving its two nitrogen donors. Indeed, the stability constant for this system (Table 1) indicates that **2** binds copper(II) the most strongly of the O_2N_2-donor macrocycles of type **1**–**3**.

The metal-ion compositions of the respective organic phases at the termination of each experiment after 24 hours are also listed in Table 2. In each case the values were calculated using the concentration difference between the source and receiving phases at the termination of the experiment (for the metal ions of interest). Owing to the additivity of errors inherent in this process, calculated metal-ion values for the membrane phase of less than 5 percent of the total metal originally present in the source phase were disregarded. Somewhat unexpectedly, a significant amount of nickel(II), between 16 and 20 percent of the total nickel originally present in the source phase, was found in the respective organic phases for each of the O_2N_2-donor systems investigated. Clearly, nickel is extracted from the source phase but does not cross the organic–receiving phase interface under the conditions employed. This result serves to demonstrate a subtlety that influences competitive metal ion transport in systems of the present type. The thermodynamic binding constants for the nickel(II) complexes of compounds **1**–**3** (Table 1) are all considerably lower than the corresponding values for copper(II). In view of this, it seems likely that the above 'partial' transport (that is, loss of nickel from the source phase) is a reflection of the previously documented relatively sluggish dissociation kinetics observed for nickel complexes[12] of the present type relative to their copper(II) analogues.[13]

Behaviour of the above type, in which a metal ion (or metal ions) is kinetically 'locked' in the organic membrane phase, appears to have received little attention previously in competitive transport studies. This is somewhat surprising since clearly such partial 'blockage' of the membrane phase has implications for the overall efficiency of the metal ion transport process as well as potential for influencing the observed selectivity pattern.

The stability constants for the complexes of compounds **4** (R = H), **4** (R = *t*-Bu) and **5** (all of which incorporate an O_2N_3-donor set) for a given metal show only relatively minor variation, even though all values, as expected, are significantly higher than for the corresponding complexes of the related O_2N_2-donor systems discussed above. In particular, it is noted that, where values were obtainable, the stabilities of the nickel(II) complexes are very similar, as are those observed for the corresponding copper(II) complexes.

Comparison of the *J* values (Table 2) for the copper(II) complexes of the 17-membered ring systems **4** (R = H) and **4** (R = *t*-Bu) shows that only a quite minor increase in transport occurs in the latter case. While an increase might be expected because of the additional lipophilicity, the overall effect of appending the *t*-Bu substituents is much attenuated in these larger ring systems. However, closer inspection of the data in Table 2 for the system incorporating **4** (R = *t*-Bu) indicates that the amount of copper remaining in the organic phase (31 percent of the total) is very much higher than that for the system based on the corresponding unsubstituted ring, **4** (R = H). Thus, in the case of **4** (R = *t*-Bu), the effect of the added lipophilicity is to promote loss of copper from the source phase while inhibiting its loss from the membrane phase.

Incorporation of an extra methylene group between the oxygen donors of compound **4** (R = *t*-Bu) to yield **5** leads to an overall decrease in transport efficiency towards copper(II). However, as above, this *t*-butyl derivative promotes retention of copper in the membrane phase (26 percent of the total) so that, while loss of this cation from the source phase is promoted, loss from the membrane phase to the receiving phase is again inhibited. As before, all three membrane phases incorporating the O_2N_3-donor rings of types **4** and **5** were found to incorporate nickel(II) after 24 hours; for these cases the amount of nickel retained ranged from 12 to 17 percent.

Studies involving the double ring spiro-linked macrocycles of types 6–8

In the case of compound **7**, evidence for formation of a dinuclear nickel(II) species was obtained by spectrophotometric titration (at a wavelength of 666 nm) of nickel(II) chloride (2.5×10^{-3} mol dm^{-3}) in methanol with a methanol solution of **7** also in methanol. A sharp end point was observed at a 2:1 metal to ligand ratio. In contrast, a parallel titration involving the corresponding monomeric analogue **3** yielded the expected 1:1 end point in this case. A related spectrophotometric titration in which **7** was incrementally added to copper(II) perchlorate in dimethyl sulfoxide indicated the formation of a species of type $[Cu_2L]^{4+}$; however, in this case the formation of a 1:1 species was also observed.

In order to aid comparison between systems, transport experiments involving the spiral-linked double ring macrocycles of types **6**–**8** incorporated these rings at a concentration of 1×10^{-3} mol dm^{-3} in the membrane phase, rather than the 2×10^{-3} mol dm^{-3} used for the single ring species of types **1**–**5**. As mentioned already, the transport runs incorporating the double rings again each showed selective transport of copper(II). In each case nickel (between 13 and 20 percent of the total originally present in the source phase) was, once again, also present in the respective membrane phases after 24 hours.

Comparison of the transport efficiency towards copper(II) of compound **6** with that of **7** shows, as before, that it is the system capable of forming 5-membered chelate rings involving each pair of nitrogen donors (namely **6**) that gives rise to the higher *J* value. The values for nickel in the organic phases were 20 and 14 percent for **6** and **7**, respectively, with the former system also incorporating a small amount of silver (5 percent) in its membrane phase after 24 hours.

Since compound **6** is an especially effective ionophore for copper, it was chosen for a parallel solvent extraction experiment in order to provide results that were directly comparable with those from the transport experiment. Identical source and organic phases to those used in the transport experiment were employed. On shaking the buffered (pH 4.9) seven-metal aqueous source phase with the chloroform phase at 25 °C for 24 hours the latter phase was found to have taken up: nickel(II), 17 percent; copper(II), 55 percent; and silver(I), 18 percent of the respective available metal present. Qualitatively, but not quantitatively, this metal-ion uptake is similar to that found in the membrane phase at the completion of the corresponding transport experiment (Table 2). This result serves to confirm both the similarities (namely, the same metals occur in the organic phase in both experiments) and differences (the concentrations of these metals are not the same, except for nickel which is not lost from the organic phase in the transport runs) arising from the different natures of the solvent extraction and membrane transport experiments.

Comparison of the transport behaviour of the spiro-linked ionophore **6** with an equivalent concentration of its single ring analogue **2** reveals that the linked system results in a greater than 3-fold transport rate increase over that for **2**. However, for the system incorporating **6,** the amount of copper remaining in the membrane phase, at 1 percent, is very much smaller than that observed for the system incorporating **2** (46 percent). Once again, the effective transport behaviour for each of these systems is seen to be controlled by a subtle balance between metal uptake/metal loss into and out of the respective membrane phases.

In contrast to the behaviour of the systems incorporating compounds **2** and **6** above, comparison of the copper transport behaviour for **7** and its single ring analogue **3** indicates that both are associated with quite moderate *J* values, with the

single ring system yielding slightly higher transport efficiency ($J = 7.97 \times 10^{-6}$ mol per 24 h) than an equivalent membrane concentration of the double ring system ($J = 5.35 \times 10^{-6}$ mol 24 h). For both systems, it seems that the overall lower J values are reflected by the small amount of copper present in the respective membrane phases after 24 hours. This suggests that it is the passage of copper across the source phase–membrane phase interface that is inhibited in each of these systems, thus leading to the lower overall transport rates.

Finally, it is instructive to compare the transport results for the spiro-linked O_2N_3-donor ring derivatives **8** (R = H) and **8** (R = *t*-Bu). In the latter case the presence of *t*-butyl groups results in a drop in transport efficiency relative to the former system (Table 2). The reason is apparent on inspection of the composition of the respective membrane phases after 24 hours. While the more lipophilic system effectively extracts copper(II) into the membrane phase, once there it is not so readily lost to the receiving phase as occurs for the system incorporating **8** (R = H). The result is, as before, a build up of copper in the membrane phase. For these two systems, silver was also present in each membrane phase at 20 and 5 percent, respectively.

The transport behaviour involving the spiro-linked ligand **8** (R = *t*-Bu) and that of an equivalent concentration of the single ring analogue **5** (R = *t*-Bu) indicates that **8** is a somewhat better ionophore towards copper(II) ($J = 10.7 \times 10^{-6}$ mol per 24 h) than is **5** ($J = 9.48 \times 10^{-6}$ mol per 24 h). In this case the reason for the difference is not so readily defined in terms of a single (dominating) influence since both systems yield approximately the same concentration of copper in their membrane phases. Clearly, a subtle balance of influences controls the respective copper transport rates observed for these systems. Each system was also found to take up a small amount of silver(I) in its membrane phase together with the usual nickel [14 percent (for **5**) and 18 percent (for **8**) percent of the total available].

Concluding remarks

Although there have now been many studies involving the transport of transition and post-transition metal ions across bulk organic membranes, the majority of these have given emphasis to the efficiency of the transport process, as indicated by the metal ion concentration(s) in the (aqueous) receiving phase on termination of the experiment. The present investigation confirms earlier observations[28] that consideration of the composition of all three phases in a transport experiment can lead to a greater insight into the nature of the process occurring. Appreciation of the factors discussed should assist in the future design of 'tailor made' ionophores for use in a wide variety of metal-ion transport systems.

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