# Silver Selectivity: A Study of Metal Recognition in Single and Multiple Phases

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Thiaalkane-bridge bis(benzimidazoles) varying both in the nature of the bridge and in the pendant groups attached to secondary nitrogen have been synthesised to assess metal selectivity in single and multiple phases. The single-phase studies ($^1H$ NMR, fast atom bombardment mass spectroscopy) and molecular modelling were intended primarily to rationalise the trends observed in the multiple-phase (bulk liquid-membrane) experiments. Selectivity for silver ion was studied by all of these techniques, whilst the membrane experiments were extended to assess selectivity for cadmium, zinc, lead and copper ions. All of these metal salts (as nitrates) were assessed in the membrane experiments or in pairwise competition experiments. Some useful separations were effected, the most striking being that for silver ions over lead. The lack of comparison amongst the results from the methods chosen indicates that a full understanding of the complex kinetics of three-phase transport is still to be attained.

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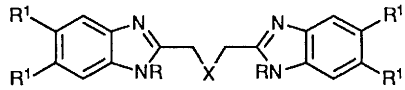
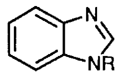
A substantial amount of work has been directed towards the correlation of thermodynamic data for cation–macrocycle interaction with the transport rates of metal ions through artifical membranes.[1] A popular method used to assess the transporting capability of ligands for metal ions has been the bulk liquid membrane.[2] Attempts[3,4] have been made to rationalise the factors that result in observed transport rates of metal cations from solutions containing either just one metal salt or pairwise mixtures. These studies have tended to concentrate on correlating the rate of transport with the thermodynamics of interaction between the carrier ligand and metal salt (usually from data measured in a single phase). Typically measurements of equilibrium constants have been made in solvents such as methanol, whereas the process we have measured is occurring at a chloroform–water interface. Although this approach appears to predict the qualitative nature of transport through a bulk liquid membrane quite well, it has been argued that an assessment of the kinetics of interaction between the ligand and metal is required.[5,6] Since the equilibrium constant can be described as a ratio of the forward and reverse rate constants for the process(es), there are situations in which rates can be important. Behr *et al.*[4] considered the possibilities for transport being limited by complexation kinetics, and decided against such possibilities in many systems, based on the consideration of experimental measurements of $V_{max}$ divided by carrier concentration. However, they noted that for complexes with low dissociation rates (instancing the transport of transition-metal cations with polyazamacrocycles as a possible example) a change to a reaction-limited process could not be excluded. Lockhart's paper on the synergic effect of mixed carriers (one optimum and one poor carrier) found the description of these results in terms of rate more natural;[7] the arguments of the earlier papers on selectivity in complexation suggest a lower limit to the viable dissociation rate, below which dissociation may not be fast enough to permit transport in the membrane.[6]

In this paper we attempt to correlate the selectivity results obtained from single-phase experiments in which different ligands are competing for the silver ion, and details of the relative kinetic selectivity of ligands obtained from NMR exchange rates of single-ligand mixtures with silver ion, with findings from the bulk liquid-membrane experiments, and with molecular modelling predictions.



| Ligand | X | R | R′ |
|---|---|---|---|
| $L^1$ | S | H | H |
| $L^2$ | $CH_2SCH_2$ | H | H |
| $L^3$ | $S(CH_2)_2S$ | H | H |
| $L^4$ | $S(CH_2)_2S$ | H | Me |
| $L^5$ | $S(CH_2)_3S$ | H | H |
| $L^6$ | $SCH_2S$ | H | H |
| $L^7$ | $CH_2SCH_2SCH_2$ | H | H |
| $L^8$ | S | $C_{12}H_{25}$ | H |
| $L^9$ | $S(CH_2)_2S$ | $C_{12}H_{25}$ | H |
| $L^{10}$ | $S(CH_2)_2S$ | $C_{12}H_{25}$ | Me |
| $L^{11}$ | $S(CH_2)_2S$ | $C_8H_{17}$ | H |
| $L^{12}$ | $S(CH_2)_3S$ | $C_{12}H_{25}$ | H |



$L^{13}$ $R = C_{12}H_{25}$

The principal aim of this work was to design a ligand that would transport silver selectively through a liquid membrane. Silver is classed as a soft metal, binding preferentially to soft donor atoms such as sulphur, and is frequently found in linear co-ordination with powerful nitrogen donors. An apparent lack of a macrocyclic effect was noted in thermodynamic studies.[8–10] Silver is frequently found as a minor component in lead ores,[11] so an emphasis was placed on the separation of these two metals. Other metal separations which were investigated in this work were Ag/Cd, Ag/Cu, Ag/Zn, Cd/Zn and Cu/Zn.

## Experimental

The bis(benzimidazoles) $L^1$–$L^7$ were prepared by means of a Phillips condensation reaction,[12] following literature methods. Ligands $L^4$, $L^6$ and $L^7$ have not been made previously.

1,6-*Bis(5′,6′-dimethylbenzimidazol-2-yl)-2,5-dithiahexane*, $L^4$.—$^1H$ NMR in $(CD_3)_2SO$–$CDCl_3$ (1:1): δ 2.04 (s, 12 H), 2.36 (s, 4 H), 3.61 (s, 4 H) and 7.01 (m, 4 H). Mass spectrum: *m/z* 411 ($HL^+$).

1,5-*Bis(benzimidazol-2-yl)-2,4-dithiapentane*, $L^6$.—$^1H$ NMR in $(CD_3)_2SO$: δ 4.07 (s, 2 H), 4.20 (s, 2 H), 7.22–7.28 (m, 4 H), 7.60–7.63 (m, 4 H) and 12.64 (NH). Mass spectrum: *m/z* 341 ($HL^+$).

1,7-*Bis(benzimidazol-2-yl)-3,5-dithiaheptane*, $L^7$.—$^1H$ NMR in $(CD_3)_2SO$: δ 3.14–3.26 (m, 8 H), 3.97 (s, 2 H), 7.18–7.24 (m, 4 H), 7.50–7.59 (m, 4 H) and 12.42 (NH). Mass spectrum: *m/z* 369 ($HL^+$).

Condensation between the bis(benzimidazoles) $L^1$, $L^3$, $L^4$ and $L^5$ and the required bromoalkane in the presence of NaH afforded the *N*-alkylated bis(benzimidazoles) $L^8$–$L^{12}$. Ligand $L^{13}$ was prepared in a similar manner.

1,3-*Bis(1′-dodecylbenzimidazol-2-yl)-2-thiapropane*, $L^8$.—To 1,3-bis(benzimidazol-2-yl)-2-thiapropane $L^1$ (2.07 g, 7.04 mmol) in freshly distilled, dry tetrahydrofuran (thf) (500 $cm^3$) under $N_2$ was added sodium hydride (0.68 g, 22.3 mmol of an 80% oil suspension). The mixture was heated to gentle reflux and a solution in dry thf (50 $cm^3$) of dry dodecyl bromide (3.68 g, 14.79 mmol) was added over a period of about 30 min. Reflux overnight afforded a bright orange solution. The solution was concentrated *in vacuo* to yield an orange syrup which was dissolved in chloroform, washed with water and dried over magnesium sulphate. Subsequent filtration followed by removal of solvent resulted in a yellow oil which was dissolved in ethanol. A cream-white solid was precipitated by the slow addition of water. Recrystallisation from an ethanol–water mixture yielded a cream solid (2.25 g, 51%). $^1H$ NMR in $(CD_3)_2SO$: δ 0.93 (t, 6 H), 1.27 (m, 36 H), 1.73 (m, 4 H), 4.23 (t, 4 H), 4.32 (s, 4 H), 7.23–7.34 (m, 4 H) and 7.57–7.70 (m, 4 H). Mass spectrum: *m/z* 631 ($HL^+$).

1,6-*Bis(1′-octylbenzimidazol-2-yl)-2,5-dithiahexane*, $L^{11}$.—Sodium hydride (0.056 g, 2.33 mmol of an 80% oil suspension) was added to a solution of 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane, $L^3$ (0.11 g, 31.1 mmol), in dry thf (40 $cm^3$) under $N_2$. After about 10 min the mixture was heated to gentle reflux and octyl bromide (0.120 g, 66.3 mmol) in dry thf (20 $cm^3$) was added dropwise over a period of 1 h to the brown mixture. Overnight reflux resulted in a deep orange-brown suspension. A small amount of water was added to the partially cooled solution to destroy any unreacted sodium hydride, followed by filtration and concentration *in vacuo* to yield an orange-brown syrup. The syrup was dissolved in chloroform (60 $cm^3$) and washed with water. The organic extracts were dried over magnesium sulphate and decolourised with charcoal. Further to purify the product, trituration with $Et_2O$ was performed (0.44 g, 38%). $^1H$ NMR in $CDCl_3$: δ 0.88 (t, 6 H), 1.21 (m, 20 H), 1.82 (m, 4 H), 2.78 (s, 4 H), 3.95 (s, 4 H), 4.15 (t, 4 H), 7.17–7.36 (m, 4 H) and 7.63–7.72 (m, 4 H). Mass spectrum: *m/z* 579 ($HL^+$).

1,6-*Bis(1′-dodecylbenzimidazol-2-yl)-2,5-dithiahexane*, $L^9$.—The general procedure described for $L^{11}$ was employed (yield 0.75 g, 35%). $^1H$ NMR in $CDCl_3$–$(CD_3)_2SO$ (1:1): δ 0.88 (t, 6 H), 1.26 (m, 36 H), 1.82 (m, 4 H), 2.81 (s, 4 H), 4.05 (s, 4 H), 4.19 (t, 4 H), 7.16–7.26 (m, 4 H), 7.39–7.41 (m, 2 H) and 7.58–7.60 (m, 2 H). Mass spectrum: *m/z* 691 ($HL^+$).

1,6-*Bis(1′-dodecyl-5′,6′-dimethylbenzimidazol-2-yl)-2,5-dithiahexane*, $L^{10}$.—The general procedure described for $L^{11}$ was employed, the final product being recrystallised from $Et_2O$ (yield 1.49 g, 75%). $^1H$ NMR in $CDCl_3$: δ 0.88 (t, 6 H), 1.25 (t, 36 H), 1.80 (t, 4 H), 2.35 (s, 6 H), 2.38 (s, 6 H), 2.73 (s, 4 H), 3.92 (s, 4 H), 4.09 (t, 4 H) and 7.44 (m, 4 H). Mass spectrum: *m/z* 747 ($HL^+$).

1,7-*Bis(1″-dodecylbenzimidazol-2-yl)-2,6-dithiaheptane*, $L^{12}$.—This ligand, prepared in a similar manner to $L^{11}$ was isolated after chromatography [eluent, ethyl acetate–light petroleum (7:3)], as an oil (0.88 g, 45%). $^1H$ NMR in $CDCl_3$–$(CD_3)_2SO$: δ 0.82 (t, 6 H), 1.20 (m, 36 H), 2.57 (t, 4 H), 1.79 (qnt, 2 H), 3.91 (s, 4 H), 4.14 (t, 4 H), 7.15 (m, 4 H), 7.36 (m, 2 H) and 7.52 (m, 2 H). Mass spectrum: *m/z* 704 ($L^+$).

N-*Dodecylbenzimidazole*, $L^{13}$.—The general procedure outlined for $L^{10}$ was employed. The final product was isolated as a light brown oil (9.52 g, 83%). $^1H$ NMR in $CDCl_3$: δ 0.84–0.91 (t, 3 H), 1.16–1.32 (m, 18 H), 1.88 (qnt, 2 H), 4.16 (t, 2 H), 7.24–7.43 (m, 3 H), 7.79–7.83 (m, 1 H) and 7.89 (s, 1 H). Mass spectrum: *m/z* 286 ($L^+$).

For any separations the support used for column chromatography was silica gel (TLC grade).

*Complexes*.—These were made by mixing equimolar solutions of metal salts and ligands in MeOH (for nitrate salts), or EtOH (for triflate salts). Silver complexes were formed with all of the ligands $L^{1-11}$. For the other metal salts, $Pb^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Cu^{2+}$, attempts were made to synthesise complexes only with some of the ligands $L^1$–$L^7$. No lead complexes could be isolated. No crystals of sufficient quality for X-ray analysis were obtained. Elemental analyses, melting points, fast atom bombardment (FAB) mass spectral and $^1H$ NMR data are contained in Tables 1, 2 and 3.

*Three-phase Transport*.—The ability of ligands $L^{8-13}$ to transport cations in both single- and multiple-ion experiments (more than one cation in the source phase) was determined using the procedure described previously.[7,13] The results are expressed as $J_m$, the number of moles of metal ion transported per 24 h $\times 10^{7}$. For ease of comparison with our earlier work[13] the values obtained for $J_m$ are subject to the same conversion factor of 1.14; this also allows for comparison with the work of Izatt and co-workers.[14,15] The results are shown in Figs. 1 and 2.

*Molecular Modelling*.—All ligands and their silver complexes were minimised with the COSMIC force field.[16] Silver parameters were developed using the method of Hopfinger and Pearlstein.[17] The calculations were terminated when the change in energy was less than $10^{-3}$ kcal $mol^{-1}$, or when the root-mean-squared energy gradient was less than 0.1 kcal $Å^{-1}$ (cal = 4.184 J). As in previous studies[13] it was assumed that both tertiary nitrogens and sulphurs were participating in co-ordination and an arbitrary charge of +0.5 was assigned to the silver. The organic part of the complex was assigned charges *via* a complete neglect of differential overlap (CNDO) calculation.

*Mass Spectral Competition Studies*.—All experiments were conducted on a Kratos MS80 instrument. A typical experiment involved two ligands both at a concentration of 0.017 mol $dm^{-3}$ and an equimolar amount of $AgNO_3$, all in dimethyl sulphoxide (dmso), together with $8 \times 10^{-1}$ mol $dm^{-3}$ tetrabutylammonium chloride in dmso (0.05 $cm^3$) as an internal standard. The abundance of ions at each *m/z* value corresponding to both the free ligand and cation–ligand complex was measured relative to the abundance of the internal standard tetrabutylammonium ion at *m/z* 242. The standard was assigned an arbitrary peak height of 10 units. Corrections were not made for sensitivity differences of the mass spectrometer at various *m/z* values. As discussed by Johnstone *et al.*[18] for the situation

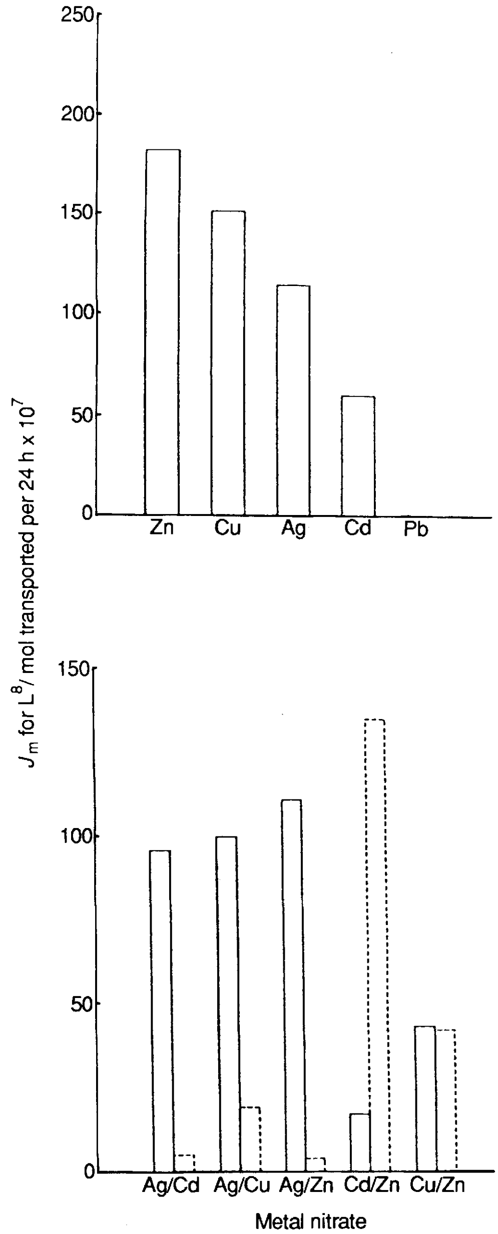


**Fig. 1** Bar charts illustrating transport of various nitrate salts in both isolation and competition by ligand $L^8$

corresponding to one metal cation and a number of ligands in any one experiment, these corrections would lead to small changes in relative abundances and are not necessary, particularly in a qualitative study.

*NMR Kinetic Studies.*—Separate mixtures were made up containing $AgNO_3$ and one of the ligands $L^1$–$L^7$ as a 1:1 mixture in $(CD_3)_2SO$. An assessment of the ABCD $\rightleftharpoons$ DCBA rates of exchange[19] (using DNMR3[20]) was then made. Only $L^1$, $L^2$, $L^5$ and $L^7$ exchanged sufficiently slowly on the NMR time-scale at room temperature for accurate shifts of protons A and D to be ascertained. Suitable shifts for the remaining ligands were taken from ligand $L^7$.

*Spectra.*—The NMR spectra were obtained on Brüker WB300 or WP200 spectrometers. Atomic absorption measurements were carried out on a Perkin-Elmer model 2380 spectrophotometer at the following wavelengths (in nm): Ag, 328.1; Pb, 283.3; Cu, 324.8; Zn, 213.9; Cd, 228.8. All samples were referenced against BDH standards. Fast atom bombardment mass spectra were obtained for the metal complexes on a Kratos MS80 instrument.

## Results and Discussion

A number of techniques have been employed to assess the selectivity of the ligands described ($L^{1-7}$) and their alkylated versions ($L^{8-13}$), in both single and multiple phases. The results obtained from the bulk liquid-membrane experiments show promise for the selective extraction of a number of metal nitrates, particularly for silver. However, a number of lipophilising syntheses had to be undertaken in order to render ligands $L^{1-7}$ suitable for use in the bulk liquid-membrane experiments (as $L^{8-12}$); accordingly, we sought possible alternative ways to assess metal selectivity, which might be applied in future, thus avoiding the need for lipophilisation of ligands under test.

The results pertaining to the silver transport are considered first. Ligands $L^1$, $L^3$, $L^4$ and $L^5$ were alkylated (*N*-dodecylated to $L^8$, $L^9$, $L^{10}$ and $L^{12}$ respectively), while $L^3$ was also octylated to $L^{11}$. The $J_m$ values (in parentheses) for transport of $AgNO_3$ in bulk chloroform liquid membranes were $L^{10}$(350), $L^9$(320), $L^{12}$(220), $L^{11}$(220), $L^8$(110) compared with the best ligands of the series we prepared previously,[13] $L^{14}$(280) and $L^{15}$(278), in units of mol per 24 h times $10^{7}$.

Membrane studies carried out on other cations indicated that some potentially useful separations had been effected. For ligand $L^8$ the order of transport ability was Zn > Cu > Ag > Cd $\gg$ Pb when the metals were present as single cation solutions, as may be seen in Fig. 1. For ligand $L^{10}$ the order, shown in Fig. 2, was Ag > Cu > Zn > Cd $\gg$ Pb. The longer bridge length of $L^{10}$ would appear more suitable for silver transport, while the shorter $L^8$ was apparently better for the smaller cations Cu and Zn. However, in competition experiments (see Figs. 1 and 2), where pairs of metal ions (equimolar) compete for transport by the ligand, $L^8$ selectively extracts Ag in preference to Cu or Zn. A selective extraction of Zn from Cd appears possible with ligand $L^8$, while ligand $L^{10}$ shows good selectivity for Ag over the other cations in pairwise competition, and a good Cu/Zn separation (see Fig. 2).

The results from FAB mass spectrometric competition experiments would suggest an order of complexing ability for the unalkylated ligands (see Table 4) of $L^5 > L^3 > L^6 > L^7 > L^2 > L^1$ from the provisional stability constant or selectivity ratio *R* [equation (1)]. From the values of *R* the order of

$$R = \frac{[ML][L']}{[ML'][L]} \tag{1}$$

stability constants in the chosen solvent dimethylformamide may be approximated, with the assumption that there are no major volatility differences between the individual ligands, nor between the individual silver complexes.

In order to make molecular mechanics calculations, a roughly tetrahedral geometry was assumed for the silver complexes. Conformations were found corresponding to energy minima for the free ligands, and also for the silver complexes in the assumed geometry, from several different starting conformations. The molecular dynamics technique was not available to us, thus the conformations sampled may not approach the global minimum. The ligands in order of least reorganisation energy were $L^6 > L^2 > L^5 \geqslant L^1 > L^3 > L^7$.

The unfunctionalised ligands had NMR spectra for the aromatic ABCD protons which could be interpreted in terms of an ABCD $\longleftrightarrow$ DCBA exchange. Earlier work[19] has shown that ligand exchange in such systems [in the presence of a metal ion, in that case cadmium(II)] is dependent on the rate of dissociation of the ML complex. The slowest exchange should thus denote the complex which is kinetically the most stable. In this work, the series of ligands $L^{1-7}$ (as 1:1 mixtures with $AgNO_3$) exhibited a clear gradation from slow exchange at room temperature to a fast exchange which could be slowed only at low temperatures. In a two-dimensional excitation spectroscopy (EXSY) experiment, with equimolar $AgNO_3$ and ligand in dimethyl sulphoxide–chloroform, an exchange correlation

**Table 1** Elemental analyses (calculated values in parentheses) and melting points of free ligands and complexes

| | | | Analysis (%) | | |
|---|---|---|---|---|---|
| Ligand or complex | M.p./°C | Formula | C | H | N |
| $L^2 + AgCF_3SO_3$ | 264–267 | $C_{18}H_{18}N_4S{\cdot}AgCF_3SO_3$ | 40.00 (39.40) | 3.40 (3.15) | 9.40 (9.65) |
| $L^3 + AgCF_3SO_3$ | 172–175 | $C_{18}H_{18}N_4S_2{\cdot}AgCF_3SO_3$ | 37.40 (37.75) | 2.95 (2.95) | 8.55 (9.15) |
| $L^5 + AgNO_3$ | 215–217 | $C_{19}H_{20}N_4S_2{\cdot}AgNO_3$ | 42.05 (42.40) | 3.75 (3.75) | 12.90 (13.00) |
| $L^6$ | 234–236 | $C_{17}H_{16}N_4S_2$ | 59.75 (59.95) | 4.70 (4.75) | 16.30 (16.45) |
| $L^6 + AgNO_3$ | 160–162 | $C_{17}H_{16}N_4S_2{\cdot}AgNO_3$ | 39.65 (40.00) | 3.00 (3.15) | 13.55 (13.70) |
| $L^6 + Cu(NO_3)_2{\cdot}2H_2O$ | 225–227 | $C_{17}H_{16}N_4S_2{\cdot}Cu(NO_3)_2{\cdot}2H_2O$ | 36.40 (36.20) | 3.35 (3.55) | 14.80 (14.90) |
| $L^7$ | 192–194 | $C_{19}H_{20}N_4S_2$ | 61.20 (61.95) | 5.40 (5.45) | 14.55 (14.55) |
| $L^7 + AgNO_3{\cdot}2H_2O$ | 160–162 | $C_{19}H_{20}N_4S_2{\cdot}AgNO_3{\cdot}2H_2O$ | 39.60 (39.75) | 3.35 (3.55) | 12.15 (12.20) |
| $L^7 + Cu(NO_3)_2{\cdot}2H_2O$ | 370* | $C_{19}H_{20}N_4S_2{\cdot}Cu(NO_3)_2{\cdot}2H_2O$ | 40.30 (39.75) | 3.70 (3.85) | 13.85 (14.65) |
| $L^8$ | 72–75 | $C_{40}H_{62}N_4S$ | 76.20 (76.15) | 10.30 (9.90) | 8.60 (8.90) |
| $L^8 + AgCF_3SO_3$ | 189–190 | $C_{40}H_{62}N_4S{\cdot}AgCF_3SO_3$ | 55.35 (55.45) | 7.05 (7.05) | 6.25 (6.30) |
| $L^9$ | 88–89 | $C_{42}H_{66}N_4S_2$ | 73.15 (73.00) | 9.80 (9.65) | 8.15 (8.10) |
| $L^9 + AgCF_3SO_3$ | 248–249 | $C_{42}H_{66}N_4S_2{\cdot}AgCF_3SO_3$ | 53.90 (54.50) | 6.95 (7.00) | 5.60 (5.90) |
| $L^{10}$ | 140–142 | $C_{46}H_{74}N_4S_2$ | 73.70 (73.95) | 10.05 (10.00) | 7.50 (7.50) |
| $L^{10} + AgCF_3SO_3$ | 179–180 | $C_{46}H_{74}N_4S_2{\cdot}AgCF_3SO_3$ | 55.40 (56.20) | 7.40 (7.45) | 5.45 (5.60) |
| $L^{11} + AgCF_3SO_3$ | 235–237 | $C_{34}H_{50}N_4S_2{\cdot}AgCF_3SO_3$ | 50.30 (50.30) | 5.85 (6.05) | 6.60 (6.70) |
| $L^{12}$ | Oil | | | | |
| $L^{13}$ | Oil | | | | |

* Decomposed.

**Table 2** NMR absorptions of complexed ligands (all complexes are 1:1 mixtures)

| Ligand | Aromatics | $SCH_2$ | Aryl–$CH_2$ | $R^1$ | R | NH | Solvent, salt |
|---|---|---|---|---|---|---|---|
| $L^2$ | 7.82–7.64 | | 3.43–3.30 | | | | *a*,*b* |
| $L^3$ | 7.85–7.76 | 3.03 | 4.32 | | | | *a*,*b* |
| | 7.50–7.41 | | | | | | |
| $L^5$ | 7.91–7.74 | 2.78(t) | 4.38 | | | 13.51 | *a*,*c* |
| | 7.50–7.42 | 2.11(q) | | | | | |
| $L^6$ | 7.81 | 4.18 | 4.41 | | | | *a*,*c* |
| | 7.43–7.37 | | | | | | |
| $L^7$ | 7.96–7.72 | 4.29 | 3.57 | | | | |
| | 7.47–7.45 | | 3.31 | | | 13.33 | *a*,*c* |
| $L^7$ | 7.61–7.50 | 3.96 | 3.27–3.16 | | | | |
| | 7.25–7.19 | | | | | | *a*,*d* |
| $L^8$ | 7.89–7.79 | | 4.27 | | 4.40 | | *a*,*b* |
| | 7.51–7.43 | | | | 1.94 | | |
| | | | | | 1.32 | | |
| | | | | | 0.94 | | |
| $L^9$ | 7.85–7.82 | 3.61 | 4.15 | | 4.32 | | *e*,*b* |
| | 7.61–7.58 | | | | 1.87 | | |
| | 7.41–7.32 | | | | 1.25 | | |
| | | | | | 0.87 | | |
| $L^{10}$ | 7.36 | 3.01 | 4.27 | 2.38 | 4.23 | | *e*,*b* |
| | 7.29 | | | 2.28 | 1.83 | | |
| | | | | | 1.24 | | |
| | | | | | 0.87 | | |
| $L^{11}$ | 7.71–7.66 | 2.93 | 4.27 | | 4.33 | | *a*,*b* |
| | 7.38–7.26 | | | | 1.84 | | |
| | | | | | 1.30 | | |
| | | | | | 0.92 | | |

[a] $(CD_3)_2SO$. [b] $AgCF_3SO_3$. [c] $AgNO_3$. [d] $Zn(NO_3)_2$. [e] $(CD_3)_2SO$–$CDCl_3$ (1:1).

was demonstrated between the AD protons and also between the B and C protons of the slowly exchanging $L^8$. A strong correlation of the solvent water and the exchangeable benzimidazole NH peak was also seen. Rates of exchange were compared for one-dimensional spectra at room temperature (using DNMR3) giving the order of exchange $L^1 > L^7 \geqslant L^5 > L^6 \gg L^3$.

No immediate method of assessing competition in a kinetic sense between any two ligands suggested itself. A more thorough comparison would require a more detailed study of the variation of exchange rates with composition, and would require separation of possible dissociative and associative contributions to the mechanism. However, qualitatively we can say that ligand $L^1$ forms the most kinetically stable silver complex, with $L^3$ the least stable, given similar formation rates for all complexes, and similar structures. Ligand $L^1$ would then be predicted to be the superior transporting agent for Ag in the bulk liquid membranes of those investigated here.

A similar technique was used to assess the kinetics of interaction of a number of different metal salts with one ligand ($L^3$). The exchange kinetics showed an order of kinetic stability Ag > Cd $\gg$ Pb. This is indeed the order in which cations are transported in three-phase membranes by the alkylated ligand $L^9$.

*Comparison of Methods.*—Given the limitations described in the earlier discussions, the results from the different methods may be compared. The mass spectrometric method described should give an approximate ordering related to the ligands $L^{1-7}$ in thermodynamic equilibrium with silver nitrate in dimethyl-

**Table 3** FAB mass spectrometry data for complexed ligands

| Complex | *m/z* |
|---|---|
| $L^2$ + $AgCF_3SO_3$[a] | 431 [L + $^{109}$Ag]$^+$<br>429 [L + $^{107}$Ag]$^+$ |
| $L^3$ + $AgCF_3SO_3$[a] | 463 [L + $^{109}$Ag]$^+$<br>461 [L + $^{107}$Ag]$^+$ |
| $L^5$ + $AgNO_3$[b] | 477 [L + $^{109}$Ag]$^+$<br>475 [L + $^{107}$Ag]$^+$ |
| $L^6$ + $AgNO_3$[b] | 449 [L + $^{109}$Ag]$^+$<br>447 [L + $^{107}$Ag]$^+$ |
| $L^6$ + $Cu(NO_3)_2$[c] | 403 [L + $^{63}$Cu]$^+$ |
| $L^7$ + $AgNO_3$[b] | 477 [L + $^{109}$Ag]$^+$<br>475 [L + $^{107}$Ag]$^+$ |
| $L^7$ + $Cu(NO_3)_2$[c] | 431 [L + $^{63}$Cu]$^+$ |
| $L^8$ + $AgCF_3SO_3$[a] | 739 [L + $^{109}$Ag]$^+$<br>737 [L + $^{107}$Ag]$^+$ |
| $L^{10}$ + $AgCF_3SO_3$[a] | 799 [L + $^{109}$Ag]$^+$<br>797 [L + $^{107}$Ag]$^+$ |
| $L^{11}$ + $AgCF_3SO_3$[a] | 855 [L + $^{109}$Ag]$^+$<br>853 [L + $^{107}$Ag]$^+$ |

[a] EtOH. [b] dmso. [c] MeOH.

**Table 4** Selectivity ratio *R* observed in competition between pairs of ligands for silver nitrate (analysed by FAB mass spectrometry)

| L | L′ | *R* |
|---|---|---|
| 1 | 2 | 1.45 |
| 1 | 3 | 0.24 |
| 1 | 5 | 0.06 |
| 1 | 6 | 0.35 |
| 1 | 7 | 0.62 |
| 2 | 3 | 0.23 |
| 2 | 5 | 0.04 |
| 2 | 6 | 0.47 |
| 2 | 7 | 0.16 |
| 3 | 5 | 0.18 |
| 3 | 6 | 1.87 |
| 3 | 7 | 1.55 |
| 5 | 6 | 5.17 |
| 6 | 7 | 0.93 |

formamide solution. The NMR method should give an indication of the kinetic ordering of the same ligands in solution in the mixed solvent dimethyl sulphoxide–chloroform. It is clear that the order of the ability of the alkylated ligands to transport silver in a three-phase transport (chloroform membrane) does not correspond to either of these. One explanation might be that the dodecylated versions of $L^1$ and $L^5$ (namely $L^8$ and $L^{12}$) are forming complexes with silver which are too stable to operate successfully in three-phase membrane transport. The molecular modelling results were not helpful in a predictive sense, probably reflecting the inadequacy of the tetrahedral geometry chosen. In general, the lack of common trends amongst the results indicates that neither thermodynamic data nor single-phase kinetic data alone are a reliable predictor of the selectivity of these alkylated ligands for $Ag^I$.

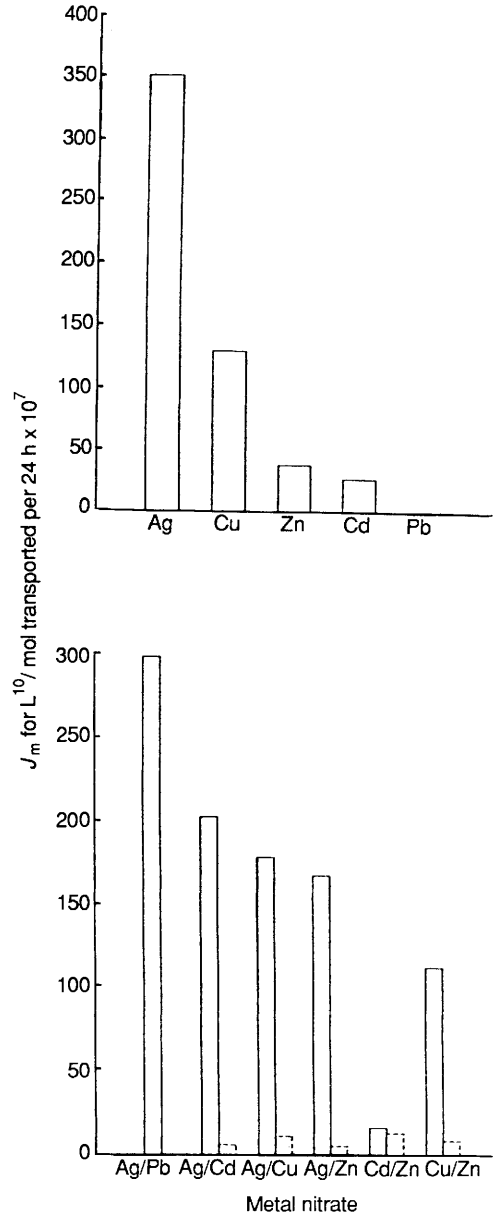


**Fig. 2** Bar charts illustrating transport of various nitrate salts in both isolation and competition by ligand $L^{10}$

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## References

1 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271; J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; G. W. Liesegang and E. M. Eyring, in *Synthetic Multidentate Compounds*, eds. R. M. Izatt and J. J. Christensen, Academic Press, New York, 1978, 289; J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Nelson, Plenum, New York, 1979, 145; N. S. Poonia and A. V. Bajaj, *Chem. Rev.*, 1979, **79**, 389; F. de Jong and D. N. Reinhoudt, *Adv. Phys. Org. Chem.*, 1980, **17**, 279.
2 E. L. Cressler and D. L. Evans, *Sep. Purif. Methods*, 1974, **3**, 399.
3 J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Neilsen, B. W. Asay and R. M. Izatt, *J. Am. Chem. Soc.*, 1980, **102**, 6820.
4 J. P. Behr, M. Kirch and J. M. Lehn, *J. Am. Chem. Soc.*, 1985, **107**, 241.
5 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103**, 1054, 1384.
6 J. C. Lockhart, in *Advances in Inorganic Bioinorganic Mechanisms*, ed. A. G. Sykes, Academic Press, New York, 1982, **1**, 217; J. C. Lockhart, *J. Chem. Soc., Faraday Trans. 1*, 1986, 1161.
7 J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1988, 1293.
8 R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen and J. J. Christensen, *Inorg. Chim. Acta*, 1978, **30**, 1.
9 L. F. Lindoy, *Prog. Macrocyclic Chem.*, 1987, **3**.
10 F. Arnaud-Neu, B. Spiess and M. J. Schwing-Weill, *Helv. Chim. Acta*, 1977, **60**, 2633.
11 R. F. Tylecote, *Metallurgy in Archaeology: A Prehistory of Metallurgy in the British Isles*, Edward Arnold, London, 1962.
12 M. A. Phillips, *J. Chem. Soc.*, 1928, 2393.

13 K. I. Kinnear, J. C. Lockhart and D. J. Rushton, *J. Chem. Soc., Dalton Trans.*, 1990, 1365.

14 R. M. Izatt, D. V. Dearden, P. R. Brown, J. S. Bradshaw, J. D. Lamb and J. J. Christensen, *J. Am. Chem. Soc.*, 1983, **105**, 1785.

15 J. D. Lamb, R. M. Izatt, D. G. Garrick, J. S. Bradshaw and J. J. Christensen, *J. Membr. Sci.*, 1981, **9**, 3.

16 J. G. Vinter, A. Davis and M. R. Saunders, *J. Computer-Aided Mol. Design*, 1987, **1**, 31.

17 A. J. Hopfinger and R. Pearlstein, *J. Comput. Chem.*, 1984, **5**, 486.

18 R. A. W. Johnstone, I. A. S. Lewis and M. E. Rose, *Tetrahedron*, 1983, **39**, 1597.

19 J. C. Lockhart, W. Clegg, M. N. S. Hill and D. J. Rushton, *J. Chem. Soc., Dalton Trans.*, 1990, 3541.

20 D. A. Kleier and G. Binsch, *J. Magn. Reson.*, 1971, **4**, 99.

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