Selectivity in Transport

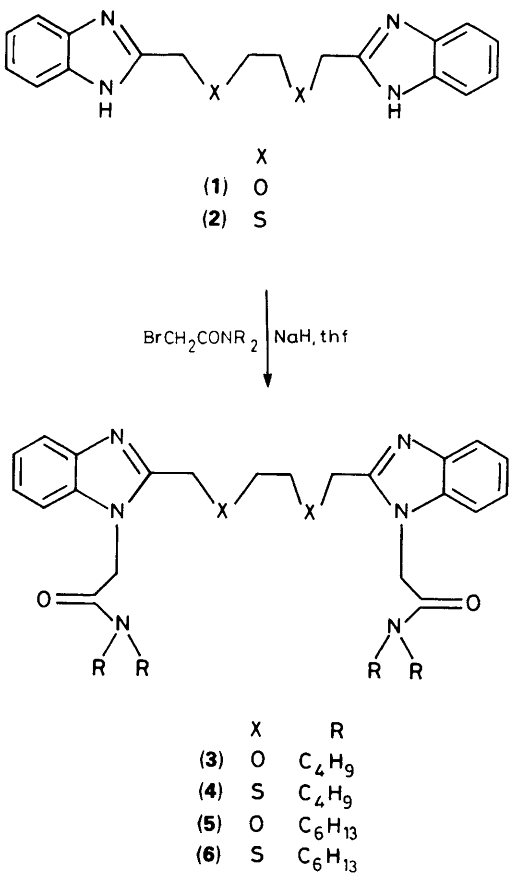
Kenneth I. Kinnear, Joyce C. Lockhart,* and David J. Rushton
Chemistry Department, The University of Newcastle upon Tyne, NE1 7RU

A series of bis benzimidazole ligands, bridged by additional donor groups (ether, thioether) and with pendant carboxylic amide groups, was prepared. In three-phase transport experiments using one quadridentate ligand and metal nitrates, the sequence $Ag^+ \approx Cu^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$ was observed for rates of single-ion transport. In pairwise comparisons of mixtures of two salts, potentially useful discriminations between Ag^+ and Pb^{2+}, Ag^+/Cu^{2+}, Ag^+/Zn^{2+}, Ag^+/Cd^{2+}, Cu^{2+}/Zn^{2+}, and Cd^{2+}/Zn^{2+} were also observed. The complexation behaviour of several ligands with Pb^{2+} and Ag^+ in a single phase was further screened in an attempt to explain the observed discrimination between these cations, either in solid or solution, with ^1H and ^{13}C n.m.r., i.r., and fast atom bombardment (f.a.b.) mass spectrometric techniques. Evidence for complexes of Ag^+ was found for each ligand, with each technique. However for Pb^{2+} only the ligands with benzimidazole plus ether donors showed any tendency to complex; although solids with a 1 : 1 ligand : metal salt composition could be isolated, only one could be verified as a complex in the f.a.b. experiment. Solid complexes with a 1 : 1 composition were isolated for the nitrate salts of Cd^{2+}, Cu^{2+}, and Zn^{2+}.

Ion recognition is the simplest form of molecular recognition, since only a simple shape has to be accommodated, and ions exhibit differences in size, charge, and softness which can be distinguished by ligands of suitable design. We have found benzimidazoles useful ligand components, since they can be multiply linked into facultative ligands with other groups.[1] The unsubstituted ones are sparingly soluble in organic solvents, but modified ligands can be produced by substitution on the secondary nitrogen.[2,3] Many benzimidazoles have been used as histidine mimics in efforts to model the environment of Zn^{2+} and Cu^{2+} in biological systems.[3,4] Ligands with carboxyl side chains[5] were originally produced as models of the A23187 ionophore[6] calcimycin, which shows discrimination for divalent ions, probably kinetic in nature, and which can distinguish Mg and Ca. Subsequently, a paper by Reed and co-workers[7] appeared, describing similarly substituted mono benzimidazoles, which were used to derivatise porphyrins. Grey's bis benzimidazoles[5] showed selectivity towards calcium, but were too hydrophilic for use in extractive processes or ion-selective electrodes. However, it has been shown that lead can be selectively complexed in preference to calcium by hydrophobic amide ligands (intended for ion-selective electrode work with calcium[8]). The ligands described here have amide side chains suitably modified with hydrophobic alkyl groups, and were tested for their ability to transport a range of ions, Ag^+, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, judged to be of current interest. The ligands and their lead and silver complexes were also examined by n.m.r. spectroscopy to examine the very high discriminatory power between lead and silver observed in three-phase transport.

Experimental

The bis benzimidazoles (**1**) and (**2**) were prepared by means of a Phillips condensation reaction,[9] following literature methods. 2-Bromo-*N*,*N*-dibutylacetamide was prepared using the method of Weaver and Whaley,[10] which was adapted to prepare the hexyl analogue 2-bromo-*N*,*N*-dihexylacetamide also. Condensation between the bis benzimidazoles (**1**) and (**2**) and the required substituted bromoacetamide in the presence of NaH base afforded the bis benzimidazole amides (**3**)—(**6**) in good yields. The preparation of (**6**) is quoted here as a representative example.



	X
(**1**)	O
(**2**)	S

	X	R
(**3**)	O	C_4H_9
(**4**)	S	C_4H_9
(**5**)	O	C_6H_{13}
(**6**)	S	C_6H_{13}

1,6-Bis[1′-(dihexylcarbamoylmethyl)benzimidazol-2′-yl]-2,5-dithiahexane (**6**).—Sodium hydride (0.36 g of an 80% oil suspension) was added to a solution of 1,6-bis(benzimidazol-2′-yl)-2,5-dithiahexane (**2**) (1.33 g, 3.74×10^{-3} mol) in dry tetrahydrofuran (500 cm^3) under N_2. After 20 min the mixture was heated to reflux and 2-bromo-*N*,*N*-dihexylacetamide (2.52 g, 8.24×10^{-3} mol) in dry tetrahydrofuran (30 cm^3) was added

Table 1. Elemental analyses and melting points of free ligands and complexes

Ligand/Complex	M.p. (°C)	Formula	Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N
(3)	Liquid	$C_{38}H_{56}N_6O_4$						
(3) + $AgNO_3$	250—251	$C_{38}H_{56}N_6O_4{\cdot}AgNO_3$	54.80	6.70	11.70	54.95	6.80	11.80
(3) + $Pb(NO_3)_2$	209—211	$C_{38}H_{56}N_6O_4{\cdot}Pb(NO_3)_2{\cdot}H_2O$	45.20	5.50	11.05	45.20	5.80	11.10
(4)	183—185	$C_{38}H_{56}N_6O_2S_2$	65.35	8.05	11.80	65.85	8.15	12.15
(4) + $AgNO_3$	212—214	$C_{38}H_{56}N_6O_2S_2{\cdot}AgNO_3$	52.60	6.40	11.25	52.90	6.55	11.35
(5)	58—60	$C_{46}H_{72}N_6O_4$	71.70	9.40	10.70	71.45	9.40	10.85
(5) + $AgNO_3$	208—210	$C_{46}H_{72}N_6O_4{\cdot}AgNO_3{\cdot}0.165\ H_2O$	56.40	7.35	9.90	56.80	7.80	10.10
(5) + $Pb(NO_3)_2$	131—133	$C_{46}H_{72}N_6O_4{\cdot}Pb(NO_3)_2$	49.80	6.45	10.05	50.05	6.55	10.15
(5) + $Zn(NO_3)_2$	222—224	$C_{46}H_{72}N_6O_4{\cdot}Zn(NO_3)_2$	56.85	7.50	11.60	57.40	7.55	11.65
(5) + $Cd(NO_3)_2$	234—238	$C_{46}H_{72}N_6O_4{\cdot}Cd(NO_3)_2$	55.15	7.00	11.70	54.75	7.20	11.10
(5) + $Cu(NO_3)_2$	151—153	$C_{46}H_{72}N_6O_4{\cdot}Cu(NO_3)_2$	57.55	7.50	11.60	57.50	7.55	11.65
(6)	81.5—82.5	$C_{46}H_{72}N_6O_2S_2$	68.90	9.00	10.45	68.60	9.00	10.45
(6) + $AgNO_3$	168—169	$C_{46}H_{72}N_6O_2S_2{\cdot}AgNO_3{\cdot}0.75\ H_2O$	55.95	7.20	9.75	55.95	7.45	9.95

Table 2. Infrared and mass spectrometry data

Ligand/salt	Measured mass Calc.	Measured mass Found	Mass spectrum (f.a.b.)	I.r. (cm^{-1})^a ν(C=O)
(3)	660.4363	660.4369	660 M^+	1 660^b
(4)	692.3902	692.3906	693.5 $[M + 1]^+$	1 650
(5)	772.5615	772.5607	772 M^+	1 660^b
(6)	No data		806 $[M + 2]^+$, 804 M^+	1 650
(3) + $AgNO_3$			769 $[M + {}^{109}Ag]^+$ 767 $[M + {}^{107}Ag]^+$, $[M - 2 + {}^{109}Ag]^+$ 765 $[M - 2 + {}^{107}Ag]^+$	1 665
(4) + $AgNO_3$			823 $[M + {}^{109}Ag + Na]^+$ 821 $[M + {}^{107}Ag + Na]^+$ 801 $[M + {}^{109}Ag]^+$ 799 $[M + {}^{107}Ag]^+$	1 650
(5) + $AgNO_3$			881 $[M + {}^{109}Ag]^+$ 879 $[M + {}^{107}Ag]^+$, $[M - 2 + {}^{109}Ag]^+$ 877 $[M - 2 + {}^{107}Ag]^+$	1 660
(6) + $AgNO_3$			913 $[M + {}^{109}Ag]^+$ 911 $[M + {}^{107}Ag]^+$	1 650
(3) + $Pb(NO_3)_2$			No sign of lead	1 660
(5) + $Pb(NO_3)_2$			1 043 $[M + {}^{208}PbHNO_3]^+$	1 650
(5) + $Zn(NO_3)_2$			898.0 $[M + Zn(NO_3)]^+$	
(5) + $Cu(NO_3)_2$			835.0 $[M + Cu]^+$	
(5) + $Cd(NO_3)_2$			948.0 $[M + Cd(NO_3)]^+$	

[a] All spectra recorded as KBr discs except where noted. [b] Capillary film.

dropwise with stirring to the bright green mixture. Overnight reflux afforded a solution with an orange-brown suspension. The solution was filtered and concentrated *in vacuo* yielding a brown syrup. Purification of this syrup (flash chromatography, eluant ethyl acetate) gave a yellow oil which crystallised from diethyl ether as a colourless powder, (6) (2.10 g, 70% yield), m.p. 81.5—82.5 °C.

Compound (4) was isolated in a similar manner as a colourless powder (1.02 g, 64% yield), m.p. 183—185 °C. Compound (5), isolated after chromatography, was an oil which crystallised after storage at 25 °C for approximately 1 month as a colourless powder (3.54 g, 98% yield), m.p. 58—60 °C. Despite numerous attempts at crystallisation, the oxygen-containing ligand (3) remained as a colourless oil (2.22 g, 93%).

Analytical and spectroscopic data used to characterise the ligands are given in Tables 1—4. Since (3) was an oil, elemental analyses for its solid metal complex derivatives were obtained for characterisation (shown in Table 1).

Complexes.—These were made by mixing equimolar solutions of metal salts and ligands in methanol or other appropriate solvents, and were sometimes obtained from solutions used for n.m.r. spectroscopy. Lead complexes are formed with the oxygen donor ligands (3) and (5) but not with the sulphur analogues. Data characterising the complexes are given in Tables 1—4. Unfortunately none of these gave crystals of sufficient quality for *X*-ray analysis.

Three-phase Transport.—The ability of several ligands to transport cations in three-phase experiments and to select between two cations in competitive experiments was determined using the apparatus [11] previously described, modified as follows. Stirrers, which were included in the receiving aqueous phase to guard against concentration gradients during sampling, assisted the faster attainment of a consistent J_m value [12] [where J_m is the (number of moles of metal ion transported per 24 h) × 10^7]. Results were reproducible within ±25%. The aqueous phase was sampled with a specially designed Teflon-tipped syringe, since it had been noted that metal syringes caused disproportionation of silver salts. Time-dependent studies were carried out to deduce the time range over which the receiving

Table 3. Proton n.m.r. absorptions of free and complexed ligands

Ligand	Aromatics	O=C–CH$_2$	XCH$_2$ (aryl)	X–CH$_2$	N–CH$_2$	CH$_2$	CH$_3$
(**3**)[a]	7.79—7.69 (2 H) 7.30—7.20 (4 H) 7.10—6.95 (2 H)	4.79	4.78	3.61	3.27—3.10	1.62—1.13	1.08—0.80
(**3**)	7.74—7.68 (2 H) 7.52—7.47 (2 H) 7.37—7.24 (4 H)	5.29	4.76	3.60	3.38—3.23	1.64—1.19	1.04—0.88
(**3**)[b]	8.10—8.05 (2 H) 7.80—7.73 (2 H) 7.60—7.45 (4 H)	5.51	5.00	3.97	3.53 (4 H) 3.38 (4 H)	1.79 (4 H) 1.60—1.45 (8 H) 1.42—1.23 (4 H)	1.10 (6 H) 0.96 (6 H)
(**3**)[c]	7.73—7.68 (2 H) 7.52—7.47 (2 H) 7.37—7.20 (4 H)	5.30	4.77	3.60	3.40—3.23	1.64—1.22	1.04—0.89
(**3**)[d]	7.73—7.70 (2 H) 7.51—7.48 (2 H) 7.34—7.25 (4 H)	5.30	4.77	3.62	3.39—3.23	1.62—1.22	1.01—0.89
(**3**)[e]	8.08—8.05 (2 H) 7.78—7.75 (2 H) 7.60—7.45 (4 H)	5.50	4.99	3.97	3.52 (4 H) 3.37 (4 H)	1.80 (4 H) 1.58—1.46 (8 H) 1.46—1.27 (4 H)	1.09 (6 H) 0.94 (6 H)
(**4**)[a]	7.72—7.64 (2 H) 7.29—7.19 (4 H) 7.18—7.10 (2 H)	5.10	3.93	2.68	3.39—3.29	1.81—1.11	1.07—0.86
(**4**)	7.67—7.64 (2 H) 7.46—7.43 (2 H) 7.32—7.22 (4 H)	5.33	4.06	2.76	3.50—3.29	1.73—1.31	1.01—0.90
(**4**)[b]	8.00—7.97 (2 H) 7.67—7.64 (2 H) 7.49—7.42 (4 H)	5.49	4.32	2.96	3.54—3.33	1.82—1.11	1.11—0.92
(**5**)[a]	7.78—7.69 (2 H) 7.31—7.20 (4 H) 7.17—7.00 (2 H)	4.81	4.80	3.61	3.26—3.10	1.62—1.23	0.97—0.81
(**5**)	7.74—7.67 (2 H) 7.51—7.46 (2 H) 7.37—7.24 (4 H)	5.29	4.77	3.61	3.41—3.23	1.64—1.30	1.02—0.88
(**5**)[b]	8.11—8.05 (2 H) 8.00—7.74 (2 H) 7.60—7.47 (4 H)	5.51	5.00	3.97	3.52 (4 H) 3.37 (4 H)	1.80—1.32	1.02 (6 H) 0.93 (6 H)
(**5**)[c]	7.73—7.62 (2 H) 7.51—7.45 (2 H) 7.37—7.24 (4 H) 7.37—7.24 (4 H)	5.29	4.77	3.61	3.36 (4 H) 3.25 (4 H)	1.63—1.29	1.00—0.88
(**5**)[f]	7.73—7.70 (2 H) 7.54—7.51 (2 H) 7.37—7.28 (4 H)	5.32	4.79	3.64	3.39 (4 H) 3.29 (4 H)	1.65—1.29	1.00—0.90
(**5**)[g]	7.81 (2 H) 7.57 (2 H) 7.40—7.35 (4 H)	5.36	4.84	3.71	3.42 (4 H) 3.29 (4 H)	1.68—1.30	0.98—0.90
(**6**)[a]	7.72—7.63 (2 H) 7.27—7.09 (6 H)	5.04	3.92	2.67	3.38—3.25	2.01—1.15	0.97—0.80
(**6**)	7.67—7.63 (2 H) 7.45—7.43 (2 H) 7.31—7.22 (4 H)	5.33	4.06	2.76	3.50—3.29	1.73—1.31	1.01—0.90
(**6**)[b]	7.90—7.87 (2 H) 7.57—7.54 (2 H) 7.39—7.32 (4 H)	5.38	4.20	2.81	3.43—3.22	1.67—1.20	0.93—0.80
(**6**)[d]	7.67—7.54 (2 H) 7.46—7.43 (2 H) 7.31—7.23 (4 H)	5.33	4.05	2.76	3.50—3.29	1.73—1.31	1.01—0.80
(**6**)[e]	7.90—7.87 (2 H) 7.57—7.53 (2 H) 7.36—7.33 (4 H)	5.38	4.21	2.84	3.43—3.22	1.67—1.21	0.93—0.80

Solvent $(CD_3)_2SO$ unless otherwise stated. Salts added in 1 mol equivalents unless otherwise stated. X = O for (**3**) and (**5**), S for (**4**) and (**6**).
[a] Solvent $CDCl_3$. [b] $AgNO_3$. [c] $Pb(NO_3)_2$. [d] 5 mol $Pb(NO_3)_2$. [e] $AgNO_3$ + 5 mol $Pb(NO_3)_2$. [f] $Zn(NO_3)_2$. [g] $Cd(NO_3)_2$.

phase should be sampled. This is significantly less when there are stirrers in the receiving phase, than for unstirred systems. For single-cation experiments the concentration of metal nitrate salt in the source phase was 1 mol dm^{-3} in metal cation, and for competition experiments both metal nitrate salts were 0.5 mol dm^{-3} in metal ion allowing ease of comparison with the results of Izatt and co-workers.[13,14] However, the results cannot be compared directly since the apparatus used was different. As standards we employed transport of Pb^{2+} and Ag^{+} by the compounds dicyclohexyl-18-crown-6{eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexa-oxacyclo-octadecine,(**A**)} and dibenzo-18-crown-6(6,7,9,10,17,18,20,21-octahydrodibenzo-

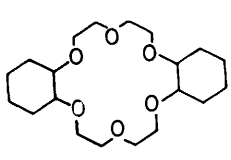
Table 4. Carbon-13 chemical shifts (p.p.m.) and relaxation times (s)[a]

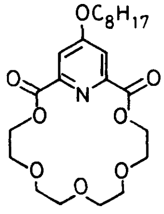
Ligand/salt[b]	Carbonyl	Aromatic	O=C–CH$_2$–N X–CH$_2$ (aryl)[c] X–CH$_2$	N–CH$_2$ (alkyl)	Aliphatic
(3)[d]	165.00 (1.99)	150.59 (2.31)	108.96 (0.24)	46.47 (0.19)	30.71 (0.30)
		141.81 (2.43)	69.16 (0.20)	45.70 (0.17)	29.35 (0.38)
		135.95 (2.64)	66.29 (0.17)	44.20 (0.14)	19.82 (0.94)
		122.86 (0.27)			19.68 (0.67)
		121.79 (0.27)			13.65 (1.35)
		119.64 (0.23)			13.50 (1.49)
(3)	169.46 (1.47)	155.05 (1.40)	114.10 (0.19)	50.06 (0.11)	34.40 (0.18)
		145.75 (1.60)		49.11 (0.14)	33.30 (0.22)
		140.38 (1.67)	72.93 (0.13)	48.44 (0.10)	23.52 (0.48)
		126.27 (0.17)	69.51 (0.11)		23.45 (0.42)
		125.35 (0.18)			17.64 (1.15)
		123.03 (0.18)			
(3)[e]	168.74 (1.88)	157.97 (1.86)	114.92 (0.19)	50.30 (0.14)	34.38 (0.25)
		143.63 (2.03)		49.27 (0.16)	33.24 (0.34)
		138.67 (2.16)	74.05 (0.17)	48.54 (0.07)	23.61 (0.52)
		127.75 (0.20)	67.21 (0.14)		23.50 (0.72)
		127.28 (0.21)			17.77 (1.35)
		122.83 (0.18)			17.69 (1.56)
(5)[d]	164.96 (2.07)	150.59 (1.96)	108.90 (0.25)	46.62 (0.13)	31.26 (0.69)
		141.73 (2.75)	69.09 (0.18)	45.89 (*f*)	31.11 (0.94)
		135.88 (1.86)	66.18 (0.16)	44.20 (0.30)	28.54 (0.22)
		122.76 (0.20)			27.18 (0.23)
		121.69 (0.22)			26.22 (0.54)
		119.56 (0.26)			26.11 (0.52)
					22.25 (1.47)
					13.68 (2.20)
(5)	169.44 (1.27)	155.03 (1.20)	114.01 (0.16)	50.26 (0.10)	35.04 (0.45)
		154.85 (1.84)	72.87 (0.13)	49.34 (0.10)	34.93 (0.62)
		145.91 (1.86)	69.49 (0.11)	48.46 (0.10)	32.29 (0.15)
		145.77 (1.52)			31.08 (0.15)
		140.33 (1.68)			29.97 (0.29)
		126.14 (0.17)			29.86 (0.26)
		125.25 (0.16)			26.04 (0.82)
		122.98 (0.15)			17.80 (1.54)
(5)[e]	168.64 (2.33)	157.87 (1.86)	114.78 (0.16)	50.45 (0.14)	34.94 (0.77)
		143.57 (2.56)	73.98 (0.15)	49.46 (0.14)	34.83 (0.88)
		138.57 (2.22)	67.18 (0.17)	48.46 (0.13)	32.22 (0.22)
		127.58 (0.19)			30.93 (0.22)
		127.17 (0.18)			29.94 (0.41)
		122.65 (0.17)			29.79 (0.55)
					26.04 (1.43)
					25.86 (1.56)
					17.77 (2.63)
					17.66 (4.46)
(5)[g]	169.51 (2.04)	155.21 (1.90)	114.15 (0.18)	50.34 (0.13)	35.04 (0.55)
		145.69 (2.08)	72.94 (0.14)	49.38 (0.14)	34.97 (0.57)
		140.36 (1.90)	69.45 (0.12)	48.50 (0.11)	32.32 (0.17)
		126.28 (0.19)			31.08 (0.19)
		125.44 (0.19)			29.97 (0.34)
		123.01 (0.17)			29.90 (0.31)
					26.11 (1.05)
					17.91 (1.77)
(6)	169.26 (1.45)	155.40 (1.45)	113.90 (0.19)	50.45 (0.10)	35.15 (0.34)
		145.91 (1.26)	34.38 (0.13)	49.68 (0.08)	35.04 (0.38)
		140.44 (1.55)	30.82 (0.11)	49.49 (0.10)	32.47 (0.14)
		140.29 (1.48)		48.53 (0.09)	31.08 (0.14)
		125.77 (0.18)			30.06 (*f*)
		125.14 (0.16)			30.01 (0.24)
		122.61 (0.17)			26.19 (0.58)
					26.11 (0.65)
					17.84 (1.42)
					17.77 (1.38)
(6)[e]	168.89 (1.33)	157.24 (1.52)	114.89 (0.18)	50.63 (0.10)	35.15 (0.40)
		143.60 (1.30)	35.60 (0.09)	49.64 (0.09)	35.04 (0.48)
		139.48 (1.26)	31.59 (0.11)	48.98 (0.10)	32.44 (0.13)
		127.46 (0.18)			31.08 (0.14)
		126.98 (0.16)			30.12 (0.23)
		122.24 (0.18)			30.01 (0.23)
					26.26 (0.71)
					26.08 (0.80)
					17.95 (1.39)
					17.88 (1.56)

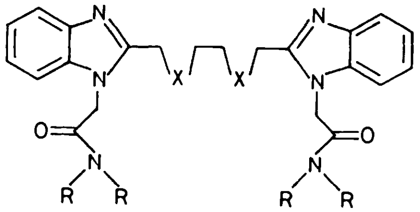
Table 4 (*continued*)

Ligand/salt[b]	Carbonyl	Aromatic	O=C–CH$_2$–N X–CH$_2$ (aryl)[c] X–CH$_2$	N–CH$_2$ (alkyl)	Aliphatic
(6)[g]	169.51 (1.31)	155.69 (1.38)	114.19 (0.21)	50.67 (0.16)	35.23 (0.52)
		145.88 (1.49)	34.64 (0.11)	49.68 (0.23)	35.16 (0.55)
		140.44 (1.44)	31.00 (0.09)	48.71 (*f*)	32.62 (0.07)
		126.32 (0.27)			31.22 (0.14)
		126.14 (0.25)			30.16 (0.33)
		125.51 (0.15)			26.30 (0.93)
		122.76 (0.29)			26.22 (0.96)
					18.02 (1.86)

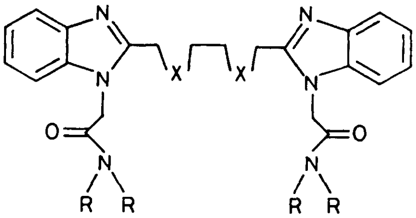
[a] All spectra run in $(CD_3)_2SO$ unless otherwise stated. [b] All salts added in 1 mol equivalents. [c] X = O for (3) and (5), S for (4) and (6). [d] In $CDCl_3$. [e] $AgNO_3$. [f] Uncertain value for T_1. [g] $Pb(NO_3)_2$.


(A)

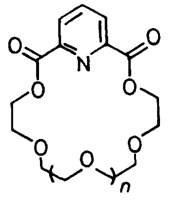

(B)

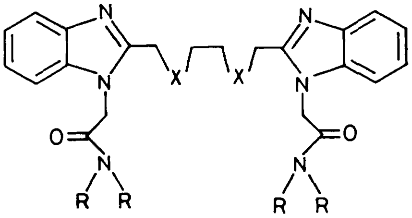

X = S, R = C_6H_{13}

(C) *i.e.* (6)

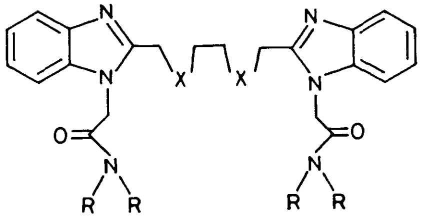

X = S, R = C_4H_9

(D) *i.e.* (4)

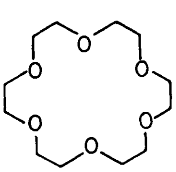

(E) *n* = 1

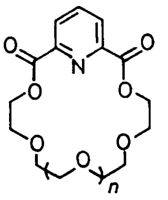

X = O, R = C_6H_{13}

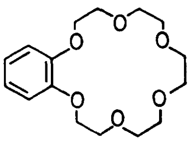
(F) *i.e.* (5)

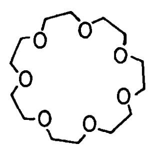

X = O, R = C_4H_9

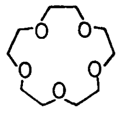
(G) *i.e.* (3)


(H)


(I) *n* = 2


(J)


(K)


(L)

[*b,k*][1,4,7,10,13,16]hexa-oxacyclo-octadecine), previously used by Izatt and co-workers,[13,14] and used a conversion factor *f*, equal to 1.14 [equation (1)], to effect the comparison. The

$$f = \frac{\text{(results from literature)}}{\text{(results from standards)}} \qquad (1)$$

results, which are shown diagrammatically in Figures 3—7, show the experimental data for our compounds multiplied by the conversion factor *f*, to allow direct comparison with those ligands investigated previously.[13,14]. Unavoidably, since Ag^+ is monovalent and the other cations are divalent, the concentration of nitrate is not constant throughout the series. To assess the effect of variable nitrate concentration, additional experiments in which $NaNO_3$ or $Pb(NO_3)_2$ was used to supply extra nitrate were carried out. Results are in Table 5. Because of the light-sensitive nature of silver compounds, all equipment containing silver salts was protected against light by aluminium foil, and placed in darkened rooms where appropriate.

Spectra.—N.m.r. spectra were obtained on Brüker WB300 or WP200 spectrometers. Some results are shown schematically in Figures 1 and 2. Atomic absorption measurements were carried out on a Perkin-Elmer model 2380 spectrophotometer at the following wavelengths: Ag, 328.1; Pb, 283.3; Cu, 324.8; Zn, 213.9; Cd, 228.8 nm. All samples were referenced against BDH standards. Infrared spectra were recorded for the ligands and their complexes on an FTIR Nicolet 20SXB instrument. Fast atom bombardment (f.a.b.) mass spectra were obtained for the metal complexes wherever feasible on a Kratos MS80 instrument.

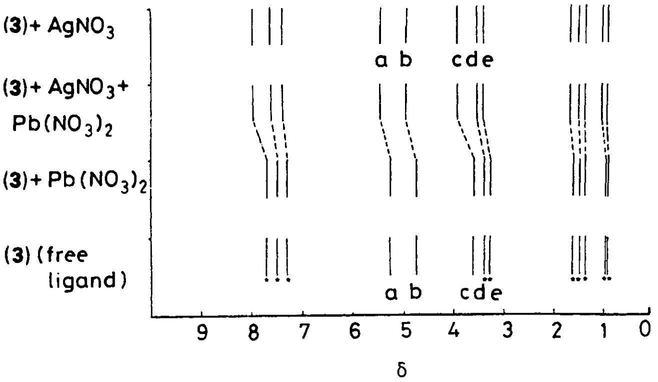


Figure 1. Bar chart illustrating chemical shifts in the ^1H n.m.r. spectra of ligand (**3**) due to the selective complexation of Ag^+ over Pb^{2+}. The δ values of the signals labelled with a * are the centres of multiplets. a = $CH_2C(O)N$, b = (aryl)CH_2X, c = XCH_2CH_2X, d and e = $CH_2NC(O)$. All spectra run in $(CD_3)_2SO$

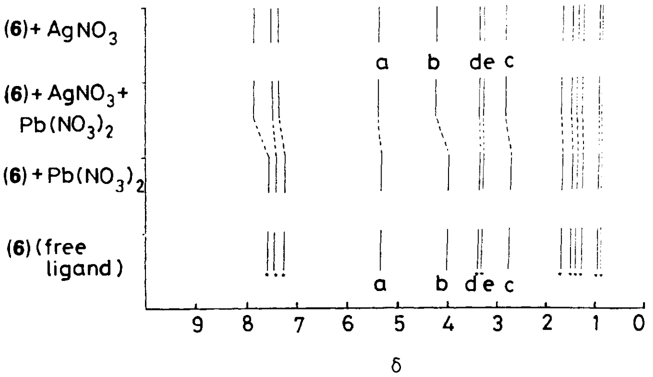


Figure 2. Bar chart illustrating chemical shifts in the ^1H n.m.r. spectra of ligand (**6**) due to the selective complexation of Ag^+ over Pb^{2+}. Details as in Figure 1

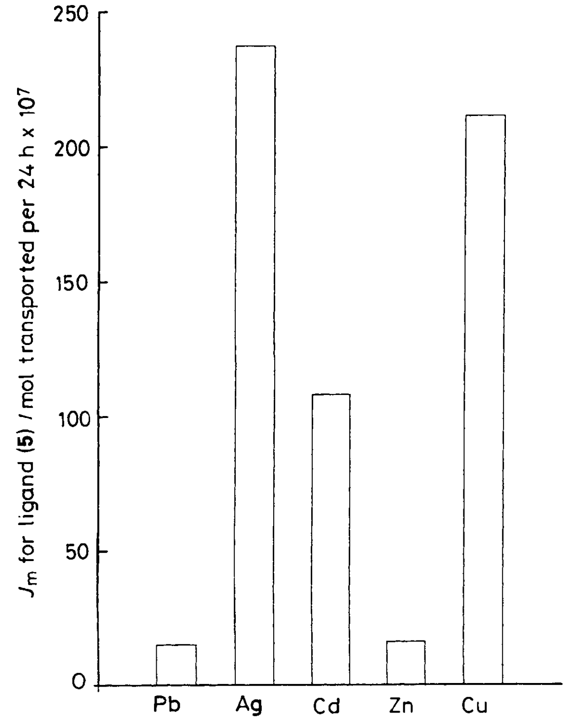


Figure 3. Bar chart illustrating transport of nitrate salts by ligand (**5**)

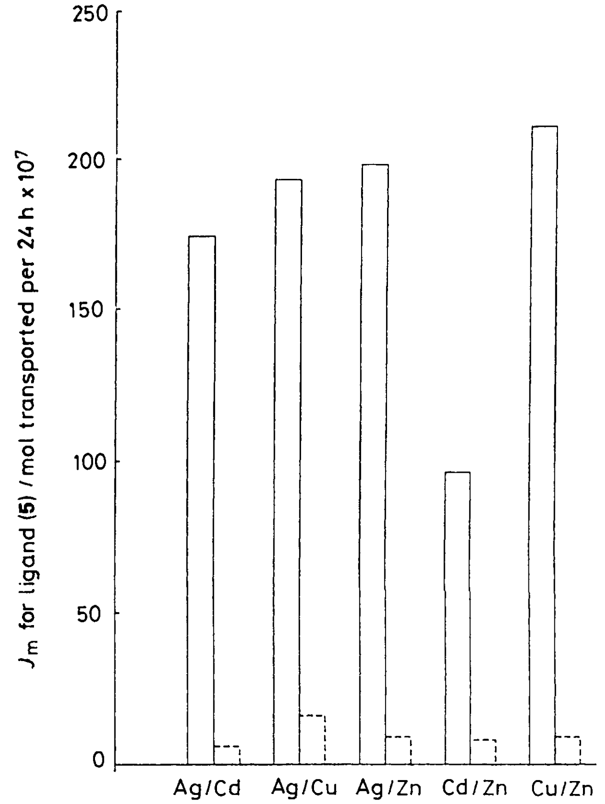


Figure 4. Bar chart illustrating competitive transport of nitrate salts by ligand (**5**)

Table 5. Effect of nitrate concentration on transport of Ag^+ by ligand (**5**)

Concentration/mol dm^{-3}			J_m/mol (24 h)$^{-1}$ × 10^7
$AgNO_3$	$Pb(NO_3)_2$	$NaNO_3$	
1.0	0.0	0.0	237
0.5	0.5	0.0	230
0.1	0.9	0.0	172
0.1	0.0	0.9	177

Results and Discussion

Some new facultative ligands (**3**)—(**6**) were synthesised, and solid 1:1 complexes of ligand (**5**) with nitrates of Ag, Pb, Cu, Zn, and Cd were prepared. Their ability to transport metal nitrates through chloroform in three-phase transport experiments was investigated. Single-ion transport was determined using ligand (**5**) for nitrates of Ag^+, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Frequently, competitive experiments between pairs of cations show suppression of transport of one ion relative to its single-ion rate.[13] Pairwise comparisons of transport rate were made for ligand (**5**) and the pairs of metals Ag/Pb, Ag/Cu, Ag/Zn, Ag/Cd, Cu/Zn, and Cd/Zn. The single-ion transport rates are shown in the bar graph of Figure 3, and the pairwise transport rates in Figure 4. The direct comparison in these bar graphs is the one of consequence in an experimental separation. The sequence $Ag^+ \approx Cu^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$is observed for single-ion transport rates with ligand (**5**). In competition experiments, transport rates for individual ions in the Ag/Pb, Cu/Pb, and Cd/Zn systems were approximately the same as in single-ion systems. A second comparison shows that increased nitrate concentration, from added $NaNO_3$ or $Pb(NO_3)_2$, keeps silver transport at a high

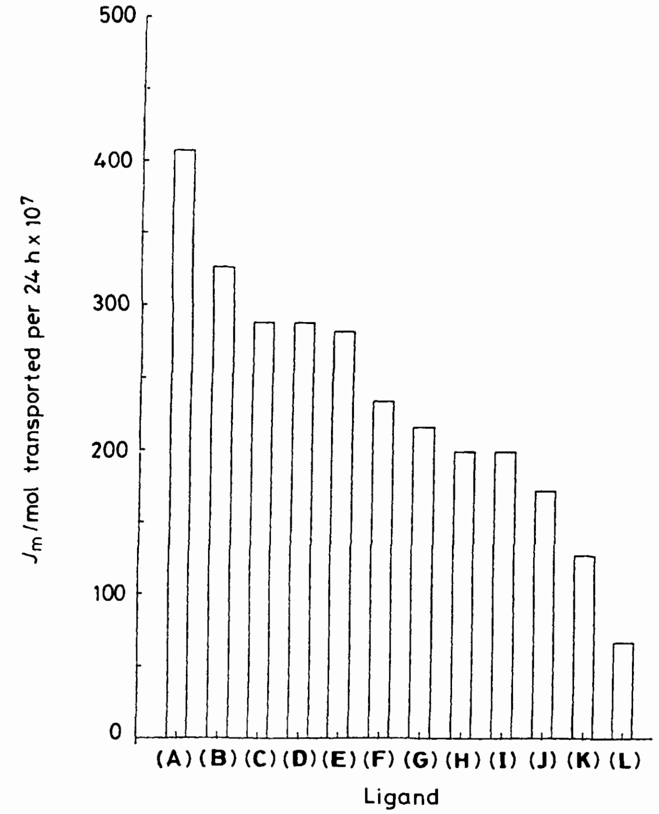


Figure 5. Bar chart illustrating transport of silver nitrate by various ligands

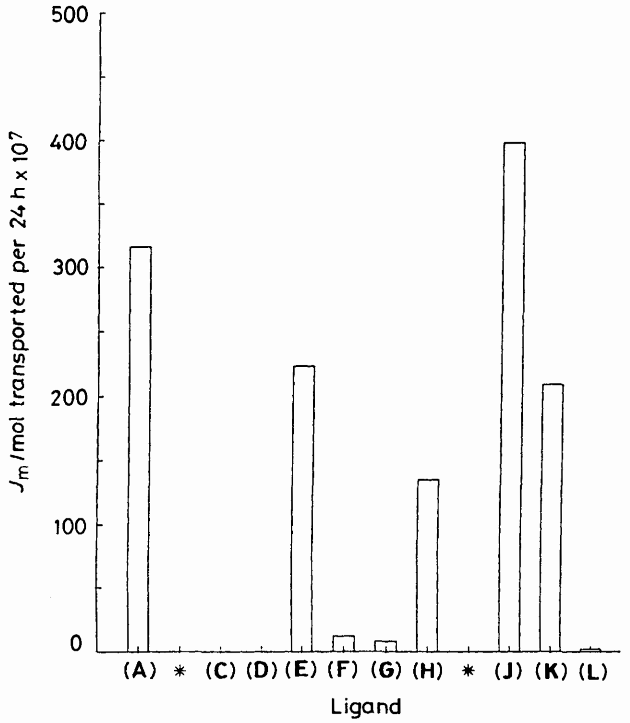


Figure 6. Bar chart illustrating transport of lead nitrate by various ligands. Asterisk indicates no data available

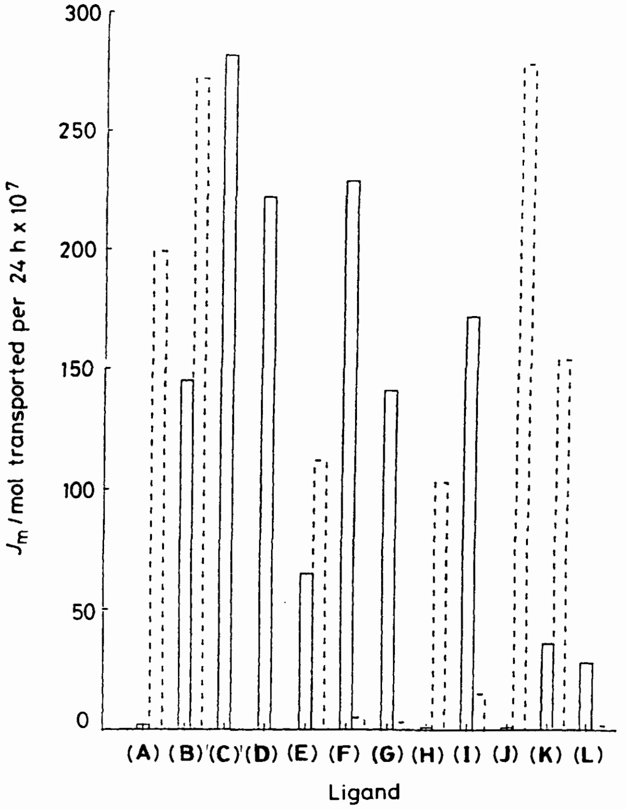


Figure 7. Bar chart illustrating transport of a mixture of silver (——) and lead(– – –) nitrates by various ligands

rate. The salt concentrations used amount to 1 mol dm^{-3} total salt with some divalent and some monovalent metal ions. Thus the activities of silver and nitrate are important, and the calculated values are shown in Table 5. The competition phenomenon can be explained in the terms used by Behr *et al.*[12] relating to cation competition in transport selectivity. Thus extraction constants for the cation pairs A/B are probably in the sequence $K_{opt} > K_A > K_B$ (or $K_B \gg K_{opt} > K_A$) where K_{opt} is the optimum extraction constant, since the relative rates (single ion) are preserved in the pairwise experiments. However, transport of both Cu^{2+} and Cd^{2+} was suppressed in binary mixtures with silver, so that this ligand offers potential separation of such mixtures. The phenomenon can best be explained in kinetic terms if ion A dissociates more slowly and so is the major entity in the organic phase, loading the ligand so as to exclude the ion B.

Many ligands have been tested for three-phase transport of Ag^+ and Pb^{2+}, especially by Izatt and Christensen and co-workers. None of these has achieved the high selectivity for silver over lead which we observed for ligand (**5**). Since silver/lead separations have been important to man for many centuries,[15] and still attract attention today,[16] we tested the other ligands (**3**), (**4**), and (**6**) described in this paper for their ability to transport Ag^+ and Pb^{2+} ions in three-phase transport, both in single-ion systems and in direct competition. The conditions used were similar to those of Izatt and co-workers,[13,14] in order to provide a comparison with the ligands used by these workers. The results of the transport experiments are shown in Figures 5—7, which give the results as bar graphs. Figure 5 places the ligands in order of of their ability to transport Ag^+ from single-ion solutions, while Figure 6 illustrates how the same ligands transport Pb^{2+} from single-ion solutions. The bar charts of Figure 7 show the relative transport of silver and lead from an equimolar mixture of lead and silver ions, with metal ions of a total 1 mol dm^{-3} concentration, equal to that of the single-ion experiments. While the crown ligands (**A**) and (**B**) used previously[13,14] provide a higher overall

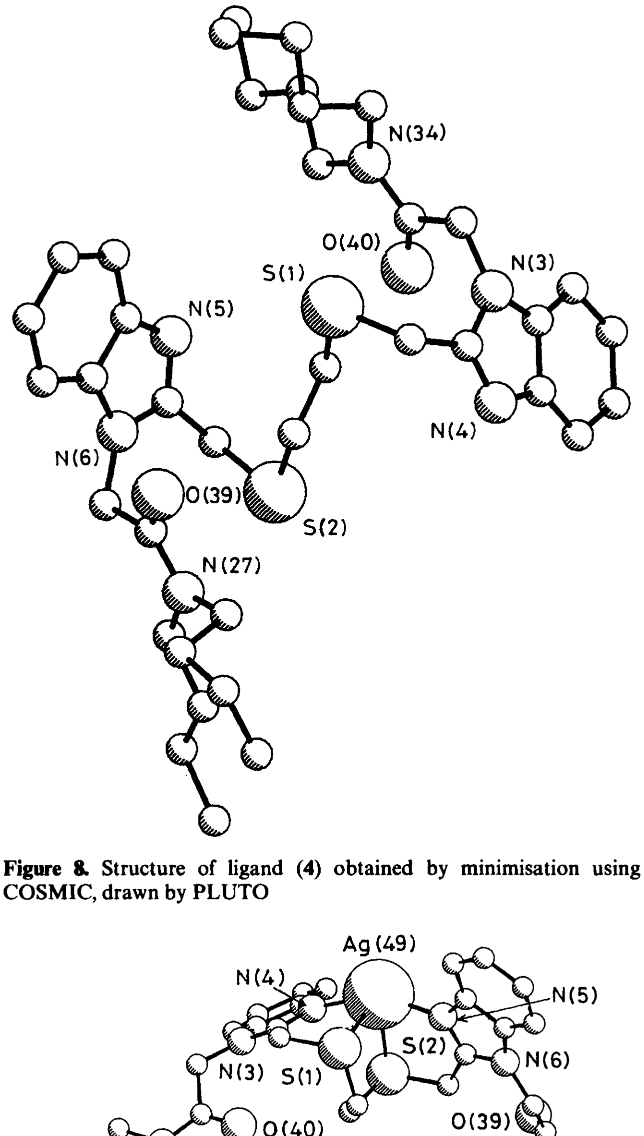


Figure 8. Structure of ligand (**4**) obtained by minimisation using COSMIC, drawn by PLUTO

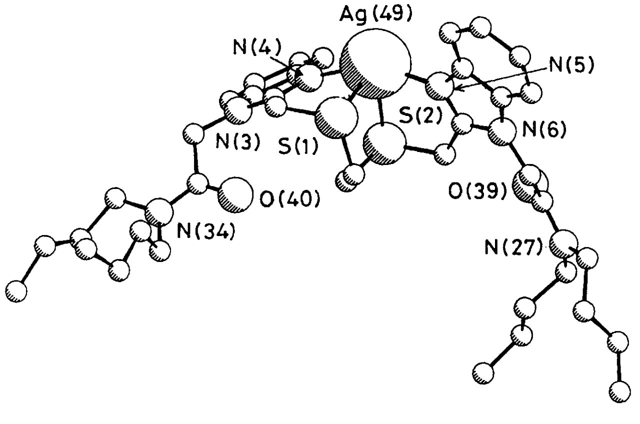


Figure 9. Structure of the complex of ligand (**4**) with Ag^+ obtained by minimisation using COSMIC (see text), drawn by PLUTO

efficiency in transport, the new ligands (**3**)—(**6**) show the better selectivity for silver, scarcely moving lead at all. This motivated us to examine the relative strengths of complexation as indicated later in this paper. The thioether ligands (**4**) and (**6**) were more effective than the ether ones, and the longer hydrocarbon chain (hexyl) was more effective than butyl in promoting the transport of silver ions through the three-phase system, as expected.

Complexation of Silver and Lead Salts with Ligands (**3**)—(**6**).—The lack of transport of lead by a nitrogen-donor ligand was intriguing, and we investigated two hypotheses, namely (1) that lead did not complex these ligands strongly or (2) that lead complexes were too strong, *i.e.* the behaviour of the ligands was at either extreme of the bell-curve used by Lehn and co-workers[12] to describe the results. This entailed attempts to examine the complexing behaviour of the ligands with silver and lead. Silver nitrate complexes were obtained in the solid state from ligands (**3**)—(**6**) but only the ether ligands (**3**) and (**5**) gave solid complexes with lead nitrate. Assignment of the ^1H and ^{13}C n.m.r. spectra of the ligands and complexes appears in Tables 3 and 4. The ^1H spectra of the free ligand (L), the 1:1 complex AgL and 1:5 mixture of L:Pb, and the 1:5:1 mixture of L:Pb:Ag, all in $(CD_3)_2SO_2$ are compared in Figures 1 and 2. The spectra of the lead systems (protons and carbons in the region of the donor atoms) were virtually identical to those of the free ligand, while addition of Ag^+ ions shifted several such signals substantially. Comparison suggests that silver is co-ordinated in $(CD_3)_2SO$ solution to each of ligands (**3**)—(**6**) while lead is not, and that silver competes effectively even with five-fold excess of lead ions for the ligands. The interpretation is complicated by the obvious solvent effect on the n.m.r. spectra.

In general the same conclusion may be drawn from the ^{13}C n.m.r. data; the C=O carbon shifts upfield, while the aryl CH_2SCH_2 carbons move down and up respectively. The n.m.r. spectra indicate changes in protons and carbons near the amide group, while the i.r. evidence gave no indication of co-ordination of the C=O group. Signals of the hexyl or butyl groups were significantly shifted in the n.m.r. spectra, in solution in $CDCl_3$ or on addition of the metal salts to $(CD_3)_2SO$. This is probably attributable to the change in the nature of solvation, rather than to direct co-ordination of metal ion in the vicinity of the groups mentioned. The ^{13}C spectral assignments are shown in Table 4. The relaxation times T_1 were measured for free and complexed ligands; the T_1 data in general show slight changes (10—50%) either on changing the solvent from chloroform to dimethyl sulphoxide, or on addition of silver nitrate. The effect of adding lead nitrate is less, but still apparent.

The findings from the f.a.b. mass spectra of the ligand plus metal salt mixtures are consistent with the general picture emerging from the other results, in that the molecular ion plus silver was seen for each ligand, while ions containing ligand plus lead ions were observed only for ligand (**5**). For the Ag^+ complexes of (**3**), (**5**), and (**6**), some unusual ions were detected. Instead of the simple Ag^{107}/Ag^{109} isotope pattern, we observed a more complex pattern superposed on the expected one, having a pair of silver isotope peaks associated with the $[M - 2]^+$ ion. Since this was not observed for other metal-ligand mixtures, it may be associated with the loss of molecular hydrogen, perhaps from the CH_2CH_2 linking the oxygen or sulphur atoms in the presence of Ag^+. We have been unable to find any similar observation in the literature, although loss of hydrogen is common in organometallic chemistry.[17]

The general impression is that lead is bound more weakly than silver. Figure 3 indicates that Ag and Cu are transported best in single-ion experiments, and that Cd is preferred over Zn and Pb, all for ligand (**5**). Figure 4 indicates that Ag is transported better by the thioether ligand (**6**). The results may be viewed in terms of the softness, size, and charge of the cations. In size terms the ionic radii[18] are in the sequence Pb^{2+} (1.18), Ag^+ (1.15), Cd^{2+} (0.97), Zn^{2+} (0.74), and Cu^{2+} (0.70 Å), while in softness[19] Ag^+ and Cd^{2+} are soft, and Cu^{2+}, Zn^{2+}, and Pb^{2+} are borderline. In general the latter metals will prefer N donors over O donors, and S donors are preferred by Ag^+ and Cd^{2+}. In transport measurements, however, Ag seems to be transported more effectively by oxygen-containing ligands; dicyclohexyl-18-crown-6 being the most efficient carrier for Ag^+. However, oxygen macrocycles are selective[13] for many other cations over Ag^+, while the introduction of pyridine-type and aza-type N and thioether S atoms may decrease the flux of Ag^+ but with enhanced selectivity. It would seem that a combination of soft and hard donor atoms is required to effect selectivity for Ag^+. The ligands (**3**)—(**6**) seem to be most effective for Ag^+ among the cations chosen and this combination of donor atoms must provide a ligand appropriate in size and softness for silver transport. The ligands are quite ineffective for lead, despite its borderline character. The co-ordination number of lead usually exceeds six, and may approach eight, nine, or ten. Possibly the ligands we used were not large enough to wrap around the large Pb^{2+}. Hancock *et al.*[20] have reported on the effectiveness of a large number of co-ordinating N in activating the lone pair on Pb^{2+} so that the ion behaves less like a large ionic cation, but effectively shrinks, in doing so exhibiting more covalent character. Zinc is also classed as a borderline metal, and, as expected, interacts with a variety of donor types. It is not transported by ligand (**5**) nor does it suppress the transport of either Ag^+ or Cd^{2+}, which suggests the interaction of zinc with this ligand is weak. Existing transport data for zinc (and copper) are not so well documented as for silver, lead, and cadmium. Zinc(II) however does have an affinity for imidazole N in biological situations. The only plausible argument is that the ligand is too large for Zn^{2+} or Cu^{2+}, but the strong affinity of Cu for benzimidazole N allows it to be transported. The K_{Cu} value is close to but less than the K_{opt} value for the ligand, but greater than the K_{Zn} value. However, the pairwise competition Ag/Cu shows that K_{Ag} is even closer to the optimum. A consideration of size may explain the improved transport of the soft Cd^{2+} with ligand (**5**) over that of the similar Zn^{2+}. Izatt *et al.*[21] were only able to observe transport of Cd^{2+} with ligands containing O and N donor atoms, which gave good selectivity over Zn^{2+} but not over the other ions studied in this paper.

Modelled Ligands.—Ligand (**4**) and its silver complex were minimised with the COSMIC force field,[22] in order to look for any possible co-ordinating role for the amide carbonyl. Parameters for silver are not available in the literature, but were developed using related systems. We assumed an approximately tetrahedral geometry around the silver, since from n.m.r. studies it appeared likely that the silver was bound to both the pyridine-type nitrogens and the sulphurs in the thioether bridge. The nitrate anion was not considered in this study and an arbitrary charge of +0.5 was assigned to the silver. The charges on the ligand were calculated by a complete neglect of differential overlap (CNDO) calculation and the structure subsequently minimised. The fully minimised structure confirmed our suspicions that the carbonyl donor group could not get close enough to the metal to co-ordinate intramolecularly to its co-ordination sphere. The closest distance of approach of either carbonyl oxygen to the Ag^+ was 5.5 Å. The free ligand is shown in Figure 8 and the silver complex in Figure 9. The free ligand would seem to be admirably suited for extraction, with its polar groups located in one area, capable of enclosing a metal ion at an interface, while the long hydrophobic tails anchor the ligand firmly in the organic phase. N.m.r. studies had also indicated that the side chains of the ether ligands were interacting differently in the presence of silver. The subsequent minimisation of the free ligand gave no indication as to how this might be happening. We did not attempt to construct a model for the intermolecular co-ordination of the amide oxygen on one co-ordinated ligand to an adjacent ligated silver ion.

The general conclusion from this work is that the multidentate benzimidazole ligands are good transporting agents for several metal ions in the three-phase transport studies, where some useful discrimination is obtained. In particular, the results suggest that the ligands may be employed to remove silver ions selectively from mixtures containing lead ions. Only the ether ligands appeared to complex lead; the resultant complexes are not strong, and there was little tendency to transport lead ions in three-phase transport studies.

Acknowledgements

The authors are grateful to the S.E.R.C. for support (to K. I. K. and D. J. R.) and provision of high-field n.m.r. and mass spectroscopic facilities. Dr. M. N. S. Hill and Mr. P. Kelly are thanked for the n.m.r. and mass spectra respectively and Mr. P. J. J. Walsh for his work during the synthesis of compound (**5**) (undergraduate research project).

References

1 W. Clegg, J. C. Lockhart, and F. Musa, *J. Chem. Soc., Dalton Trans.*, 1986, 47.
2 J. V. Dagdigian and C. A. Reed, *Inorg. Chem.*, 1979, **18**, 2623.
3 P. J. M. W. L. Birker, J. Helder, G. Henkel, B. Krebs, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 357.
4 E. Bouwman, W. L. Driessen, and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1988, 1337.
5 H. Grey, Ph. D. Thesis, Newcastle upon Tyne, 1986.
6 D. R. Pfeiffer, R. W. Taylor, and H. A. Lardy, *Ann. N. Y. Acad. Sci.*, 1978, **307**, 402.
7 N. G. Larsen, P. D. W. Boyd, S. J. Rodgers, G. S. Wuenschell, C. A. Koch, S. Rasmussen, J. R. Tate, B. S. Erler, and C. A. Reed, *J. Am. Chem. Soc.*, 1986, **108**, 6950.
8 E. Linder, K. Toth, E. Pungor, F. Behm, P. Oggenfuss, D. H. Welti, D. Amman, W. E. Morf, E. Pretsch, and W. Simon, *Anal. Chem.*, 1984, **56**, 1127.
9 M. A. Phillips, *J. Chem. Soc.*, 1928, 2393.
10 W. E. Weaver and W. M. Whaley, *J. Am. Chem. Soc.*, 1947, **69**, 515.
11 J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1988, 1293.
12 J. P. Behr, M. Kirch, and J. M. Lehn, *J. Am. Chem. Soc.*, 1985, **107**, 241.
13 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.
14 J. D. Lamb, R. M. Izatt, D. G. Garrick, J. S. Bradshaw, and J. J. Christensen, *J. Membr. Sci.*, 1981, **9**, 3.
15 R. F. Tylecote, 'Metallurgy in Archaeology: A Prehistory of Metallurgy in the British Isles,' E. Arnold, London, 1962.
16 L. F. Lindoy, *Prog. Macrocyclic Chem.*, 1987, **3**.
17 'Mass Spectrometry of Metal Compounds,' ed. J. Charalambous, Butterworths, London, 1975.
18 R. D. Shannon and C. D. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925.
19 R. G. Pearson, *J. Chem. Educ.*, 1963, **45**, 581.
20 R. D. Hancock, M. S. Shaikjee, S. M. Dobson, and J. C. A. Boeyens, *Inorg. Chim. Acta*, 1988, **154**, 229.
21 R. M. Izatt, S. R. Izatt, D. W. McBride, jun., J. S. Bradshaw, J. J. Christensen, *Isr. J. Chem.*, 1985, **25**, 27.
22 J. G. Vinter, A. Davis, and M. R. Saunders, *J. Computer-Aided Mol. Design*, 1987, **1**, 31.

Received 26th June 1989; Paper 9/02677K