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Metal-ion recognition. The interaction of copper(II), silver(I) and lead(II) with 22-membered macrocycles incorporating O_4N_2-, $O_2S_2N_2$- and S_4N_2-donor sets

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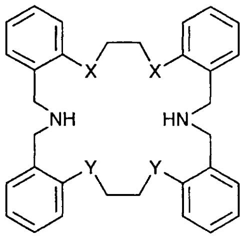
A comparative potentiometric investigation in 95% methanol of the complexation of 22-membered macrocyclic rings incorporating mixed (O_4N_2, $O_2S_2N_2$ and N_2S_4) donor-atom sets towards copper(II), silver(I) and lead(II) has been made. As expected, the introduction of 'soft' sulfur donors into the macrocycle framework increases the discrimination for silver(I) over lead(II) with that incorporating an N_2S_4 donor set showing discrimination of at least 10^8 in favour of silver(I). Details of the binding of silver(I) and lead(II) to the O_4N_2 and $O_2S_2N_2$ systems have been assessed in $CDCl_3$–$(CD_3)_2SO$ (1:4) using ^{13}C NMR spin–lattice relaxation (T_1) studies as well as observation of the induced chemical shifts of ligand resonances on complex formation. Overall, the NMR results correlate well with the observed thermodynamic stabilities of the individual complexes. Competitive mixed-metal transport experiments across a bulk chloroform membrane have been performed using each of the three macrocycles as the ionophore. For each experiment the source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) as their nitrate salts. In each case the silver(I) ion was the only one to exhibit significant transport under the conditions employed, with both macrocycles incorporating sulfur donors being more efficient ionophores than the O_4N_2-donor system.

Metal-ion recognition is a fundamental property of many processes in nature, but the factors influencing such recognition are often not well understood, especially when substrates incorporating mixed donor sets are present. Macrocycles have proved very suitable for investigating metal-ion recognition phenomena since their cyclic nature tends to restrict the number of co-ordination modes possible.[1] Further, in the case of rings large enough to encircle the metal, 1:1 (metal:ligand) stoichiometries for the resulting metal complexes tend to be promoted. Both factors serve to simplify the study of metal complexation in solution.

As a continuation of our previous studies in the area of ligand design for heavy-metal-ion recognition,[2,3] we now present the results of an investigation of the interaction of copper(II), silver(I) and lead(II) with the potentially hexadentate macrocycles L^1–L^3. The behaviour towards silver(I) was of particular interest since inherent in the design of these systems are structural features which appeared likely to enhance their relative affinity for this ion over other ions of interest. Thus, when the co-ordination chemistry of silver(I) is considered two characteristics seem amenable for exploitation in macrocyclic ligand design. The first is the preference of this ion for linear diamine co-ordination, as exemplified by the structure of $[Ag(NH_3)_2]^+$, while the second is its well documented affinity for soft donors such as thioether sulfur.[4] In view of this, the above 22-membered rings incorporating O_4N_2-, $O_2S_2N_2$- or S_4N_2-donor sets, and 'opposing' amine donors, were synthesized. This work represents an extension of our previous studies concerned with investigating the factors which influence (macrocyclic) ligand discrimination for silver(I).[3]



L^1 X = Y = O
L^2 X = O, Y = S
L^3 X = Y = S

Experimental

Physical measurements

Proton and ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer. Melting points are uncorrected.

Macrocycle syntheses

The preparation of compound L^1, *via* Schiff-base condensation of equimolar amounts of the corresponding diamine and dialdehyde precursors followed by sodium tetrahydroborate reduction of the intermediate diimine, has been reported previously.[5]

1,2-Bis[2-(hydroxyiminomethyl)phenylsulfanyl]ethane. 1,2-Bis(2-formylphenylsulfanyl)ethane[6] (1.95 g, 6.4 mmol) was added to a mixture of hydroxylamine hydrochloride (1.40 g, 20 mmol), ethanol (20 cm^3) and water (3 cm^3). Sodium hydroxide (2.5 g, 62.5 mmol) was slowly added and the mixture refluxed for 5 min. After cooling to room temperature the reaction mixture was poured into a solution of hydrochloric acid (2 mol dm^{-3}, 60 cm^3) and the resulting precipitate collected and dried in a vacuum to yield off-white crystals (2.09 g, 98%), m.p. 155 °C (Found: C, 57.9; H, 4.9; N, 8.0. $C_{16}H_{16}N_2O_2S_2$ requires C, 57.8; H, 4.9; N, 8.4%); δ_H[300 MHz, $(CD_3)_2CO$] 3.10 (4 H, s, SCH_2), 7.26–7.79 (8 H, m, aryl H) and 8.61 (2 H, s, CH=N); δ_C[75 MHz, $(CD_3)_2CO$] 34.7, 127.4, 128.1, 130.7, 132.6, 134.8, 135.0 and 147.5.

1,2-Bis[2-(aminomethyl)phenylsulfanyl]ethane. Lithium aluminium hydride (1.00 g, 26.4 mmol) was added slowly to a stirred, cooled (0 °C) solution of the above freshly prepared compound (2.00 g, 6.0 mmol) in dry tetrahydrofuran (30 cm^3). After the mixture had warmed to room temperature it was heated at the reflux temperature for 1 h. The mixture was allowed to cool to room temperature then water (1 cm^3), 20% aqueous sodium hydroxide (1 cm^3) and water (3 cm^3) were added and the mixture filtered. The white granular precipitate was washed with hot dichloromethane (2 × 40 cm^3) and the solvent removed from the filtrate by evaporation. The residue was diluted with dichloromethane (20 cm^3) then washed with half-saturated sodium carbonate, half-saturated sodium chloride and water. The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure to yield a viscous brown oil (0.95 g, 52%). δ_H(300 MHz, $CDCl_3$) 1.65 (4 H, br s, NH_2), 3.10 (4 H, s, SCH_2), 3.93 (4 H, s, CH_2N) and 7.20–7.34 (8 H, m, aryl H); δ_C(75 MHz, $CDCl_3$) 33.1, 44.9, 127.0, 127.6, 128.4, 129.7, 133.4 and 143.6. The dihydrochloride salt of the diamine was produced by dissolving a small amount of the free base in hot absolute ethanol and adding a few drops of concentrated hydrochloric acid. After cooling (4 °C) overnight a crystalline solid had formed, m.p. 261 °C (decomp.) (Found: C, 50.6; H, 5.8; N, 7.0. $C_{16}H_{22}Cl_2N_2S_2$ requires C, 50.9; H, 5.9; N, 7.4%).

Macrocycle L^2. 1,2-Bis[2-(aminomethyl)phenylsulfanyl]ethane (1.00 g, 3.3 mmol) dissolved in hot absolute ethanol (20 cm^3) was added over 10 min to a stirred, boiling solution of 1,2-bis(2-formylphenoxy)ethane[7] (0.89 g, 3.3 mmol) dissolved in absolute ethanol (200 cm^3). The reaction mixture was stirred at its boiling point for 30 min then $NaBH_4$ (3.2 g, 84.6 mmol) was added slowly. The volume of the solution was then reduced to 100 cm^3 after which ice–water (500 cm^3) was added slowly. Stirring was continued overnight and the white precipitate which had formed was collected, washed with water and recrystallised from hot acetonitrile (70 cm^3) to yield compound L^2 (1.3 g, 73%) as a white solid, m.p. 146 °C (Found: C, 70.6; H, 6.5; N, 5.1. $C_{32}H_{34}N_2O_2S_2$ requires C, 70.8; H, 6.3; N, 5.2%); δ_H(300 MHz, $CDCl_3$) 1.88 (2 H, br s, NH), 2.98 (4 H, s, CH_2S), 3.83 (4 H, s, CH_2N), 3.88 (4 H, s, CH_2N), 4.36 (4 H, s, CH_2O) and 6.88–7.33 (16 H, m, aryl H); δ_C(75 MHz, $CDCl_3$) 34.1, 48.7, 51.4, 66.2, 111.1, 120.9, 127.1, 127.5, 128.0, 128.9, 129.7, 129.8, 131.4, 133.9, 141.9 and 156.5.

Macrocycle L^3. 1,2-Bis[2-(aminomethyl)phenylsulfanyl]ethane (0.68 g, 2.2 mmol) dissolved in hot absolute ethanol (25 cm^3) was added over 10 min to a stirred, boiling solution of 1,2-bis(2-formylphenylsulfanyl)ethane (0.67 g, 2.2 mmol) dissolved in absolute ethanol (150 cm^3). The reaction mixture was stirred and boiled for 30 min during which time a white crystalline precipitate formed. This was collected and washed thoroughly with water to yield the intermediate diimine macrocycle (0.92 g, 73%) as a colourless powder. δ_H(300 MHz, $CDCl_3$) 2.96 (4 H, s, CH_2S), 3.07 (4 H, s, CH_2S), 5.00 (4 H, s, CH_2N), 7.20–8.03 (16 H, m, aryl H) and 8.98 (2 H, s, CH=N); δ_C(75 MHz, $CDCl_3$) 34.1, 34.8, 62.9, 127.5, 127.7, 127.8, 128.3, 129.9, 130.8, 131.7, 132.5, 133.7, 137.1, 140.6 and 161.1.

Lithium aluminium hydride (0.5 g, 13 mmol) was slowly added to a cooled (0 °C) stirred solution of the above product (0.34 g, 0.6 mmol) in tetrahydrofuran (20 cm^3). The resulting suspension was refluxed under nitrogen for 4 h then cooled to room temperature and water (0.5 cm^3), 20% aqueous sodium hydroxide (0.5 cm^3) then water (1.5 cm^3) were added sequentially. The resulting white precipitate was filtered off and washed with hot dichloromethane (4 × 20 cm^3). The combined filtrates were reduced to dryness on a rotary evaporator then redissolved in dichloromethane (50 cm^3). This solution was washed with dilute sodium hydroxide. The organic layer was collected, dried (Na_2SO_4) and the solvent evaporated to yield a solid which was recrystallised from dichloromethane to afford compound L^3 (0.32 g, 94%) as a yellow powder, m.p. 141 °C (Found: C, 66.3; H, 5.8; N, 4.7. $C_{32}H_{34}N_2S_4$ requires C, 66.9; H, 6.0; N, 4.9%); δ_H(300 MHz, $CDCl_3$) 1.70 (2 H, br s, NH), 3.01 (8 H, s, SCH_2), 3.92 (8 H, s, CH_2NH) and 7.19–7.45 (16 H, m, aryl H); δ_C(75 MHz, $CDCl_3$) 33.8, 51.4, 127.0, 127.7, 129.8, 130.8 and 141.0.

Stability constants

The potentiometric (pH titration) log *K* data were processed as described previously.[3] All metal complex log *K* values are the mean of between two and four individual determinations at varying metal : macrocycle ratios. All measurements were performed in 95% methanol at 25 ± 0.1 °C. Analytical grade methanol was fractionated and distilled over magnesium before use. The potentiometric titration apparatus consisted of 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. This solution was also used in the salt bridge, while the calomel reference contained NEt_4ClO_4 (0.09 mol dm^{-3}) and tetraethylammonium chloride (0.01 mol dm^{-3}) in 95% methanol. Methanol-saturated nitrogen was bubbled through the solution in the measuring cell; tetraethylammonium hydroxide solution was introduced into the cell using a Metrohm Dosimat 655 automatic titration apparatus. A Corning model 130 Research pH meter was employed for the pH determinations. The personal computer-controlled apparatus was calibrated daily by titration with a solution of standardised base. In nearly all cases it was not possible to obtain complete titration curves because of either precipitation or competing hydrolysis reactions. The titration data corresponding to the lower portions of the respective titration curves refined satisfactorily assuming 1 : 1 metal to macrocycle complexation.

T_1 measurements

These employed the macrocycle in $CDCl_3$–$(CD_3)_2SO$ (1 : 4) (0.5 cm^3) held in 5 mm tubes. The macrocycle concentration was *ca.* 0.10 mol dm^{-3} in each case. For the metal complex studies a stoichiometric amount of silver(I) or lead(II) nitrate was added to the tube. The ^{13}C NMR spectra were obtained using a Bruker AM300 spectrometer fitted with a BUT-1000 temperature controller. Relaxation times were determined by the inversion-recovery technique, with at least eight points being used for each T_1 determination.[8,9] Relaxation delays of 1.5 or 2.0 s were applied; these were sufficient to achieve full relaxation. All spectra were recorded at 25 °C; 128 scans were employed in obtaining the free macrocycle spectra with 400 scans used in the case of the metal complex. The relative T_1 values were estimated to have errors of no more than ± 5–10%. Studies were performed for L^1 and L^2; unfortunately, the corresponding silver and lead complexes of L^3 were not sufficiently soluble in $CDCl_3$–$(CD_3)_2SO$ (1 : 4) to allow a similar investigation.

Membrane-transport experiments

The transport experiments employed a 'concentric cell' 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.[10] For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 revolutions min^{-1}; the cell was enclosed by a water jacket and thermostatted at 25 °C. The aqueous source phase was buffered at pH 5.0 (2 mol dm^{-3} $MeCO_2H$–2 mol dm^{-3} NaO_2CMe) and contained an equimolar mixture of the metal ions (see Results and Discussion section), each at a

Table 1 Ligand protonation constants[a] and stability constants[a,b] for the copper(II), silver(I) and lead(II) complexes of L^1–L^3

	Free macrocycle[c]		$\log K_{ML}$[d]		
Macrocycle	$\log K_1^H$	$\log K_2^H$	Cu^{II}	Ag^{I}	Pb^{II}
L^1	9.36	8.30	7.5(1)	8.4(1)	5.9(1)
L^2	8.66	7.63	8.8(1)	9.5(1)	< 4.5
L^3	7.91	6.90	9.7(1)	12.5(1)	< 4.5

[a] In 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4) at 25 °C. [b] The values quoted are the mean of two to four separate determinations at different concentrations; unless otherwise indicated, individual errors represent the average deviation from the mean, rounded to the first significant figure. For all metal complex systems, precipitation and/or competing hydrolysis restricted the pH range that could be used for the log K calculations. [c] $K_1 = [HL^+]/[L][H^+]$ and $K_2 = [H_2L^{2+}]/[HL][H^+]$. [d] $K_{ML} = [ML^{n+}]/[M^{n+}][L]$.

concentration of 10^{-2} mol dm^{-3}. The chloroform phase contained the macrocycle (1×10^{-3} mol dm^{-3}) as well as hexadecanoic acid (4×10^{-3} mol dm^{-3}). The major role of the latter is to aid the transport process by providing a lipophilic counter ion in the organic phase (after proton loss to the aqueous source phase) for charge neutralisation of the metal cation being transported; in this manner the need for uptake of lipophobic nitrate anions into the organic phase is avoided. The receiving phase was buffered at pH 3.0 (1.0 mol dm^{-3} HCO_2H–1.0 mol dm^{-3} NaOH). All transport runs were terminated after 24 h and atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period. The transport results are quoted as the average values obtained from duplicate runs (errors ±15%). Transport rates (J values) are in mol h^{-1} and represent mean values measured over 24 h.

Results and Discussion

Relative to studies involving macrocyclic ligand complexes incorporating a single donor type, systematic studies of the effects of donor-atom variation on the stabilities of mixed-donor systems have received less attention. Macrocycles L^1–L^3 represent a series of 22-membered rings in which the donor-atom set varies systematically from O_4N_2 in L^1 through $O_2S_2N_2$ in L^2 to S_4N_2 in L^3. Thermodynamic stability constants for the complexes of these macrocycles with silver(I), lead(II) and copper(II) were determined potentiometrically in 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4, 25 °C) by the pH-titration procedure. The log K values for the respective 1 : 1 complexes are summarised in Table 1. The stepwise replacement of the oxygen donors by sulfurs in L^1–L^3 results in a moderate increase in copper(II) complex stability along the series indicating a weak preference of copper(II) for thioether sulfur over ether oxygen donors. For silver(I) the increase is much greater, in keeping with the b-class (soft)[11] nature of this ion. In contrast, the stabilities of the lead(II) complexes of L^2 and L^3 are *lower* than for the corresponding complex of L^1, an observation in keeping with the 'borderline' classification of this ion. A tendency towards lower stability has been observed previously for the lead(II) complexes of macrocyclic ligands on replacement of oxygen by sulfur donors.[3] The opposite trends towards silver(I) and lead(II) along the L^1–L^3 series (Table 1) is thus reflected in the exceptional thermodynamic discrimination (by a factor of at least 10^8) exhibited by L^3 for silver(I) over lead(II).

In further potentiometric studies the determination of the log K values for the cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes of L^1–L^3 was attempted; however, in each of these cases low stabilities coupled with low solubilities and/or competing hydrolysis reactions precluded the reliable determination of individual constants. Nevertheless, it is clear from the limited data obtained that each of these complexes has a log K value which is less than about 4.

Spin–lattice relaxation (T_1) studies

In an attempt to probe more fully the nature of respective silver and lead complexes in solution, ^{13}C NMR spin–lattice relaxation time (T_1) determinations were undertaken in $CDCl_3$–$(CD_3)_2SO$ (1 : 4) for L^1 and L^2, both in the presence and absence of a 1 : 1 stoichiometric ratio of silver(I) or lead(II) ions. Specifically, the aim of these experiments was to gain information about the co-ordination tendencies of the individual donor groups of L^1 and L^2 towards these ions in solution. It is noted that Izatt and co-workers[12] have successfully demonstrated the use of this technique for probing the relative donor affinities of thia and aza derivatives of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) towards silver(I), lead(II) and mercury(II).

Since T_1 values are dependent on the number of internal degrees of freedom of the molecule, on co-ordination the ability of the molecule to tumble will be reduced leading to an increase in correlation times and a corresponding decrease in T_1 values. That is, upon complexation of silver(I) or lead(II) the reduced mobility of the carbon backbone might be expected to result in a decrease in the respective relaxation times for the individual carbons adjacent to bound donor sites. In this manner the technique offers a convenient means for assessing specific binding interactions. Comparison of the T_1 values for the methylene carbon atoms adjacent to the oxygen donors shows that little change occurs upon complexation of L^1 to silver(I) (Table 2). In contrast, the methylene carbons adjacent to the amine donors show significantly decreased T_1 values on formation of the corresponding silver(I) complexes (Table 2). Taken together with the ^{13}C NMR chemical shift data which show a change in chemical shift of $NCH_2 > OCH_2$ (Table 2), the observed behaviour is in accord with co-ordination of the amine groups, with the ether oxygens being, at best, only weakly bound under the conditions used for the experiment.

For lead(II) the T_1 and chemical shift data suggest that in this case both the oxygen and nitrogen donors of L^1 interact quite weakly with this ion (Table 2). The increase in the T_1 value for the NCH_2 carbon is similar to that noted for other systems (and rationalised in terms of molecular compression and/or desolvation upon complexation).[8,13] However, in the absence of further data it seems inappropriate to speculate on the reasons for such behaviour in the present case. The small induced changes in the chemical shifts of the above resonances on complexation (Table 2) also suggest that the interactions with lead(II) appear very weak in the solvent mixture used for the measurements. Overall, the results are consistent with the observed relative stabilities for these silver(I) and lead(II) complexes, determined in 95% methanol (Table 1).

For L^2 the T_1 values for the methylene carbons adjacent to the thioether sulfurs and for the methylenes adjacent to the amine groups on the same side as the thioether sulfur groups again decrease on addition of silver(I), strongly suggesting that both donor types have significant interaction with the metal ion (Table 2). In contrast, the T_1 values for the methylene groups adjacent to the ether oxygen donors were found to increase on complex formation while the value for the remaining methylene groups adjacent to nitrogen were unchanged within experimental error. These results appear best interpreted in terms of silver binding to the nitrogen and sulfur donors of L^2 with little evidence for other than weak ether oxygen interaction with the silver ion under the conditions employed. In general, the induced chemical shifts for the respective methylene carbons also fit the suggested pattern although the shift (1.67 ppm) for the methylene signals adjacent to the ether oxygens suggests that a clear interaction of these donors with silver(I) does exist.

The T_1 values for the lead(II) complex of L^2 (Table 2) show

Table 2 Relaxation times[a] T_1 and induced chemical shifts for the silver(I) and lead(II) complexes of L^1 and L^2 (25 °C)

	T_1[b]/s				Chemical shift (ppm)[c]			
Compound	OCH_2	NCH_2	NCH_2[d]	SCH_2	OCH_2	NCH_2	NCH_2[d]	SCH_2
L^1	0.152	0.174	—	—	65.81	47.39	—	—
$[AgL^1]^+$	0.147 (−3)	0.142 (−21)	—	—	67.36 (+1.55)	49.52 (+2.13)	—	—
$[PbL^1]^{2+}$	0.153 (+1)	0.192 (+10)	—	—	65.88 (+0.07)	47.35 (−0.04)	—	—
L^2	0.157	0.204	0.195	0.178	66.06	50.65	47.41	32.76
$[AgL^2]^+$	0.192 (+22)	0.206 (+1)	0.154 (−21)	0.108 (−39)	67.73 (+1.67)	52.51 (+1.86)	47.98 (+0.57)	28.18 (−4.58)
$[PbL^2]^{2+}$	0.157 (0)	0.167 (−18)	0.155 (−21)	0.180 (+1)	66.07 (+0.01)	50.61 (−0.04)	47.40 (−0.01)	32.82 (+0.06)

[a] In $CDCl_3$–$(CD_3)_2SO$ (1 : 4). [b] Percent change in T_1 relative to free macrocycle value given in parentheses. [c] Change in chemical shift relative to free macrocycle in parentheses. [d] Corresponds to methylene carbons in structure of L^2 that are closest to sulfur heteroatoms.

little change for the carbons adjacent to the ether oxygen or the thioether donors, with significant decreases for the methylene carbons adjacent to the amine donors. These results suggest weak interaction of the ether oxygens and thioether donors with lead(II), with the interaction of the amine donors being somewhat stronger; the chemical shift data are in accord with a weak interaction occurring with all donors. Comparison of the corresponding silver(I)- and lead(II)-induced chemical shifts suggest, overall, a stronger interaction with silver(I) than lead(II). Again, this result is consistent with the observed log *K* pattern (Table 1).

Bulk membrane-transport studies

Competitive mixed-metal transport experiments have been undertaken involving a chloroform membrane phase containing each of the respective macrocycles as the ionophore. 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), the individual metal-ion concentrations were each 10^{-2} mol dm^{-3}. As mentioned in the Experimental section, transport was performed against a back gradient of protons, with hexadecanoic acid also being present in the organic phase. Under the conditions employed all three ionophores yielded highly selective transport of silver(I), with the efficiency being highest (and, within experimental error, about the same) for L^2 and L^3, the sulfur-containing macrocycles. The perhaps unexpected similarity in the transport rates for the L^2 and L^3 systems may, in fact, reflect the stronger binding of silver by L^3. The stability constant (log $K = 12.5$) may be sufficiently high to inhibit the final step in the transport process, the loss of silver ion from the organic membrane phase into the aqueous receiving phase.

In each case silver was observed to be transported between about fifty and several hundred times more efficiently than the next metal appearing in the receiving phase. While caution needs to be exercised since a number of factors (beside thermodynamic stability) may influence observed transport behaviour, the present results nevertheless parallel the results from the log *K* studies. Namely, for the series of metals investigated, each of L^1, L^2 and L^3 has its strongest affinity for silver(I).

Acknowledgements

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