

Hexa Schiff-base cryptands: solution thermodynamic and X-ray crystallographic studies of main group, transition and heavy metal ion complexes

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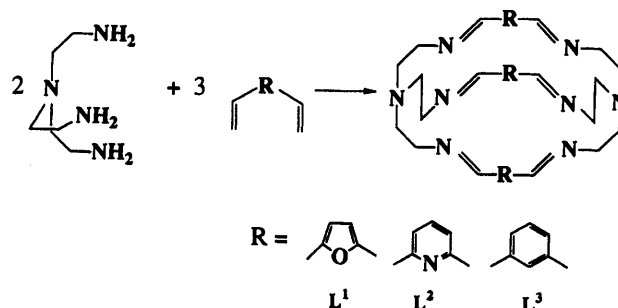
The complexing properties of three hexaimino cryptands bearing furan (L^1), pyridine (L^2) and *meta*-xylyl (L^3) groups towards alkali, alkaline earth, Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cu^+ , Cd^{2+} and Ag^+ cations have been investigated in acetonitrile, by means of UV-VIS spectrophotometry and/or potentiometry. The formation of both mononuclear (1 : 1) and binuclear (2 : 1) complexes is ligand and cation dependent. L^1 and L^2 form predominantly 1 : 1 species. However, additional 2 : 1 complexes are found between Cu^+ and both ligands and between Ag^+ and L^1 , whereas only 2 : 1 species are formed with Mg^{2+} . With L^3 , there is generally formation of both the mono- and the bi-nuclear species. The stoichiometries detected in solution are in agreement with those of the solid complexes when they could be isolated. The structures of the monosilver complex with L^2 and the disilver complex with L^1 are presented. The former shows the silver cation in an unexpected position, as being bonded to three pyridine nitrogen atoms as well as to two imine nitrogen atoms of one side of the macrocycle. The latter shows that the two silver cations are in close proximity [$d_{Ag-Ag} = 3.115(2)$ Å]. The stability of the complexes, which increases when going from alkali to alkaline earth, transition and heavy metal cations, is always lower than that found for the corresponding diazapolyoxa cryptates in the same medium. Although L^2 shows a marked preference for Mg^{2+} over Ca^{2+} within the alkaline earths, a lack of selectivity is observed in each series of cations and even between alkaline earth and heavy metal ions, resulting from a remarkable enthalpy-entropy compensation effect demonstrated by the results of the calorimetric study of the complexation of Ca^{2+} , Sr^{2+} , Ba^{2+} and Ag^+ by the two ligands L^1 and L^2 . With regards to the formation of binuclear complexes, no positive cooperative effect has been observed, except for the Mg^{2+} complexes with L^1 and L^2 and the Cu^+ complex with L^3 . The calorimetric study of the disilver complexes of L^1 shows that there is actually a strongly positive enthalpic cooperativity which is completely offset by the entropic change.

As conclusively demonstrated by the elegant work of Lehn,¹ there are many advantages to be gained from the use of cryptands, as against acyclic or macrocyclic receptors, in the complexation of cations. Thus, cryptand complexes are associated with relatively high kinetic and thermodynamic stability together with the good lipophilicity required for extraction processes. In many cases also, exact complementarity of fit of cationic guest with cryptand host can be achieved, generating maximum selectivity for a particular desired cation as against other potentially interfering ions.

Complexation properties of the diazapolyoxacryptands 222, 221 and 211 have been well studied,^{1,2} particularly in respect to their host function towards group 1 and 2 cations. The predominance of the relatively hard ether-O donors in these cryptands makes them excellent hosts for such hard cations, but less effective towards the softer groups 12–14 or transition cations, which are known to prefer N-donor ligands. Apart from a description of the ligating properties of the all sp^3 N-donor ligand O-bistren,³ the systematic study of all-aza cryptand complexation has been less thoroughly pursued than that of the diazapolyoxa analogues, perhaps because of the greater difficulty of synthesis of the all-aza cryptand ligands. However, it has been noted that stability constants of transition ion complexes with mixed N, O donor cryptands increase as each O-donor is replaced by an amino-N donor.⁴ It thus seems of interest to examine the quantitative solution complexation properties of

hexa Schiff-base ligands which incorporate at least six soft sp^2 imino-N donors; such hosts might be expected to stabilise transition and group 12–14 cation cryptates relative to those of group 1 and 2.

Schiff-base cryptands L^1 , L^2 and L^3 were generated in good purity and high yield⁵ by the [2 + 3] condensation of the triamine tris(2-aminoethyl)amine (tren) with the appropriate dialdehyde^{5–8} (Scheme 1) in the absence of template cation, as



Scheme 1 Schiff-based cryptand formation

described earlier. We have reported the isolation of dinuclear cryptates of Ag^+ ^{7–9} and Cu^+ ^{16–10} with these and other Schiff-base cryptands, while with the larger group 1 and 2 cations,^{6,11,12}

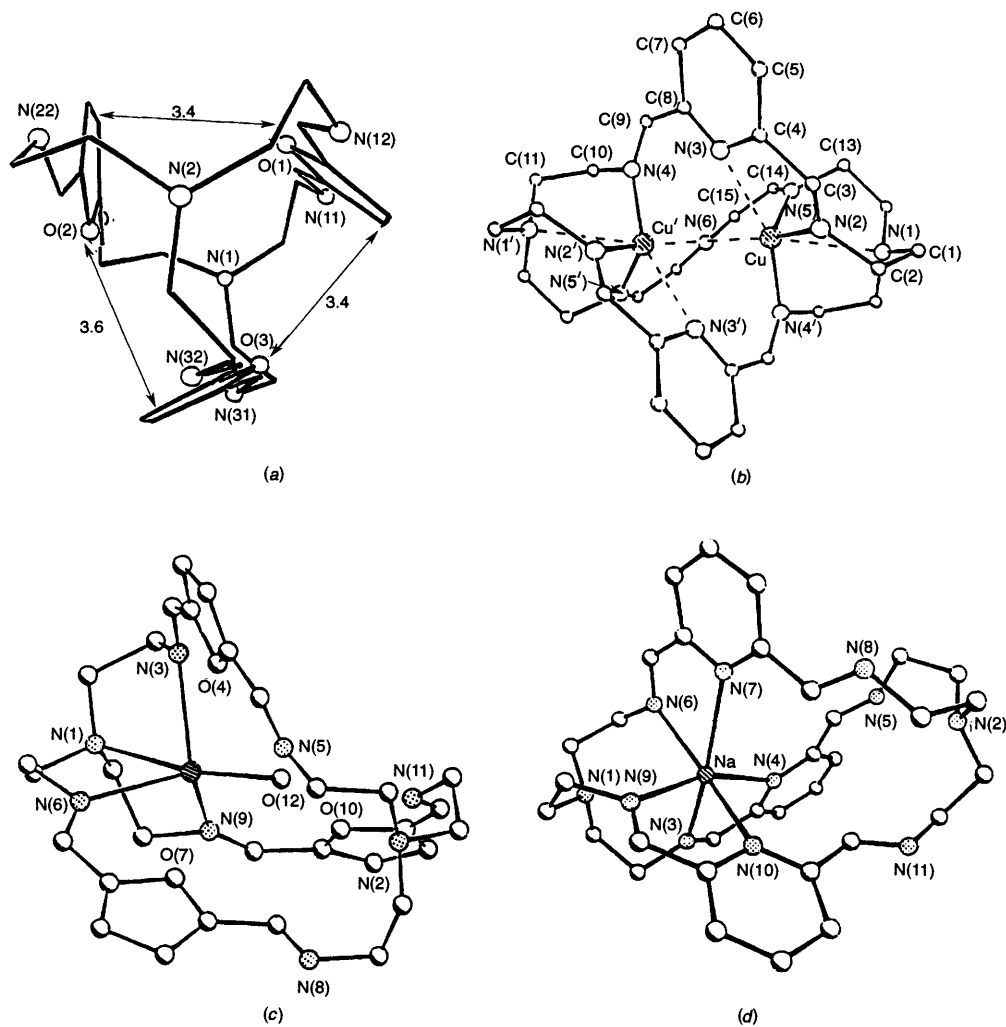


Fig. 1 (a) View showing the approximate three-fold axis of L^1 (from ref. 12); (b) view of $[Cu_2L^2]^{2+}$ cation (from ref. 6); (c) X-ray structure of $[NaL^1 \cdot H_2O]^+$ (from ref. 2) and (d) X-ray structure of $[NaL^2]^+$ cations (from ref. 2)

mononuclear cryptates are normally obtained. All three free cryptands L^1 – L^3 ^{12–14} and many of their cryptates^{6–9,11} have been structurally characterised.

In the metal-free state, the aza cryptands adopt a divergent conformation,¹⁴ with aromatic rings triangularly disposed about the N_{br} – N_{br} axis [Fig. 1(a)], while in the presence of a pair of guests [Fig. 1(b)] the cryptand converts to a symmetric convergent conformation with trigonally disposed aromatic rings. In mononuclear cryptates, on the other hand, X-ray crystallographic^{11,15} [Figs. 1(c) and 1(d)] and/or NMR evidence frequently indicates an unsymmetric conformation where the cationic guest is sited closer to one bridgehead than the other, differentiating the two ends of the cryptand host and generating complex NMR spectra.^{8b,8c,15,16}

As shown by the virtual superpossibility of structures and the similarity of solution 1H NMR^{6,12,13} spectra for L^1 – L^3 , the three free ligands differ little from each other in conformation,¹⁴ both in the solid state and in solution. A high degree of similarity likewise exists between such cryptate structures as have been reported. The main difference to be noted between L^1 and L^2 structures derives from the tendency of the pyridine-N in the spacer link of L^2 to coordinate the cationic guest(s), encouraging location of these towards the centre of the cryptand host, away from the bridgehead nitrogen. 1H NMR spectra of disilver cryptates of L^1 and L^3 are very similar,^{7,8} as are also those of dicopper(I) cryptates of all three ligands, but with minor differences in chemical shifts or coupling constants which affect the degree of overlapping, and thus complexity, of the methylene pattern. These minor changes presumably reflect

small alterations in torsion angles in the methylene caps; there is no suggestion of inequivalence in the two ends or three strands of the cryptand which would generate splitting of imino (C)H or aromatic resonances.^{15,16}

It is possible, in L^3 cryptates, that the presence of three aromatic CH groups tending to protrude into the cavity in the convergent conformation may generate some degree of steric strain, resulting in the adoption of a more open conformation than that displayed in the convergent form of L^1 or L^2 . It is perhaps worth noting, in this connection, the difference between L^3 and the other two cryptands as single cation host: Ba^{2+} is a good template ion for L^1 and L^2 , but not L^3 , and Na^+ cryptates of L^1 and L^2 , but not L^3 , can be isolated.

We have not yet attempted the isolation of cryptates L^1 – L^3 with all group 1, 2 or transition series cations, so a comprehensive description of solid state complexation is not available; work on the synthesis and characterisation of many of the cryptates is still in progress. However, we have evidence^{8b} that L^2 , in particular, can encapsulate transition cations.

In favourable circumstances, NMR data can provide evidence regarding the rate of exchange of cation between the cryptated and solvated state, *i.e.* the kinetic stability of the cryptate, once formed, towards decomplexation.^{9,11,15,16} All three dicopper cryptates show sharply resolved 1H NMR spectra at all accessible temperatures in CD_3CN , showing that no exchange process rapid on the 1H NMR timescale is in operation. The disilver cryptates, on the other hand, show broadened resonances at ambient temperature, which sharpen as temperatures decrease toward 233 K, at that temperature dis-

playing coupling $^3J\{^{109,107}\text{Ag}-^1\text{H}\}$ of the imino (C)H to the magnetic isotopes of silver. The observation of this coupling,^{7,9} which is only rarely observed in silver complexes,¹⁷ is evidence for kinetic stabilisation of the disilver cryptates. The monosodium cryptates of L¹ and L² exhibit splitting of the ²³Na resonance in the presence of free Na⁺ at temperatures below ambient, also demonstrating a relatively low rate of exchange between solvated and cryptated states for this normally labile cation.

Our preliminary investigations thus confirm the expectation of kinetic stabilisation of cationic guest within the aza cavity, while leaving unanswered the crucial question of selectivity of the host for particular heavy metal cations *versus* the common biological cations which may interfere. To answer this question, which is all-important in connection with any potential biomedical or environmental application of these systems, requires a quantitative study of complexation properties of the cryptands with a range of cations. In this paper we describe the complexation in acetonitrile (MeCN) of a variety of metal ions: alkali and alkaline earth cations, transition and other heavy metal cations (Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Cu⁺, Cd²⁺ and Ag⁺) by cryptands L¹–L³, together with crystal structures of two silver cryptates.

Experimental

Materials

The ligands were synthesised according to the procedure already described.^{5a,14} The solvent, acetonitrile (Merck 'Uvasol' or Fluka 'for UV spectroscopy') was used without further purification. The ionic strength was held constant at 10⁻² mol dm⁻³ by addition of tetraethylammonium perchlorate (Et₄NClO₄, Fluka) recrystallised twice from methanol and dried under vacuum for 24 h.

The metal salts were either perchlorates, nitrates or chlorides: LiClO₄ (Fluka, purum), NaClO₄ (Merck, p.a.), KClO₄ (Prolabo, Normapur), RbClO₄ (Sigma), CsCl (Fluka, purum), Mg(ClO₄)₂ · xH₂O (Merck, p.a.), Ca(ClO₄)₂ · 4H₂O (Fluka, purum), Sr(ClO₄)₂ · 6H₂O (Alfa), Ba(ClO₄)₂ (Prolabo, Normapur), Co(ClO₄)₂ · 6H₂O (Fluka, purum), Ni(ClO₄)₂ · 6H₂O (Fluka, purum), Cu(ClO₄)₂ · 6H₂O (Fluka, purum), Zn(ClO₄)₂ · 6H₂O (Fluka, purum), Cd(NO₃)₂ · 4H₂O (Merck), and AgClO₄ · H₂O (Fluka, puriss.). Cu^I was provided as the tetrafluoroborate Cu(BF₄)₂ · 4MeCN obtained by stirring Cu(BF₄)₂ with Cu⁰, previously purified with acetone and iodine, in acetonitrile under an argon atmosphere. The white product thus obtained was filtered, washed with diethyl ether and then dried. Some calorimetric measurements were performed using copper(I) perchlorate which is more soluble than the tetrafluoroborate. CuClO₄ solutions (0.02 mol dm⁻³) were obtained by reaction of a 0.01 mol dm⁻³ solution of copper(II) perchlorate with a slight excess of copper powder, under nitrogen, followed by filtration of the metal in excess.

All the solid salts were dried *in vacuo*, at ambient temperature, for 24 h before use. Their stock solutions (except for alkali and silver cations) were standardised with ethylenediaminetetraacetic acid (EDTA), using the appropriate indicators.¹⁸ The stock solutions of silver perchlorate were standardised against NaCl, using a silver electrode.

Synthesis of the complexes—Ag₂L¹(CF₃SO₃)₂ (1)

To 0.25 mmol L¹ in 40 cm³ CH₂Cl₂ was added 0.9 mmol AgCF₃SO₃ in 20 cm³ MeCN, and the solution stirred at 40 °C for 30 min. 50 cm³ EtOH was then added and the solution rotary evaporated to the first ring of solid. After filtering, pale yellow crystals of product were obtained by slow evaporation in air (Found: C, 35.5; H, 3.3; N, 10.7. Calc. for C₃₂H₃₆Ag₂F₆N₈O₉S₂, C, 35.9; H, 3.4; N, 10.7%).

AgL²BPh₄ (2)

To 0.05 mmol L² in 10 cm³ CH₂Cl₂ was added 0.1 mmol

AgClO₄ in 10 cm³ MeCN and 0.1 mmol NaBPh₄ in 10 cm³ EtOH. The solution was filtered, and on standing in air to evaporate, pale yellow crystals of product were obtained (Found: C, 66.7; H, 5.7; N, 15.7. Calc. for C₆₂H₆₂AgBN₉, C, 67.3; H, 5.8; N, 15.2%).

On slow recrystallisation from EtOH–MeCN, X-ray quality crystals of the MeCN solvate were obtained, which were used for structure determination.

Complexation studies

Stability constant measurements

The stability constants β_{xy} , β_{xy} being the molar ratio $[\text{M}_x\text{L}_y]/[\text{M}]^x[\text{L}]^y$ corresponding to the general equilibrium $x\text{M} + y\text{L} \rightleftharpoons \text{M}_x\text{L}_y$, with M = metal ion and L = ligand, have been determined by UV absorption spectrophotometry in all cases, except for the complexation of Cu^I by L² and L³ which was followed in the visible region. The values were checked by potentiometry in the case of the silver complexes with L¹ and L².

The UV spectra of a series of solutions of a given ligand concentration ($c_L = 5\text{--}6 \times 10^{-6}$ mol dm⁻³) and increasing concentration of metal ion were recorded with a Shimadzu UV-2101 spectrophotometer between 200 and 350 nm with L² and L³ and between 250 and 400 nm with L¹. Suprasil cells of 0.2, 1 or 4 cm path length, thermostatted at 25 ± 0.01 °C, were used. The visible spectra were recorded between 300 and 500 nm from solution with c_L around 10⁻⁵ mol dm⁻³. In every case, a high ratio *R* of the metal-to-ligand concentrations was utilised in order to promote the formation of different species in particular the binuclear species. With alkali cations and ligands L¹ and L², the equilibria were quasi-instantaneous as with alkaline earth cations and ligand L³. However, with the latter cations and ligands L¹ and L², it was necessary to wait between 1 and 5 h, respectively, to obtain stable spectra. With transition and heavy metal ions, the equilibria were sometimes even more sluggish, in particular with L³ and Co²⁺, Ni²⁺ and Zn²⁺. Although they led to coherent spectra, these measurements could not be taken into account because of the possible opening of the macrocycle during this time in the presence of the Lewis-acidic bivalent cations. For the complexation of Ag⁺ by L³, the spectra were recorded 7 d after the preparation of the solutions. Fig. 2 illustrates the case of the complexation of barium by L² and of Cu^I by L³. Spectrophotometric data were interpreted by the programs LETAGROP-SPEFO¹⁹ or SIRKO.²⁰

Potentiometric measurements were performed with the following electrochemical cell: Ag_s/AgClO₄, C_{Ag}, Et₄NClO₄ 0.01 mol dm⁻³//Et₄NClO₄ 0.01 mol dm⁻³//AgClO₄ 0.01 mol dm⁻³/Ag_s. The reference and measurement compartments were thermoregulated at 25 ± 0.01 °C. Prior to each measurement the electrode was calibrated by incremental addition of AgClO₄ solution to 10 cm³ of the supporting electrolyte in acetonitrile. After calibration a ligand solution ($c_L = 10^{-4}$ mol dm⁻³ for L² and 2 × 10⁻⁴ mol dm⁻³ for L¹) was added up to *R* values of at least 2. Potentiometric data were interpreted by the program SIRKO.²⁰

Calorimetric measurements

The calorimetric measurements were made at 25 °C, using a precision isoperibol titration calorimeter (Tronac 450, Orem, Utah). The calorimeter was equipped with a 2 cm³ burette linked by Teflon tubes to the reaction vessel and connected to a computing system which allowed precise injections of the titrant during an accurately known amount of time. The whole assembly was then immersed into the calorimeter bath and left for several minutes until thermal equilibrium was reached. The burette was connected to a motor, the rotating rate of which (400 steps s⁻¹) corresponded to a burette delivery rate of 0.333 cm³ s⁻¹. The metallic salts ($c_M = 7 \times 10^{-3}$ mol dm⁻³ for alkaline

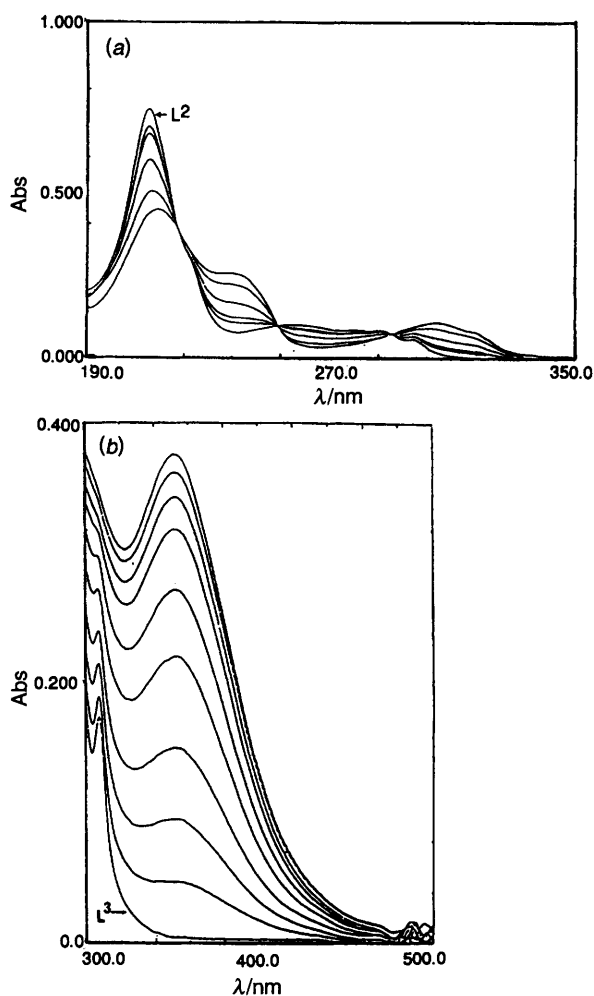


Fig. 2 Changes in the absorption spectrum of (a) a L^2 solution ($c_L = 5.0 \times 10^{-6} \text{ mol dm}^{-3}$) on increase of the Ba^{2+} concentration ($0 < c_M/c_L < 5$) and (b) a L^3 solution ($c_L = 8.45 \times 10^{-6} \text{ mol dm}^{-3}$) on increase of the copper(I) concentration ($0 < c_M/c_L < 38$)

earth cations, 0.01 mol dm^{-3} for Ag^+ and $ca. 2 \times 10^{-2} \text{ mol dm}^{-3}$ for Cu^+) were titrated into 40 or 50 cm^3 of a solution of cryptand L^1 or L^2 ($c_L = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$) in acetonitrile. Using these concentrations, the equilibria were found to be quasi-instantaneous. The low solubility of L^3 prevented similar studies with this ligand. The temperature *versus* time curve was automatically converted into a heat *versus* mole of titrant added curve. An electrical calibration (Joule effect) was made after each experiment. The measured heat was corrected by an appropriate program for the non-chemical heat effects, and for heats of dilution, after their determination by titration of the metal ion solution into the solvent. Because of the high stability of the complexes, the corrected heats are directly related to the enthalpies of complexation and to the number of moles of cation added, up to the stoichiometric amount. However, in the case of silver and L^1 where two complexes are formed simultaneously, the corresponding ΔH_{xy} values were refined using the program SIRKO.²⁰ The large uncertainties observed in some cases on ΔH_{xy} values with alkaline earths could be ascribed either to the small heat measured, due to the small ΔH_{xy} and the small ligand concentration used, as in the case of Ba^{2+} with L^1 , or to the fact that the very high and positive heats of dilution of alkaline earths represented the major contributions to the measured heats, as in the case of Sr^{2+} and Mg^{2+} with both ligands. The values of the entropy of complexation ΔS_{xy} were derived from the Gibbs equation, $\Delta G_{xy} = \Delta H_{xy} - T\Delta S_{xy}$, knowing $\Delta G_{xy} = -RT \ln \beta_{xy}$.

X-Ray structure determinations

Crystal data and refinement details for $[\text{AgL}^2]\text{BPh}_4$, NCMe (1) and $[\text{Ag}_2\text{L}^1](\text{CF}_3\text{SO}_3)_2$ (2) are given in Table 1. Complex 1 was mounted on a STOE2 diffractometer to rotate around the a axis. Data were measured *via* ω scan with a 2θ maximum of 50° . Background counts were for 20 s and a scan rate of $0.0333^\circ \text{ s}^{-1}$ was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. No decay in intensity was observed for the standard reflections. Data for 2 were collected using the MARresearch Image Plate. The crystal was positioned at 75 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.²¹ Both structures were solved using heavy atom method with the SHELXS-86 program.²² For both structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and refined with isotropic thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. The structures were refined by full-matrix least-squares analysis, 1 on F using SHELX76²³ and 2 on F^2 using SHELXL-93.²⁴ All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. The dimensions in the silver coordination spheres in the two structures are listed in Tables 1 and 2.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/30.

Results and discussion

The logarithms of the stability constants for the different species formed in acetonitrile are given in Table 3.

Alkali cation complexes

Only 1 : 1 complexes have been found between L^1 and any group 1 cation, and between L^2 and the cations Li^+ and Na^+ . No complexation could be detected for L^2 with the larger cations, from K^+ on, or for L^3 with any group 1 cation, since no significant spectral changes were observed during the titration of the ligands by the metal ions even in large excess. This is in agreement—at least for L^3 —with the fact that no complex could be detected by NMR and no solid complex could be isolated with this ligand. Treatment of L^3 with group 1 salts failed to alter the ^1H NMR spectrum and resulted in recovery of the free ligand.

With $\log \beta$ values ranging from 2.1 to 3.9, these ligands are much looser binders than Lehn's diaza-polyoxa-macrobicycles such as 222 (Table 3).²⁵ The following conclusions can also be drawn.

(i) The stabilities of the L^1 complexes vary irregularly along the series. $\log \beta_{11}$ values decrease according to the sequence: $\text{Li}^+ > \text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Rb}^+$. There is no complexation of the larger cations with ligand L^2 although this ligand is similar in size to L^1 . This suggests that the size match between the cavity of the ligand and the cation is not the predominant factor in determining the stability of these complexes. The highest stability of the Li^+ complex of L^1 can be ascribed to the weaker solvation of this cation in acetonitrile, as compared to the other group 1 cations. A similar result had been observed with cryptands 22, 221 and 211²⁶ and with calixarene-esters.²⁷

(ii) Contrary to what can be expected from the higher affinity of sodium for O-donor atoms than for N-donor atoms, the sodium complex of L^2 is 3.4 times more stable than its homologue of L^1 . However, this result is consistent with the structural data which showed no coordination of the cation to the

Table 1 Crystal data and structure refinement for **1** and **2**

Compound	1	2
Formula	[AgL ²], BPh ₄ MeCN	[Ag ₂ L ¹], 2CF ₃ SO ₃
Empirical formula	C ₆₂ H ₆₂ AgBN ₉	C ₃₂ H ₃₆ Ag ₂ F ₆ N ₈ O ₉ S ₂
Formula mass	1051.88	1070.55
<i>T</i> /K	293(2)	293(2)
Wavelength/Å	0.71070	0.7107
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions/Å		
<i>a</i> /Å	11.527(2)	13.727(9)
<i>b</i> /Å	13.849(2)	22.42(2)
<i>c</i> /Å	16.813(2)	14.738(9)
<i>a</i> ^o	97.81(1)	(90)
<i>β</i> ^o	94.44(1)	97.13(1)
<i>γ</i> ^o	102.22(1)	(90)
<i>V</i> /Å ³	2583	4039
<i>Z</i>	2	4
<i>D_c</i> /Mg m ⁻³	1.352	1.761
Absorption coefficient/mm ⁻¹	0.441	1.162
<i>F</i> (000)	1098	2144
Crystal size/mm	0.3 × 0.3 × 0.3	0.3 × 0.25 × 0.17
<i>θ</i> range for data collection/ ^o	2.08–25.74	1.68–25.07
Index ranges	–13 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 15 –19 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 16, –26 ≤ <i>k</i> ≤ 26, –17 ≤ <i>l</i> ≤ 14
Reflections collected	8529	11674
Independent reflections	8529	6758 [<i>R</i> (int) = 0.0351]
Refinement method	<i>F</i> on 3050 obs data	<i>F</i> ² on all data
Weighting Scheme <i>w</i>	1/[σ ² (<i>F</i>) + 0.003 <i>F</i> ²]	<i>a</i> = 0.21, <i>b</i> = 35.43 ^a
Data/restraints/parameters	3050/0/651	6755/0/533
Goodness-of-fit	1.267	0.607
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.057 <i>R</i> _w = 0.059	<i>R</i> ₁ = 0.0582, <i>wR</i> ₂ = 0.1701 <i>R</i> ₁ = 0.0760, <i>wR</i> ₂ = 0.1972
<i>R</i> indices (all data)		
Largest diff. peak and hole/e Å ⁻³	0.59, –0.29	0.817, –1.123

^a Weight = 1/[σ²(*F_o*²) + (*aP*)² + *bP*], where *P* = [max(*F_o*², 0) + 2*F_c*²]/3.

furan oxygens in the Na⁺L¹ complex, but strong interaction with the pyridine nitrogens in Na⁺L² (Fig. 1).¹¹

Alkaline earth cation complexes

In acetonitrile, ligands L¹ and L² form only 1 : 1 complexes with all alkaline earth cations except Mg²⁺. Only binuclear complexes are found with the latter cation. This is in agreement with the stoichiometries of the complexes isolated in the solid state.^{8b,28} With L³ there is evidence for the formation in solution of both mono- and bi-nuclear complexes with all cations of the series but Ba²⁺. In the latter case, no complex could be detected in solution nor isolated in the solid state, as noted earlier.

1 : 1 complexes with alkaline earth cations are more stable than their homologues with alkali cations, log β₁₁ in the range 4.2–6.6, but less stable than the corresponding 222 cryptates. Their stability does not vary significantly within the series, except with L¹. In this case, there is a marked minimum of stability with Sr²⁺, Ca²⁺ forming a slightly more stable complex than Ba²⁺. Therefore, again no cation-based specificity seems to operate with alkaline earths.

With regard to the dinuclear complexes observed with Mg²⁺, the most stable is formed with L². The fact that we did not detect the formation of any 1 : 1 complexes with ligands L¹ and L², at least under our experimental conditions, suggests an important positive cooperative effect in the formation of the binuclear complexes. With ligand L³, however, evidence was found for the formation of a mononuclear species. The value of the stepwise stability constant, *K*₂, for the formation of the binuclear species, which could thus be calculated was found to be 3.2 log units,²⁹ *i.e.* lower than β₁₁. The value of Δ = log *K*₂/β₁₁ = –1.02, which is a measure of the relative stability of the binuclear complex as compared to the mononuclear complex, indicates a certain electrostatic interaction between the two cations in the binuclear complex, as expected with divalent

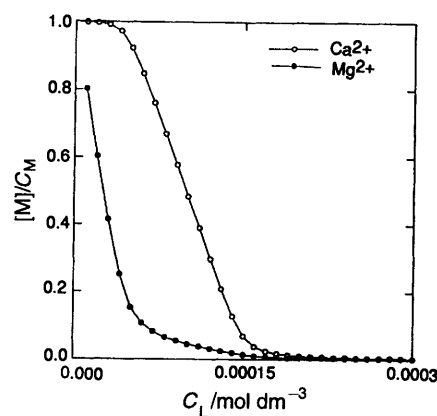


Fig. 3 Calculated percentages of free Mg²⁺ and Ca²⁺ as a function of the ligand L² concentration (*c_M* = 10⁻⁴ mol dm⁻³)

cations in close proximity. This interaction is maximum for the Ca²⁺ complex (Δ = –2.7) and minimum for Sr²⁺ (Δ = 0.5).

On the other hand, it is difficult to compare the complexing power of L¹ and L² towards magnesium and the other alkaline earths from the simple view of the stability constants, since the species involved have different stoichiometries. The real selectivity of the ligands is better described by the calculated percentages of free cation left as a function of the ligand concentration. Fig. 3, which represents such curves for an equimolar mixture of Mg²⁺ and Ca²⁺ (*c_{Mg}* = *c_{Ca}* = 10⁻⁴ mol dm⁻³) in the presence of L², shows that the free Mg²⁺ concentration is much lower than the free Ca²⁺ concentration over a wide range of ligand concentration. For instance for *c_L* = 10⁻⁴ mol dm⁻³, the percentages of free Mg²⁺ and Ca²⁺ are respectively 4.5 and 48. The difference is lower but still exists with L¹. Thus, it is obvious

Table 2 Selected bond lengths (Å) and angles (°) for **1** and **2**

In (1)		
Ag(1)–N(3A)	2.274(12)	
Ag(1)–N(3C)	2.418(14)	
Ag(1)–N(6C)	2.430(10)	
Ag(1)–N(6B)	2.510(12)	
Ag(1)–N(6A)	2.750(14)	
N(3A)–Ag(1)–N(3C)		97.2(5)
N(3A)–Ag(1)–N(6C)		119.4(4)
N(3C)–Ag(1)–N(6C)		69.1(4)
N(3A)–Ag(1)–N(6B)		129.6(4)
N(3C)–Ag(1)–N(6B)		98.4(4)
N(6C)–Ag(1)–N(6B)		111.0(4)
N(6A)–Ag(1)–N(3A)		66.0(4)
N(6A)–Ag(1)–N(3C)		162.5(4)
N(6A)–Ag(1)–N(6C)		113.9(5)
N(6A)–Ag(1)–N(6B)		96.3(4)
In (2)		
Ag(1)–(3B)	2.262(5)	
Ag(1)–N(3A)	2.301(5)	
Ag(1)–N(3C)	2.326(5)	
Ag(1)–N(100)	2.656(5)	
Ag(2)–(11B)		2.254(6)
Ag(2)–N(11A)		2.281(5)
Ag(2)–N(11C)		2.311(6)
Ag(2)–(200)		2.708(6)
N(3B)–Ag(1)–N(3A)		114.7(2)
N(3B)–Ag(1)–N(3C)		112.0(2)
N(3A)–Ag(1)–N(3C)		105.8(2)
N(3A)–Ag(1)–N(100)		70.9(2)
N(3B)–Ag(1)–N(100)		72.8(2)
N(3C)–Ag(1)–N(100)		72.2(2)
N(11B)–Ag(2)–N(11A)		113.9(2)
N(11B)–Ag(2)–N(11C)		110.5(2)
N(11A)–Ag(2)–N(11C)		104.7(2)
N(11A)–Ag(2)–N(200)		72.0(2)
N(11B)–Ag(2)–N(200)		70.8(2)
N(11C)–Ag(2)–N(200)		69.4(2)
Ag(1)...Ag(2)		3.115(2)

that L^2 and, to a lesser extent, L^1 are selective for Mg^{2+} over Ca^{2+} .

Table 4 gives the values of the thermodynamic parameters of complexation ΔG_{xy} , ΔH_{xy} and $T\Delta S_{xy}$ for the alkaline earth complexes with L^1 and L^2 . With both ligands and all group 2 cations except in the case of L^2 with Ca^{2+} and Ba^{2+} , the stabilisation of the complexes is entropy controlled ($\Delta S_{xy} > 0$ and dominant). Such positive entropy changes have often been observed with strongly solvated cations like alkaline earths.³⁰ The particularly high values observed for Mg^{2+} complexes can be explained by the fact that, first, they correspond to different overall parameters (describing the fixation of two cations) and, secondly, this cation is the best solvated among the alkaline earths. In addition, $T\Delta S_{21}$ is almost two times higher with L^2 than with L^1 , suggesting a more important desolvation of the cation when complexed by the former ligand and/or a more complete desolvation of the ligand L^2 itself.

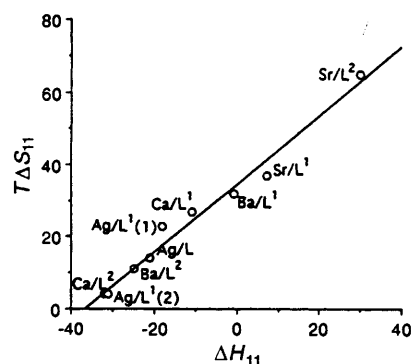
The enthalpy changes ($-\Delta H_{xy}$) are low or close to zero and they even become negative and unfavourable in the case of Sr^{2+} with both ligands, and in the case of Mg^{2+} with L^2 . The Ca^{2+} and Ba^{2+} complexes with L^2 are an exception, since their stability is enthalpy driven ($-\Delta H_{11} > 0$ and dominant).

As regards the 1 : 1 complexes with both ligands, the same trends are observed within the series, *i.e.* a decrease of $-\Delta H_{11}$ from Ca^{2+} to Sr^{2+} and an increase thereafter for Ba^{2+} . This variation is associated with a maximum of $T\Delta S_{11}$ for Sr^{2+} . In fact, the small variations in the free energy observed with L^1 and particularly with L^2 result from a remarkable enthalpy–entropy

Table 3 Stability constants (as $\log \beta_{xy} \pm \sigma_{n-1}$)^a of metallic complexes with ligands L^1 , L^2 , L^3 and cryptand 222, in acetonitrile, at 25 °C, $I = 0.01 \text{ mol dm}^{-3}$ (Et_4NClO_4)

Cations	Species	L^1	L^2	L^3	222 ^b
Li^+	ML	3.91 ± 0.05	2.36 ± 0.07	<i>e</i>	6.97
Na^+	ML	2.47 ± 0.01	3.0 ± 0.2	<i>e</i>	9.63
K^+	ML	2.6 ± 0.1	<i>e</i>	<i>e</i>	11.30
Rb^+	ML	2.1 ± 0.2	<i>e</i>	<i>e</i>	≥ 7
Cs^+	ML	3.3 ± 0.2	<i>e</i>	<i>e</i>	4.57
Mg^{2+}	ML	<i>e</i>	<i>e</i>	4.26 ± 0.05	
	M_2L	11.1 ± 0.1	12.6 ± 0.2	7.5 ± 0.1	
Ca^{2+}	ML	6.64 ± 0.05	6.26 ± 0.01	4.5 ± 0.2	10.5
	M_2L	<i>e</i>	<i>e</i>	6.29 ± 0.05	
Sr^{2+}	ML	5.3 ± 0.1	6.01 ± 0.01	4.2 ± 0.1	
	M_2L	<i>e</i>	<i>e</i>	7.86 ± 0.05	
Ba^{2+}	ML	5.8	6.22	<i>e</i>	≥ 9
Co^{2+}	ML	6.2 ± 0.1	7.2 ± 0.4	<i>c</i>	
Ni^{2+}	ML	5.42 ± 0.01	6.24 ± 0.01	<i>c</i>	
Cu^{2+}	ML	<i>d</i>	<i>d</i>	7.2 ± 0.1	17.8 ^f
	M_2L			12.4 ± 0.3	
Zn^{2+}	ML	5.39 ± 0.02	5.4 ± 0.2	<i>c</i>	≤ 9.5
Cd^{2+}	ML	4.13 ± 0.01	6.50 ± 0.04	6.5 ± 0.1	19.8
	M_2L	<i>e</i>	<i>e</i>	12.8 ± 0.1	
Cu^+	ML	7.1 ± 0.3	4.77 ± 0.01	<i>e</i>	
	M_2L	12.6 ± 0.2	8.6 ± 0.1	8.65 ± 0.07	
Ag^+	ML	7.2 ± 0.2	6.0 ± 0.1	4.8 ± 0.1	
	M_2L	13.3 ± 0.2	<i>e</i>	8.77 ± 0.02	

^a Precision: standard deviation σ_{n-1} on the mean of n experiments ($n \geq 3$). ^b Ref. 8. ^c Hydrolysis of the ligand may be suspected because of slow equilibria. ^d No reproducible spectra. ^e Not detected. ^f Calculated value, from ref. 34.

**Fig. 4** Plot of $T\Delta S_{11}$ vs. ΔH_{11} for the complexation of alkaline earth and Ag^+ cations with L^1 and L^2

compensation effect, as shown on Fig. 4, by the linear dependence of $T\Delta S_{11}$ with ΔH_{11} ($r^2 = 0.979$, when data for the silver complexes are included in the correlation). Such an effect, which can be expressed by eqn. (1), has already been encountered

$$T\Delta S_{11} = a\Delta H_{11} + T\Delta S_0 \quad (1)$$

with different types of macrocyclic and acyclic ligands as well as with antibiotics and thoroughly discussed by Inoue *et al.*³¹ According to these authors, the value a of the slope means that only a proportion of the increment in ΔH_{11} contributes to raise the stability. It thus represents a quantitative measure of the entropic cancelling effect, characteristic of the ligand. $T\Delta S_0$ is the intrinsic entropy gain upon complexation and is related to the desolvation of the cation. In our case, a value (0.94) corresponds to an important entropic loss since only 6% of the increment of ΔH_{11} contributes to raise the stability. This reveals the importance of the rearrangement of the ligand upon complexation. The large positive value found for $T\Delta S_0$ (34.8 kJ mol^{-1}) indicates the importance of the solvation of the cations. This also suggests that the interactions, taking place between alka-

Table 4 Thermodynamic parameters of complexation of alkaline earth cations by L¹ and L² in acetonitrile^a (ΔG_{xy} , ΔH_{xy} and $T\Delta S_{xy}$ in kJ mol⁻¹ and ΔS_c in J K⁻¹ mol⁻¹)

Ligands	Cations	Species	$-\Delta G_{xy}$	$-\Delta H_{xy}$	$T\Delta S_{xy}$	ΔS_c
L ¹	Mg ²⁺	M ₂ L	63.3 ± 0.6	18 ± 4	46 ± 4	150 ± 20
	Ca ²⁺	ML	37.8 ± 0.3	11 ± 1	27 ± 1	92 ± 5
	Sr ²⁺	ML	30.2 ± 0.6	-7 ± 4	37 ± 5	120 ± 20
	Ba ²⁺	ML	33.1 ± 0.6	1 ± 3	32 ± 4	110 ± 10
	Ag ⁺	ML	41 ± 1	18 ± 2	23 ± 3	77 ± 10
		M ₂ L	76 ± 1	49 ± 1	27 ± 2	91 ± 7
L ²	Mg ²⁺	M ₂ L	71.8 ± 1.1	-12 ± 8	85 ± 10	280 ± 30
	Ca ²⁺	ML	35.68 ± 0.06	32 ± 1	4 ± 1	12 ± 4
	Sr ²⁺	ML	34.26 ± 0.06	-30 ± 10	65 ± 10	210 ± 40
	Ba ²⁺	ML	35.45 ± 0.06	25 ± 6	11 ± 6	40 ± 20
	Ag ⁺	ML	34.2 ± 0.6	21 ± 3	13 ± 4	4 ± 13

line earth and silver cations and the two ligands, despite the latter cation's softer character, are similar in nature.

With both ligands, the lowest entropy change is observed for Ca²⁺ though it is more solvated than Sr²⁺ or Ba²⁺. This suggests an incomplete desolvation of the cation upon complexation which is also consistent with the high $-\Delta H_{11}$ values observed with this cation. With Sr²⁺, although it is less solvated than Ca²⁺, $T\Delta S_{11}$ is higher indicating a more pronounced or even a complete desolvation. Consequently, the enthalpy term becomes positive and hence unfavourable. For Ba²⁺, the largest and least solvated cation of the alkaline earth series, $T\Delta S_{11}$ is lower than for Sr²⁺. However, it remains higher than for Ca²⁺, indicating a still important desolvation, at least more important than for Ca²⁺. The fact that $-\Delta H_{11}$ remains high would suggest a high coordination number of the cation in the complex. This result is consistent with the indications of IR data on the solid complexes. The absorption frequency, $\nu_{C=N}$, in [CaL¹]²⁺ is unsplit and unshifted relative to L¹, while [BaL¹]²⁺ is unsplit but shifted suggesting that all imino nitrogens are coordinated in the latter and none in the former case. [SrL¹]²⁺, with a split $\nu_{C=N}$ imino absorption, appears to be intermediate.

Transition and heavy metal ion complexes

Only 1 : 1 complexes are formed between Co²⁺, Ni²⁺ and Zn²⁺ and ligands L¹ and L² (Table 3). With L³ and the same bivalent cations, we had to wait more than 12 h to reach the equilibria. In such conditions, the ligand probably undergoes hydrolysis leading to the opening of one branch of the bicycle. Thus, it was not realistic to consider the stability constant values which could be obtained from the interpretation of the experimental spectra as corresponding to L³ complexes. Complexation of Cu²⁺ by L¹ and L² did not lead to reproducible spectral changes. This could be related to the instability of Cu²⁺ in acetonitrile solutions and, in the case of L¹, to possible hydrolysis of the ligand. However, with L³, the equilibrium was quasi-instantaneous and both mono- and bi-nuclear complexes could be detected owing to the presence of several isosbestic points. At higher *R* values, the presence of an additional isosbestic point suggested the formation of a third species. In such conditions, the water introduced in solution by the metal ion in excess can interact with the dinuclear species and form another complex, similar to that isolated in the solid state,^{8a} in which the two cations are bridged by a OH group.

In general the 1 : 1 complexes of Co²⁺, Ni²⁺ and Zn²⁺ have similar stabilities as the corresponding complexes of alkaline earths. The L² complexes are slightly more stable than their L¹ homologues because of the presence of the nitrogen donor atoms which have a higher affinity for transition cations than oxygen atoms. Co²⁺ complexes of L¹ and L² are about ten times more stable than Ni²⁺ complexes, in contradiction with the Irving-Williams stability order.³² As regard the Cu²⁺ binuclear species found with L³, its stepwise stability constant $\log K_2 = 5.2$ is lower than $\log \beta_{11}$ ($\Delta = -2$), showing an important

electrostatic interaction between the two copper ions in the complex.

The formation of a 1 : 1 complex of Cd²⁺ has been shown unambiguously with L². With L¹, the spectra show a unique well defined isosbestic point and could be well interpreted by taking into account the presence of either a 1 : 1 or a 1 : 2 species. However, it was not possible to obtain a satisfactory fit when considering both complexes together. On the other hand, the FAB spectrum of a mixture of L¹ and cadmium perchlorate in acetonitrile in a 1 : 2 ratio revealed the existence of two complexes with the 1 : 1 and 2 : 1 stoichiometry. The simplest species has been considered in Table 3, *i.e.* the mononuclear one, also present in the mass spectrum. In the solid state, only 1 : 1 stoichiometry is found with L¹ and L², although 1 : 2 stoichiometry occurs with L³.²⁸ With L³, the mononuclear and the binuclear species have to be taken into account in order to obtain a satisfactory interpretation of the experimental data. The 1 : 1 complexes with L¹ and L² are the most stable ones ($\log \beta_{11} = 6.5$) but they are much less stable than their homologue with 222 ($\log \beta_{11} = 19.8$).²⁵ These ligands do not display any remarkable selectivity for Cd²⁺ over Zn²⁺ or other transition metal ion of biological relevance.

The interpretation of the experimental spectra recorded during the complexation of Cu^I indicates the formation of binuclear complexes with the three ligands. Mononuclear species are formed in significant amount with L¹ and L² only. Although such 1 : 1 complexes had never been isolated in the solid state, 2 : 1 complexes had been prepared and studied by ¹H NMR and X-ray crystallography.⁶⁻⁸ The fact that the mononuclear species is disfavoured with L³ can be related to the absence of donor sites at the centre of the cavity. Two distinct chelation sites, formed each by one bridgehead nitrogen and three imines, are thus defined, which favour the formation of binuclear species. The ¹H NMR spectra also suggest that in the convergent (coordinating) form of L³, three aromatic CH groups are pointing in the direction of the centre of the cavity leading to steric constraint which may favour a more open conformation than that displayed in the L¹ and L² cryptates. The crystal structure of the dicopper(I) cryptate of L³, which has been solved, does show evidence of steric strain.³³

L¹ forms the most stable Cu⁺ complexes, while L² and L³ binuclear complexes have similar lower stabilities. With L¹ and L², the formation of the binuclear complexes is less favoured than that of the mononuclear complexes, as shown by the Δ values, respectively, -1.6 and -0.94. This indicates electrostatic interaction between the two metal ions, in agreement with the rather short Cu^I-Cu^I distances observed in the solid complexes,¹⁰ which appears stronger with L¹ than L². However, this is in contradiction with the shorter Cu^I-Cu^I distance in the L² complex (3.04 instead of 4.2 Å in the L¹ complex) and the electrochemical results in *N,N*-dimethylformamide showing a single (irreversible) two-electron oxidation wave for [Cu₂L¹]²⁺ and two (quasi-reversible) one-electron oxidation waves for [Cu₂L²]²⁺.¹⁰ It appears that solvation effects may be an important factor in determining the cooperativity in these systems.

As regards the complexation of Ag⁺, mono- and bi-nuclear complexes have been found with L¹ and L³, whereas only the mononuclear species could be detected with L². The stoichiometries are again the same as those of the complexes isolated in the solid state. In particular the existence of the 1 : 1 complex with L² has been confirmed although a binuclear complex had been previously isolated by Lehn *et al.*, after reaction of silver hexafluorophosphate with this ligand, and characterised by its ¹H NMR spectrum in CD₂Cl₂.^{5b}

The structure of AgL²(BPh₄) provides an ultimate proof of the existence of a mononuclear silver complex with L². It contains discrete cations [AgL²]⁺, anions BPh₄⁻ and solvent molecules MeCN. The position of the MeCN is unremarkable having no close contacts to cation or anion. The structure of the

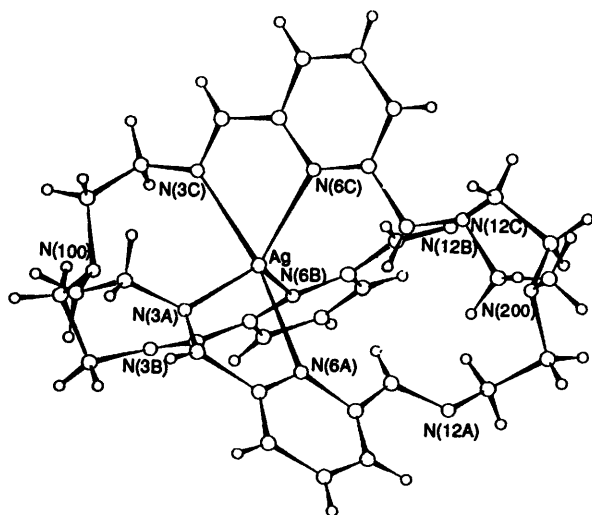


Fig. 5 Structure of $[\text{AgL}^2]^+$ cation; for interatomic distances see Table 4

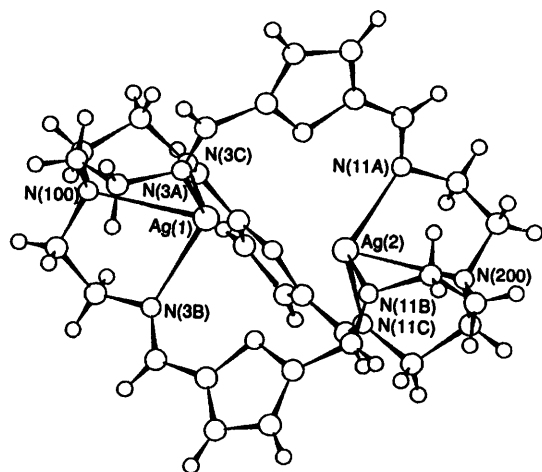


Fig. 6 Structure of $[\text{Ag}_2\text{L}^1]^{2+}$ cation; for interatomic distances see Table 4

cation is shown in Fig. 5 together with the atomic numbering scheme. The position of the silver atom within the macrocycle is unexpected as the metal is bonded to all three pyridine atoms [2.750(10), 2.430(10), 2.510(12) Å] as well as to two of the three imine nitrogen atoms to one side of the macrocycle [2.274(12), 2.430(10) Å]. The geometry of the coordination sphere is irregular though it could be described as a trigonal bipyramid with N(3C) and N(6A) in axial positions and N(3A), N(6C) and N(6B) in equatorial sites. The fact that only one silver is found in the macrocycle contrasts with the structure of $[\text{Ag}_2\text{L}^1]^{2+}$ shown in Fig. 6 together with the atomic numbering scheme. The two silver atoms are both four-coordinate being strongly bound to three imino nitrogen atoms [2.265(6) to 2.326(5) Å] and more weakly to the bridgehead nitrogen at 2.656(5), 2.708(6) Å. The Ag(1) \cdots Ag(2) distance is 3.115(2) Å. The distances from the silver atoms to the furan oxygen atoms are too long to be considered as bonds [3.07(2) to 3.20(2) Å]. Although there are no structural data available for the disilver complex of L^3 , the structure of $[\text{Ag}_2\text{L}^4]^{2+}$, where L^4 is the similar macrocycle with *p*-phenyl bridging links, is known. In that structure, the intercationic distance is 6.06 Å, *i.e.* much longer than in the present structure.

The stability of the 1 : 1 silver complexes decreases according to the sequence: $\text{L}^1 > \text{L}^2 > \text{L}^3$. However, the most stable complex AgL^1 ($\log \beta_{11} = 7.1$) is less stable than the corresponding 222 and 221 cryptates ($\log \beta_{11} = 8.99$ and 11.24, respectively).²⁵ L^1 also forms the most stable dinuclear complex. Its room temp.

^1H NMR spectrum shows that, in contrast to that of the L^3 complex, the two silver cations are not in rapid exchange between cryptand and solvent but are retained in the cavity of the ligand.^{8b,9} As was the case for the binuclear Cu^1 complexes of L^1 and L^2 , there is no positive cooperative effect during the formation of the disilver complexes of L^1 and L^3 , since $\Delta = -1.1$ and -0.83 , respectively.

In order to allow an in-depth discussion of the stability of the silver complexes with L^1 and L^2 , a calorimetric study has been carried out. The values of the overall thermodynamic parameters ΔG_{xy} , ΔH_{xy} and $T\Delta S_{xy}$ are presented in Table 4. Attempts to determine the same parameters for the complexation of copper(I) by the same ligands were also unsuccessful. Most of the heat evolved during the complexation was due to the dilution of the metal salt and thus, no reliable values of the complexation enthalpies could be obtained. The only conclusion which could be drawn was the entropic stabilisation of the copper(I) complexes with L^1 and L^2 .

As regards Ag^1 , the results show that, for the mononuclear complex with L^1 , both the enthalpy and entropy changes are favourable. The same situation holds with L^2 , but the highest stability of the L^1 complex is mainly due to its higher entropic contribution, the enthalpy terms being very close to each other. These results are consistent with the strong solvation of silver in acetonitrile. Upon complexation, the cation should undergo desolvation, leading to a positive contribution to the entropy change. As regards the binuclear complex with L^1 , ΔH_2 and $T\Delta S_2$ values, corresponding to its stepwise formation with respect to the mononuclear complex, could be calculated from the overall values in Table 4: $-\Delta H_2 = 31 \text{ kJ mol}^{-1}$ and $T\Delta S_2 = 4 \text{ J K}^{-1} \text{ mol}^{-1}$. They show that the stabilisation of the binuclear complex is purely of enthalpic origin as the entropy change is close to zero. The fact that $-\Delta H_2 \gg -\Delta H_{11}$ shows an important cooperative effect of enthalpic nature, overcoming the repulsion of the two cations, which should lead to $-\Delta H_2 < -\Delta H_{11}$. However this effect is offset by the unfavourable entropy change ($T\Delta S_2 < T\Delta S_{11}$) leading to the observed global negative cooperative effect when comparing $\log \beta_{11}$ and $\log K_2$. It is likely that the binding of the first cation enables the ligand to adopt a conformation which is favourable to the further fixation of a second cation at a distance which may assure weak M–M bonding. During this process the ligand should undergo extensive desolvation which could explain also the high $T\Delta S_{11}$ value for the first step. The quite unfavourable entropy term for the second step could be due to a loss of freedom of the system upon complexation, resulting from its organisation and rigidification.

Acknowledgements

The authors thank Dr S. Fanni for fruitful discussions.

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Paper 6/01986B

Received 21st March 1996

Accepted 17th July 1996