Metal Complexes of Molecular Clefts. The Synthesis and *X*-Ray Crystal Structures of a Mononuclear Barium and Four Binuclear Silver(I) Complexes of Bibracchial Tetraimine Schiff-base Macrocycles†

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Mononuclear barium and binuclear silver(I) complexes of bibracchial tetraimine Schiff-base macrocycles L^1—L^4 derived from the '2 + 2' condensation of 2,6-diacetylpyridine and the functionalised triamines *N,N*-bis(2-aminoethyl)-2-(aminomethyl)pyridine, *N,N*-bis(3-aminopropyl)-2-(aminomethyl) pyridine, *N,N*-bis(3-aminopropyl)-2-methoxyethylamine, and *N,N*-(3-amino-propyl)-2-methoxybenzylamine, respectively, have been synthesised. The crystal structures of five complexes have been determined: $[BaL^1][ClO_4]_2$ crystallises in the monoclinic space group $C2/c$ (C^6_{2h}, no. 15) and has unit-cell dimensions a = 20.310(38), b = 14.453(41), c = 15.137(29) Å, β = 104.84(15)°, and Z = 4; $[Ag_2L^1][ClO_4]_2$ crystallises in the tetragonal space group $I4_1cd$ (C^{12}_{4v}, no. 110) with a = 28.11(4), c = 21.618(16) Å, and Z = 16; $[Ag_2L^2][ClO_4]_2\cdot0.5H_2O$ crystallises in the triclinic space group $P\bar{1}$ (C^1_i, no. 2) with a = 12.277(16), b = 13.899(14), c = 15.260(50) Å, α = 77.30(20), β = 70.17(20), γ = 71.27(9)°, and Z = 2; $[Ag_2L^3][ClO_4]_2\cdot 0.5\ H_2O$ crystallises in the triclinic space group $P\bar{1}$ (C^1_i, no. 2) with a = 14.171(14), b = 18.323(16), c = 12.495(23) Å, α = 99.20(12), β = 120.13(11), γ = 116.35(7)°, and Z = 2; $[Ag_2L^4][ClO_4]_2$ crystallises in the monoclinic space group $P2_1/a$ (C^5_{2h}, no. 14), a = 16.595(16), b = 13.363(11), c = 23.951(25) Å, β = 105.43(8)°, and Z = 4. The macrocycles fold to present molecular clefts into which the metals co-ordinate. Modification of the ring size and of the nature of the donor atom in the pendant arm leads to the Ag ··· Ag separation in the binuclear silver(I) complexes varying from 2.9 to 6.9 Å.

Pendant-arm macrocycles and their metal complexes have attracted much interest in recent years.[1–4] Arms bearing additional potential ligating groups have been introduced at both carbon (*C*-pendant) and nitrogen (*N*-pendant) atoms of macrocycles which have generally been based on polyaza- or polyoxa-donor sets. One potential of this area derives from the concept that the presence of two pendant arms, bearing ligating groups, attached at appropriate positions on the macrocyclic framework would result in an 'opened' cryptand thus leading to modified complexation properties relative to the corresponding clathrochelates or simple macrocyclic precursors.[5] Such doubly pendant-armed macrocycles have been designated as bibracchial.[6]

'2 + 2' Tetraimine Schiff-base macrocycles are readily prepared by the template cyclocondensation of heterocyclic dicarbonyl derivatives and 1,*n*-diaminoalkanes.[7,8] In the present work extension of this approach to include functionalised triamines bearing 2-pyridylmethyl-, 2-methoxyethyl, and 2-methoxybenzyl substituents leads to the synthesis of N,N'-bibracchial macrocyclic (L^1—L^4) complexes of the templating cation. Mono- and bi-nuclear complexes are recovered in the presence of barium and silver(I) templates respectively. The crystal structures of a mononuclear barium complex of L^1 and of four homobinuclear silver(I) complexes, one from each macrocyclic ligand, are reported and discussed.

Results and Discussion

Functionalised Triamine Precursors.—(*i*) N,N-*Bis*(*aminoalkyl*)-2-(*aminomethyl*)*pyridines*. The aminomethylpyridines were prepared as the hydrochloride salts by the following route. The primary amine functions in 3-azapentane-1,5-diamine and 4-azaheptane-1,7-diamine were selectively protected using phthalic anhydride[9] and the resulting bis(phthalimido)-derivatives were then treated with 2-(chloromethyl)pyridine to introduce the functional group at the secondary amine. The phthalimido groups were then removed from the protected triamine by heating at reflux in aqueous HCl[10] to give the corresponding hydrochloride salts.

(*ii*) N,N-*Bis*(3-*aminopropyl*)*alkylamines*. The *N,N*-bis(3-aminopropyl)alkylamines were prepared from acrylonitrile and the corresponding alkylamine by a modification of the route employed by Lotz and Kaden,[11] with the catalytic hydrogenation of the *N,N*-bis(2-cyanoethyl)alkylamines first formed being replaced by a chemical reduction utilising dissolving sodium metal in absolute ethanol.[12]

Template Synthesis of Bibracchial [2 + 2] *Tetraimine Schiff-base Macrocycles.*—A number of workers have reported the cyclization of 2,6-dicarbonylpyridines and *N,N*-bis(3-aminopropyl)alkylamines to form the [2 + 2] tetraimine Schiff-base products, where the pendant alkyl group is simply a proton or a methyl group.

Alcock *et al.*[12] found that the reaction of an equimolar amount of 2,6-diformylpyridine and *N,N*-bis(3-aminopropyl)-methylamine in dry tetrahydrofuran causes the precipitation of a colourless crystalline material and have proposed that this is the [2 + 2] tetraimine Schiff-base product (L^5). Nelson[7] found that the condensation between 2,6-diacetylpyridine and *N,N*-bis(3-aminopropyl)amine in the presence of manganese(II), cobalt(II), nickel(II), copper(II), or zinc(II) salts yields the mononuclear metal complex of the [1 + 1] tetraimine Schiff-base macrocycle. However, if the reaction is repeated with a silver(I)

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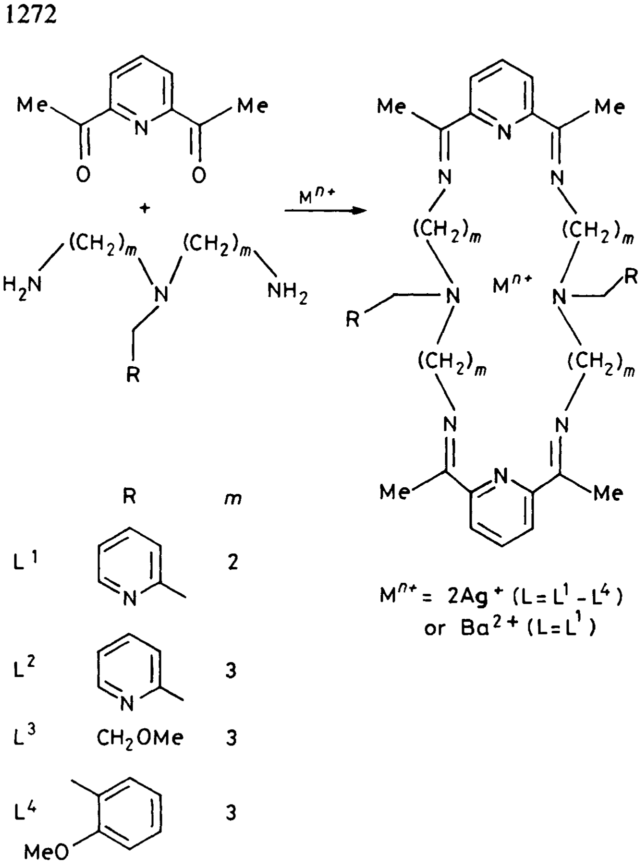
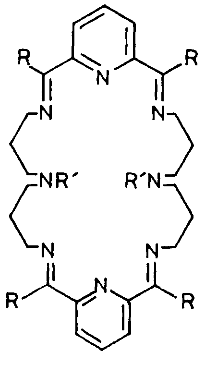
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

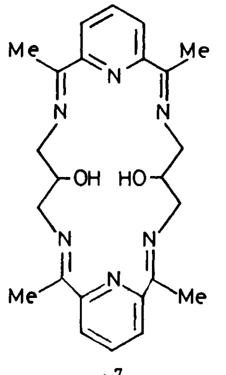
Non-S.I. unit employed: mmHg ≈ 133 Pa.



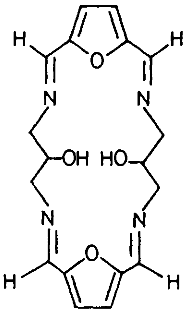
Scheme.



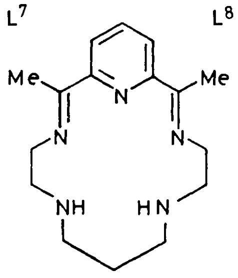
	R	R′
L^5	H	Me
L^6	Me	H



L^7



L^8



L^9

salt as the metal template the product isolated is the binuclear silver(I) complex of the [2 + 2] tetraimine Schiff-base macrocycle (L^6; R′ = H).[13] Similarly Cabral *et al.*[14] found that silver(I) and lead(II) salts can be successfully used as templates for the formation of the binuclear complexes of the [2 + 2] tetraimine Schiff-base macrocycles (L^6; R = H or Me).

When equimolar amounts of 2,6-diacetylpyridine and the *N*,*N*-bis(*n*-aminoalkyl)-2-(aminomethyl)pyridine (*n* = 2 or 3, alkyl = ethyl or propyl) are heated at reflux temperature in dry methanol, ethanol, or tetrahydrofuran a polymeric gum is isolated. When the reaction is carried out in the presence of a suitable templating cation such as barium(II) or silver(I) the [2 + 2] tetraimine Schiff-base macrocycle may be isolated as the corresponding metal complex (Scheme).

Template Formation in the Presence of Barium(II) *Salts.*—The reaction of 2,6-diacetylpyridine with *N*,*N*-bis(2-aminoethyl)-2-(aminomethyl)pyridine in the presence of barium(II) perchlorate (2:2:1 molar proportions) in refluxing methanol for 22 h leads to the isolation of white crystals. These are characterised as the mononuclear complex $[BaL^1][ClO_4]_2$. The macrocyclic nature of the ligand L^1 is confirmed using i.r. spectroscopy, positive-ion fast atom bombardment mass spectrometry (f.a.b.m.s.), and *X*-ray crystallography.

The i.r. spectrum (recorded as a KBr disc) of $[BaL^1][ClO_4]_2$ showed no bands characteristic of the stretching frequency of the carbonyl groups in the 2,6-diacetylpyridine, nor of the unsymmetrical and symmetrical stretching frequencies for the primary amine groups. Instead, the complex possesses a strong band at 1 635 cm^{-1} indicative of the stretching frequency of imino groups. It also exhibits very strong bands between 1 110 and 1 080 and at 624 cm^{-1} characteristic of the stretching frequencies of the perchlorate anions.

The positive-ion f.a.b.m.s. of the complex shows two major peaks, at *m*/*z* 879 (100) and 780 (12%). The first peak corresponds to the $[BaL^1(ClO_4)]^+$ cation, where the parent molecule has lost one perchlorate anion, to generate a positive ion. The loss of the second perchlorate anion to form $[BaL^1]^+$ corresponds to the second peak.

The reaction of 2,6-diacetylpyridine with *N*,*N*-bis(3-aminopropyl)-2-(aminomethyl)pyridine in the presence of barium(II) perchlorate (2:2:1 molar proportions) in methanol at reflux temperature for 22 h does not lead to the isolation of a macrocyclic complex. The size of the cavity in L^2 does not match that required by the barium(II) ion with the result that the template does not stabilise the formation of the macrocycle.

Template Formation in the Presence of Silver(I) *Salts.*—The reaction of 2,6-diacetylpyridine with *N*,*N*-bis(*n*-aminoalkyl)-2-(aminomethyl)pyridine (*n* = 2 or 3, alkyl = ethyl or propyl) in the presence of silver(I) nitrate (1:1:1 molar proportions) in methanol at reflux temperature for 20 h, followed by filtration of the pale yellow reaction solution into a methanolic solution containing an excess of sodium perchlorate, causes precipitation of $[Ag_2L][ClO_4]_2$ (L = L^1 or L^2) as the filtrate cools. The homobinuclear macrocyclic complexes so formed were characterised using i.r. spectroscopy, positive-ion f.a.b.m.s., and *X*-ray crystallography. It is noteworthy that changing the metal ion used in the template procedure from barium to silver(I) leads to the formation of homobinuclear rather than mononuclear complexes. It is likely that this is related to the change in ionic radius from barium (1.43 Å) to silver(I) (1.13 Å) as the formation of a mononuclear silver(I) complex would cause a collapsing of the macrocyclic structure to accommodate the silver cation with adverse accompanying steric effects.

The i.r. spectra (recorded as KBr discs) of $[Ag_2L^1][ClO_4]_2$ and $[Ag_2L^2][ClO_4]_2$ show no bands indicative of carbonyl stretching frequencies or of primary amine stretching frequencies. The spectra of $[BaL^1][ClO_4]_2$ and $[Ag_2L^1][ClO_4]_2$ are similar, with a notable exception in the imine stretching frequency region between 1 645 and 1 630 cm^{-1}. The complex $[BaL^1][ClO_4]_2$ possesses a single imine stretching frequency band at 1 635 cm^{-1}, in contrast to $[Ag_2L^1][ClO_4]_2$ which possesses two imine stretching bands at 1 630 and 1 645 cm^{-1}. The i.r. spectrum of $[Ag_2L^2][ClO_4]_2$ is very similar to that of

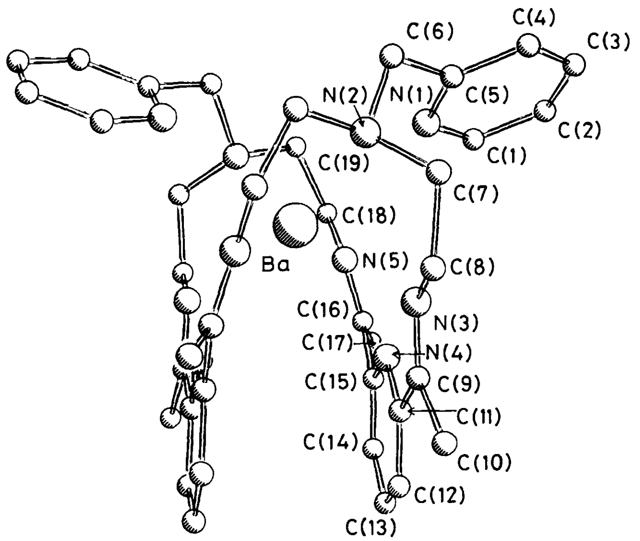


Figure 1. The molecular structure with atom labelling of the cation $[BaL^1]^{2+}$

Table 1. Atom co-ordinates (× 10^4) for $[BaL^1][ClO_4]_2$

Atom	x	y	z
Ba	0	1 822(1)	2 500
Cl(1)	1 676(3)	4 068(5)	−1 547(4)
O(1)	1 861(10)	3 717(13)	−657(8)
O(2)	983(6)	4 276(13)	−1 801(12)
O(3)	1 784(9)	3 363(15)	−2 128(14)
O(4)	2 075(8)	4 817(10)	−1 632(19)
N(1)	−327(6)	3 114(10)	886(8)
N(2)	1 122(7)	2 806(10)	1 970(11)
N(3)	750(7)	895(10)	1 303(12)
N(4)	−490(4)	195(8)	1 295(10)
N(5)	−1 452(8)	1 447(11)	1 581(13)
C(1)	−895(6)	2 993(10)	150(8)
C(2)	−895(6)	3 346(10)	−708(8)
C(3)	−326(6)	3 821(10)	−829(8)
C(4)	242(6)	3 942(10)	−92(8)
C(5)	241(6)	3 589(10)	765(8)
C(6)	811(9)	3 718(13)	1 592(12)
C(7)	1 393(10)	2 319(12)	1 259(14)
C(8)	1 431(8)	1 266(11)	1 326(15)
C(9)	680(7)	3(10)	1 258(14)
C(10)	1 252(11)	−688(15)	1 127(18)
C(11)	23(4)	−438(8)	1 266(10)
C(12)	−116(4)	−1 385(8)	1 228(10)
C(13)	−767(4)	−1 698(8)	1 219(10)
C(14)	−1 280(4)	−1 065(8)	1 247(10)
C(15)	−1 141(4)	−119(8)	1 286(10)
C(16)	−1 650(6)	618(9)	1 295(15)
C(17)	−2 420(9)	304(20)	999(19)
C(18)	−1 984(9)	2 109(12)	1 702(15)
C(19)	−1 650(10)	2 981(13)	2 194(15)

$[BaL^1][ClO_4]_2$, and unlike $[Ag_2L^1][ClO_4]_2$ only possesses one imine stretching frequency at 1 640 cm^{-1}.

The positive-ion f.a.b.m.s. of these binuclear silver complexes of L^1 and L^2 show identical initial breakdown patterns. The loss of an anionic perchlorate ion from the neutral parent molecule generates the cationic $[Ag_2L(ClO_4)]^+$ species, which is the first peak observed in the mass spectra. The loss of a second perchlorate anion occurs to generate $[Ag_2L]^+$. This in turn loses a silver ion to form $[AgL]^+$. The final major peak of interest arises in the spectra from the loss of a methylenepyridyl group from the $[AgL]^+$ species to form $[AgL']^+$ ($L' = L - CH_2C_5H_4N$). The oxidation state of the silver ions may change during the formation of these breakdown species in order to maintain a monopositive species.

When the condensation reaction between 2,6-diacetylpyridine and the *N,N*-bis(3-aminopropyl)alkylamine (alkyl = 2-methoxyethyl or 2-methoxybenzyl) is carried out in the presence of an equimolar amount of silver(I) perchlorate the product isolated is characterised as the binuclear silver(I) complex of the corresponding [2 + 2] tetraimine Schiff-base macrocycle. The condensation involves the addition of a methanolic solution of the *N,N*-bis(3-aminopropyl)alkylamine to a methanolic solution of silver perchlorate monohydrate and 2,6-diacetylpyridine and the solution is heated at reflux temperature for 18 h. Since this method involves refluxing a solution containing the potentially explosive silver(I) perchlorate[15] for 18 h it is advisable to carry it out only on a small scale.

An improved method for the preparation of these complexes involves carrying out the reaction in the presence of silver(I) nitrate. This increases the yields of the products and minimises the inherent hazards in the use of the perchlorate salt. It should however be noted that silver(I) nitrate also has the potential to detonate and has been reported as the cause of a recent explosion,[16] thus it remains prudent to adopt suitable precautions. A methanolic solution containing equimolar amounts of silver(I) nitrate, 2,6-diacetylpyridine, and the *N,N*-bis(3-aminopropyl)alkylamine is heated at reflux temperature for 16 h and then filtered into a methanolic solution containing an excess of sodium perchlorate in order to isolate the required complex (Scheme). The binuclear silver(I) complex $[Ag_2L^3][ClO_4]_2 \cdot H_2O$ is now isolated in 80% yield and $[Ag_2L^4][ClO_4]_2$ in 74% yield as compared with yields of 47 and 23% respectively when using the previous route. The nature of the binuclear silver(I) complexes of the [2 + 2] tetraimine Schiff-base macrocycles is established using i.r. spectroscopy, positive-ion f.a.b.m.s., and *X*-ray crystallography.

The i.r. spectra (recorded as KBr discs) of the $[Ag_2L][ClO_4]_2$ complexes ($L = L^3$ or L^4) show no bands ascribable to the ketone and amine stretches found for the precursors. The complex $[Ag_2L^3][ClO_4]_2 \cdot H_2O$ possesses a strong band at 1 635 cm^{-1} indicative of the imino stretching frequency in the Schiff-base linkage, while the $[Ag_2L^4][ClO_4]_2$ complex possesses an imino stretching frequency band at 1 640 cm^{-1}. Both $[Ag_2L^3][ClO_4]_2 \cdot H_2O$ and $[Ag_2L^4][ClO_4]_2$ exhibit strong bands between 1 100 and 1 080 cm^{-1}, and at 624 cm^{-1} characteristic of the stretching frequencies of the perchlorate groups.

The positive-ion f.a.b. mass spectra of $[Ag_2L^3][ClO_4]_2 \cdot H_2O$ and $[Ag_2L^4][ClO_4]_2$ show identical key intermediate breakdown species. The highest peak observed corresponds to the monocationic $[Ag_2L(ClO_4)]^+$ species, which arises from the loss of a perchlorate anion from the neutral parent molecule. The loss of a second perchlorate anion generates $[Ag_2L]^+$, with the dicationic $[Ag_2L]^{2+}$ also being observed as a peak at half the mass. The loss of a silver cation from this generates the final peak of interest in the spectra, arising from the mononuclear species $[AgL]^+$.

Attempts to remove the metals from the macrocycles in an effort to obtain the metal-free tetraimine Schiff bases were unsuccessful, generally leading to hydrolysis products.

Descriptions of the Structures.—Complexes derived from macrocycles having N-donor pendant arms. Crystals of $[BaL^1][ClO_4]_2$ were grown by slow diffusion of diethyl ether into a solution of the complex in acetonitrile. The complexes $[Ag_2L^1][ClO_4]_2$ and $[Ag_2L^2][ClO_4]_2$ were similarly crystallised by the slow diffusion of diethyl ether into a solution of the complex in CD_3CN.

Table 2. Selected bond lengths (Å) and angles (°) for $[BaL^1][ClO_4]_2$

Ba–N(1)	3.011(14)	Ba–N(2)	2.966(18)
Ba–N(3)	2.968(19)	Ba–N(4)	2.986(14)
Ba–N(5)	2.970(16)	N(2)–C(6)	1.509(23)
N(2)–C(7)	1.504(29)	N(2)–C(19a)	1.455(24)
N(3)–C(8)	1.477(23)	N(3)–C(9)	1.296(20)
N(5)–C(16)	1.302(21)	N(5)–C(18)	1.489(26)
C(5)–C(6)	1.483(19)	C(7)–C(8)	1.526(24)
C(9)–C(10)	1.582(28)	C(9)–C(11)	1.483(18)
C(15)–C(16)	1.487(17)	C(16)–C(17)	1.578(23)
C(18)–C(19)	1.530(26)		
N(1)–Ba–N(2)	60.6(4)	N(1)–Ba–N(3)	80.0(4)
N(1)–Ba–N(4)	91.3(4)	N(1)–Ba–N(5)	75.3(4)
N(1)–Ba–N(1a)	103.3(5)	N(1)–Ba–N(2a)	84.1(4)
N(1)–Ba–N(3a)	137.2(4)	N(1)–Ba–N(4a)	162.5(4)
N(1)–Ba–N(5a)	118.7(4)	N(2)–Ba–N(3)	60.1(4)
N(2)–Ba–N(4)	111.8(4)	N(2)–Ba–N(5)	134.5(5)
N(2)–Ba–N(2a)	122.7(6)	N(2)–Ba–N(3a)	158.7(4)
N(2)–Ba–N(4a)	112.6(4)	N(2)–Ba–N(5a)	58.3(5)
N(3)–Ba–N(4)	54.1(4)	N(3)–Ba–N(5)	103.6(5)
N(3)–Ba–N(3a)	126.3(6)	N(3)–Ba–N(4a)	82.8(4)
N(3)–Ba–N(5a)	66.4(5)	N(4)–Ba–N(5)	55.6(4)
N(4)–Ba–N(4a)	76.1(5)	N(4)–Ba–N(5a)	106.1(4)
N(5)–Ba–N(5a)	159.0(6)	Ba–N(1)–C(5)	113.2(3)
Ba–N(1)–C(1)	122.4(3)	Ba–N(2)–C(6)	104.2(11)
Ba–N(2)–C(7)	114.6(10)	C(6)–N(2)–C(7)	109.4(15)
Ba–N(2)–C(19a)	107.1(13)	C(6)–N(2)–C(19a)	108.8(13)
C(7)–N(2)–C(19a)	112.4(15)	Ba–N(3)–C(8)	116.5(11)
Ba–N(3)–C(9)	114.6(13)	C(8)–N(3)–C(9)	116.8(14)
Ba–N(4)–C(15)	115.4(3)	Ba–N(4)–C(11)	113.7(2)
Ba–N(5)–C(16)	120.6(10)	Ba–N(5)–C(18)	119.3(11)
C(16)–N(5)–C(18)	117.4(14)	N(1)–C(5)–C(6)	116.4(10)
C(4)–C(5)–C(6)	123.6(9)	N(2)–C(6)–C(5)	111.8(14)
N(2)–C(7)–C(8)	116.1(18)	N(3)–C(8)–C(7)	109.2(14)
N(3)–C(9)–C(10)	124.1(15)	N(3)–C(9)–C(11)	120.8(14)
C(10)–C(9)–C(11)	114.9(13)	C(9)–C(11)–N(4)	113.5(7)
C(9)–C(11)–C(12)	126.5(7)	N(4)–C(15)–C(16)	115.3(7)
C(14)–C(15)–C(16)	124.7(7)	N(5)–C(16)–C(15)	120.4(11)
N(5)–C(16)–C(17)	124.0(16)	C(15)–C(16)–C(17)	115.6(14)
N(5)–C(18)–C(19)	110.1(15)	C(18)–C(19)–N(2a)	114.6(15)

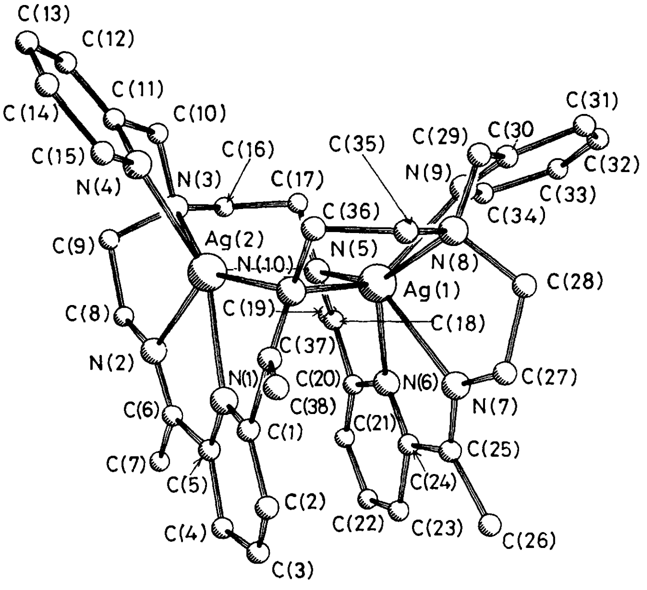


Figure 2. The molecular structure with atom labelling of the cation $[Ag_2L^1]^{2+}$

The X-ray crystallographic determination of $[BaL^1][ClO_4]_2$ confirms the macrocyclic nature of the ligand. The structure of the cation is shown in Figure 1 along with the atom labelling. Atomic co-ordinates are listed in Table 1 with bond lengths and angles, complete with estimated standard deviations (e.s.d.s), in Table 2. The cation possesses crystallographically imposed C_2 symmetry with the barium atom on the C_2 axis. The macrocycle is folded back upon itself to provide a 'molecular cleft' in which the pyridyl fragments at opposite ends lie approximately parallel (4.8°), although not 'face-to-face,' with the barium 'sandwiched,' although displaced towards the more open part of the macrocycle. All ten nitrogen atoms from the ligand are close enough to interact with the central barium ion (2.97—3.01 Å); however, the metal lies well displaced from the pyridyl planes (1.08 and 1.66 Å). In view of the constraints applied during refinement, little discussion of the bond lengths would be justified although the refined values are very acceptable. There are no short intermolecular contacts and there is no opportunity for hydrogen bonding.

The structure of the dication $[Ag_2L^1]^{2+}$ is shown in Figure 2 with atomic co-ordinates in Table 3 and bond lengths and angles in Table 4. The asymmetric unit also contains two perchlorate anions. The macrocycle retains its cleft-like appearance and co-ordinates to two silver atoms which are closely spaced [Ag $\cdots$ Ag 3.068(6) Å]. Each silver is co-ordinated 'strongly' to two pyridyl nitrogens (one in the macrocycle and one in the pendant picoline fragment), to a tertiary amino nitrogen, and to both imino nitrogens lying adjacent to the co-ordinating macrocyclic pyridyl. One silver [Ag(1)] is also close to a third imino nitrogen [N(10)], which is therefore symmetrically bridging the two silvers: the diametrically opposite imino nitrogen [N(5)] is much further from the second silver [Ag(2) $\cdots$ N(5) 3.068(25) Å]. The co-ordination geometries of the silvers are not closely related to regular polyhedra. It is noteworthy that the pendant groups are fully incorporated in the silver co-ordination spheres. Examination of the angles at the two silver atoms shows a close correspondence of all chemically equivalent pairs involving two macrocyclic heteroatoms. However, the position of the pendant pyridyl group on Ag(1) is such that N(9) subtends smaller angles to the two macrocyclic imino nitrogens (by 7.6 and 11.1°), and particularly to the macrocyclic pyridyl (by 28.3°) than does the corresponding atom N(4) at Ag(2). This leaves angular space on Ag(1) for the further incorporation of imino nitrogen N(10) fully into its co-ordination sphere, giving it a symmetrically bridging role. It is noteworthy that the Ag–N contacts to N(5) and N(10) are significantly longer than those to the other two imino nitrogens N(2) and N(7), which show no bridging tendencies. The conformation of the macrocycle is such that the two halves (defined by the macrocyclic pyridyl fragments) are almost precisely parallel (angle between mean planes 1.8°). In view of the constraints applied to chemically equivalent bonds during refinement, discussion of the macrocycle geometry must necessarily be limited: however, all bond lengths have refined to very acceptable values. The four pyridyl fragments are each planar [root mean square (r.m.s.) deviations 0.040, 0.009, 0.012, and 0.018 Å] with major displacement of the silver atoms from these mean planes by 0.27, 0.65, 0.33, and 1.09 Å; in each case, the last two values refer to the pendant pyridyl groups. There are no significant intermolecular interactions and no opportunities for hydrogen bonding.

The structure of the dication $[Ag_2L^2]^{2+}$ in which the macrocyclic ring size has been expanded from 24- to 28-membered is shown in Figure 3 with atomic co-ordinates in Table 5 and bond lengths and angles in Table 6. The asymmetric unit also contains two perchlorate anions and a half-occupancy (on the basis of electron density) water of solvation. The macrocycle co-ordinates to two silver atoms which are in very similar and

Table 3. Atom co-ordinates (× 10^4) for $[Ag_2L^1][ClO_4]_2$

Atom	*x*	*y*	*z*
Ag(1)	1 090(1)	−1 002(1)	609
Ag(2)	1 259(1)	−1 984(1)	1 189(2)
Cl(1)	−1 248(4)	−1 512(4)	−694(6)
O(1)	−1 678(11)	−1 499(11)	−1 013(13)
O(2)	−1 020(14)	−1 955(14)	−751(16)
O(3)	−953(17)	−1 160(14)	−924(13)
O(4)	−1 328(14)	−1 404(15)	−74(16)
Cl(2)	1 572(3)	843(3)	2 218(3)
O(5)	1 400(10)	444(9)	1 920(15)
O(6)	1 896(10)	708(11)	2 663(13)
O(7)	1 205(9)	1 086(9)	2 496(15)
O(8)	1 794(12)	1 134(12)	1 793(13)
N(1)	410(9)	−1 948(11)	1 183(11)
N(2)	913(7)	−2 097(11)	2 187(10)
N(3)	1 896(10)	−1 909(9)	2 004(12)
N(4)	1 902(7)	−2 484(8)	928(10)
N(5)	1 414(11)	−985(13)	1 726(15)
N(6)	548(7)	−693(12)	1 357(6)
N(7)	323(10)	−742(13)	153(9)
N(8)	1 144(3)	−983(3)	−602(9)
N(9)	1 676(11)	−428(6)	254(5)
N(10)	907(7)	−1 827(11)	97(9)
C(1)	165(4)	−1 948(14)	653(10)
C(2)	−322(4)	−1 897(15)	627(7)
C(3)	−573(12)	−1 804(15)	1 161(10)
C(4)	−322(11)	−1 855(17)	1 705(19)
C(5)	165(11)	−1 921(16)	1 712(12)
C(6)	480(6)	−1 989(16)	2 261(14)
C(7)	244(18)	−1 900(20)	2 895(16)
C(8)	1 252(8)	−2 158(13)	2 695(10)
C(9)	1 763(11)	−2 258(13)	2 474(17)
C(10)	2 332(11)	−2 085(13)	1 715(19)
C(11)	2 287(8)	−2 501(11)	1 292(13)
C(12)	2 650(11)	−2 824(12)	1 210(18)
C(13)	2 613(13)	−3 172(14)	763(16)
C(14)	2 210(13)	−3 157(16)	401(19)
C(15)	1 860(16)	−2 820(13)	493(17)
C(16)	1 997(15)	−1 459(7)	2 316(12)
C(17)	1 920(12)	−1 041(13)	1 865(20)
C(18)	1 155(4)	−756(11)	2 101(8)
C(19)	1 309(15)	−550(14)	2 731(10)
C(20)	639(4)	−707(12)	1 962(4)
C(21)	282(3)	−650(13)	2 390(7)
C(22)	−185(7)	−599(18)	2 208(20)
C(23)	−287(11)	−593(21)	1 585(16)
C(24)	94(5)	−644(10)	1 189(8)
C(25)	−18(6)	−641(15)	515(10)
C(26)	−528(7)	−534(16)	295(19)
C(27)	297(13)	−712(18)	−522(6)
C(28)	789(11)	−645(14)	−825(20)
C(29)	1 619(9)	−794(14)	−722(20)
C(30)	1 746(15)	−367(12)	−352(6)
C(31)	1 896(15)	62(5)	−595(8)
C(32)	1 949(14)	433(13)	−185(14)
C(33)	1 890(16)	376(13)	444(15)
C(34)	1 758(14)	−71(9)	649(14)
C(35)	1 077(16)	−1 434(4)	−926(8)
C(36)	1 174(15)	−1 852(15)	−483(12)
C(37)	484(6)	−1 985(13)	102(7)
C(38)	241(14)	−2 179(15)	−486(14)

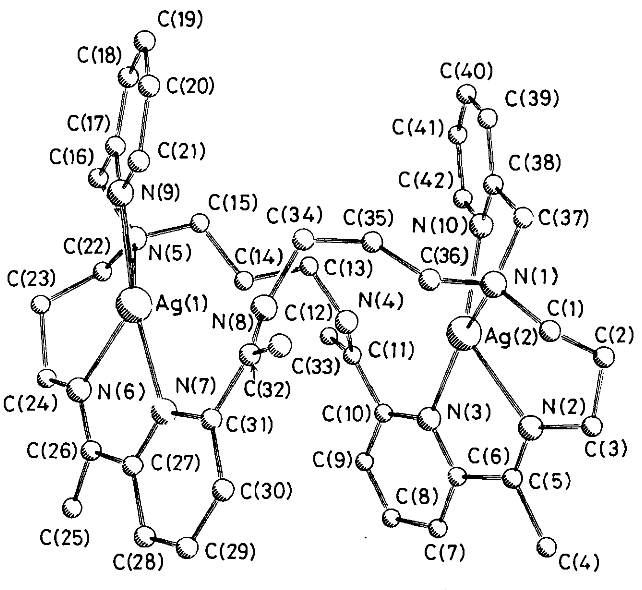


Figure 3. The molecular structure with atom labelling of the cation $[Ag_2L^2]^{2+}$

widely separated environments (Ag • • • Ag 6.824 Å). Each is co-ordinated 'strongly' to two pyridyl nitrogens (one in the macrocycle and one in the pendant picoline fragment), to a tertiary amino nitrogen, and to the imino nitrogen lying between the co-ordinating macrocyclic pyridyl and tertiary amine nitrogens: there is a 'weaker' (longer) bond to the other imino nitrogen which is adjacent to the co-ordinating macrocyclic pyridyl. The five-co-ordinate geometry is not closely related to either trigonal bipyramidal or square-based pyramidal. Again the pendant group is fully incorporated in the silver co-ordination sphere. The conformation of the macrocycle has suffered a 'concertina' expansion but leaves no obviously unfilled co-ordination site. Bond lengths and angles within the macrocycle are acceptable within the rather high e.s.d.s; the four pyridyl rings are each planar (r.m.s. deviations 0.010, 0.026, 0.013, and 0.017 Å). Those of the macrocycle are mutually inclined at 20° and the silver atoms deviate from these planes by 0.009 and 0.302 Å respectively, and from the planes of the pendant pyridyl residues by 0.645 and 0.650 Å. The half-occupancy water molecule forms a hydrogen bond to perchlorate oxygen O(1), and perhaps to O(3) of the same perchlorate anion, at distances of 2.80 and 2.98 Å respectively. Drew *et al.*[13] have reported the crystal structure of the disilver complex of a related macrocycle in which the pendant pyridyl groups are replaced simply by protons.[13] A similar large silver • • • silver separation of 6.0 Å is found for this system but the macrocycle does not form a cleft implying that the introduction of the pendant arms is perhaps a necessary criterion for cleft formation.

Complexes derived from macrocycles having O*-donor pendant arms.* The complex $[Ag_2L^3][ClO_4]_2 \cdot 0.5H_2O$ crystallises from methanol as pale yellow prisms. The structure of the $[Ag_2L^3]^{2+}$ dication is shown in Figure 4 with atomic co-ordinates in Table 7 and bond lengths and angles in Table 8. The asymmetric unit also contains two perchlorate anions (one rotationally disordered 0.524:0.476 with approximately coincident chlorine atoms), and some water of solvation disordered between two mutually incompatible sites (given occupancies 0.333 and 0.167), adjacent to a crystallographic inversion centre. The macrocycle co-ordinates to two silver atoms which are in rather different environments. One, Ag(1), is 'strongly' linked to a pyridinyl nitrogen, a tertiary amino nitrogen, and to three of the imino nitrogens; the five-co-ordinate geometry is not closely related to either trigonal bipyramidal or square-based pyramidal. The second silver, Ag(2), forms only three 'strong' links to nitrogen atoms, one each to a pyridinyl, amino, and imino

Table 4. Selected bond lengths (Å) and angles (°) for $[Ag_2L^1][ClO_4]_2$

Ag(1) · · · Ag(2)	3.068(6)	Ag(1)–N(10)	2.620(28)
Ag(1)–N(5)	2.582(32)	Ag(2)–N(10)	2.597(21)
Ag(1)–N(6)	2.385(20)	Ag(2)–N(1)	2.389(26)
Ag(1)–N(7)	2.480(29)	Ag(2)–N(2)	2.388(22)
Ag(1)–N(8)	2.622(19)	Ag(2)–N(3)	2.520(28)
Ag(1)–N(9)	2.431(25)	Ag(2)–N(4)	2.358(22)
N(2)–C(6)	1.266(28)	N(2)–C(8)	1.462(31)
N(3)–C(9)	1.461(45)	N(3)–C(10)	1.462(44)
N(3)–C(16)	1.461(34)	N(5)–C(17)	1.464(47)
N(5)–C(18)	1.266(39)	N(7)–C(25)	1.269(33)
N(7)–C(27)	1.463(23)	N(8)–C(28)	1.461(37)
N(8)–C(29)	1.459(29)	N(8)–C(35)	1.459(18)
N(10)–C(36)	1.464(38)	N(10)–C(37)	1.270(30)
Ag(2) · · · N(5)	3.068(25)		

N(5)–Ag(1)–N(6)	65.4(8)	N(1)–Ag(2)–N(10)	66.8(7)
N(5)–Ag(1)–N(7)	132.3(9)	N(2)–Ag(2)–N(10)	133.5(7)
N(5)–Ag(1)–N(8)	155.9(7)	N(3)–Ag(2)–N(10)	153.2(8)
N(5)–Ag(1)–N(9)	92.5(8)	N(4)–Ag(2)–N(10)	100.1(8)
N(6)–Ag(1)–N(7)	66.9(7)	N(1)–Ag(2)–N(2)	66.7(7)
N(6)–Ag(1)–N(8)	134.9(5)	N(1)–Ag(2)–N(3)	135.2(9)
N(6)–Ag(1)–N(9)	113.8(9)	N(1)–Ag(2)–N(4)	142.1(9)
N(7)–Ag(1)–N(8)	69.4(5)	N(2)–Ag(2)–N(3)	70.6(8)
N(7)–Ag(1)–N(9)	105.5(10)	N(2)–Ag(2)–N(4)	116.6(9)
N(8)–Ag(1)–N(9)	68.4(4)	N(3)–Ag(2)–N(4)	70.9(8)
N(5)–Ag(1)–N(10)	118.7(9)	N(6)–Ag(1)–N(10)	119.0(9)
N(7)–Ag(1)–N(10)	85.6(9)	N(8)–Ag(1)–N(10)	66.9(5)
N(9)–Ag(1)–N(10)	126.0(6)	Ag(2)–N(1)–C(1)	121.3(16)
Ag(2)–N(1)–C(5)	120.8(19)	Ag(2)–N(2)–C(6)	118.3(20)
Ag(2)–N(2)–C(8)	115.4(14)	C(6)–N(2)–C(8)	124.0(23)
Ag(2)–N(3)–C(9)	104.4(19)	Ag(2)–N(3)–C(10)	105.5(20)
Ag(2)–N(3)–C(16)	122.2(20)	Ag(2)–N(4)–C(11)	120.0(18)
Ag(2)–N(4)–C(15)	121.5(23)	Ag(1)–N(5)–C(17)	122.3(24)
Ag(1)–N(5)–C(18)	113.9(20)	C(17)–N(5)–C(18)	118.8(30)
Ag(1)–N(6)–C(20)	122.2(16)	Ag(1)–N(6)–C(24)	117.6(12)
Ag(1)–N(7)–C(25)	118.5(16)	Ag(1)–N(7)–C(27)	117.2(21)
C(25)–N(7)–C(27)	124.3(28)	Ag(1)–N(8)–C(28)	107.6(18)
Ag(1)–N(8)–C(29)	103.8(19)	Ag(1)–N(8)–C(35)	117.0(10)
Ag(1)–N(9)–C(30)	119.7(21)	Ag(1)–N(9)–C(34)	114.5(18)
Ag(1)–N(10)–Ag(2)	72.0(6)	Ag(1)–N(10)–C(36)	107.6(21)
Ag(2)–N(10)–C(36)	125.1(20)	Ag(1)–N(10)–C(37)	119.3(21)
Ag(2)–N(10)–C(37)	106.9(15)	C(36)–N(10)–C(37)	118.2(24)
N(1)–C(1)–C(37)	112.0(15)	C(2)–C(1)–C(37)	124.8(17)
N(1)–C(5)–C(6)	111.6(24)	C(4)–C(5)–C(6)	127.9(27)
N(4)–C(11)–C(10)	113.6(25)	C(10)–C(11)–C(12)	122.4(26)
N(6)–C(20)–C(18)	112.8(13)	C(18)–C(20)–C(21)	125.9(11)
N(6)–C(24)–C(25)	117.9(14)	C(23)–C(24)–C(25)	116.3(19)
N(9)–C(30)–C(29)	112.8(28)	C(29)–C(30)–C(31)	125.1(20)

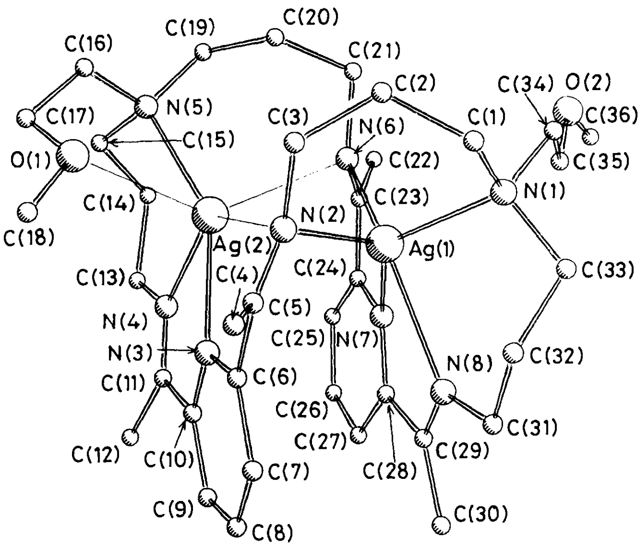


Figure 4. The molecular structure with atom labelling of the cation $[Ag_2L^3]^{2+}$

nitrogen, but additionally is involved in 'weaker' (longer) interactions with the oxygen atom of one of the pendant alkoxy groups (the other is directed away from the macrocycle), and to two (diametrically opposite) imino groups which are also linked to Ag(1). [A 'strong' link is defined as one in which the contact distance is less than the sum of the ionic radius of Ag^+ (1.12 Å)[17] and the van der Waals radius of the ligating atom, 1.50 (N) and 1.55 Å(O);[18] a 'weak' link has a contact distance in excess of this sum.] Again the five-co-ordinate geometry is not obviously symmetric. Thus, the two silver atoms are asymmetrically bridged by a pair of imino groups and the silver–silver distance is remarkably short at 2.907(4) Å. The inclusion of each silver atom in the co-ordination polyhedron of the other does not help in the description of the co-ordination geometry. The macrocycle adopts a conformation which closely resembles that of $[Ag_2L^1]^{2+}$, where the smaller 24-membered macrocycle carries pendant pyridyl substituents of a greater donor capacity, rather than that of $[Ag_2L^2]^{2+}$, where the 28-membered macrocycle also carries pendant pyridyl groups. Bond lengths and angles within the macrocycle are unexceptionable. The two pyridyl rings are each planar (r.m.s. deviations 0.007 and 0.015 Å) and are mutually inclined at 6°: the silver atoms deviate from these planes by 0.469 and 0.716 Å respectively. Both sites filled by fractional occupancy water molecules are in positions to hydrogen bond to perchlorate oxygens O(7) and O(12) on either of the components of the essentially evenly disordered perchlorate anion. One site, O(16), is rather too close to one inversion-related perchlorate oxygen [$O(7^I)$ at 2.61 Å], although not to the other [$O(12^I)$ at 3.31 Å]. The other site, O(15), is well positioned with respect to $O(7^I)$ (2.92 Å) but remote from $O(12^I)$. Of the four partial occupancy water sites clustered around the inversion centre at [0.5, 0, 0.5], three of the distinct interactions would be mutually incompatible (at separations of 1.18, 2.30, and 2.54 Å), but the fourth interaction [$O(15) \cdots O(15^I)$ of 3.15 Å] would be acceptable. These observations are all entirely consistent with the observation (on the basis of determined electron densities) that O(15) has the higher occupancy.

The complex $[Ag_2L^4][ClO_4]_2$ was crystallised by the slow diffusion of diethyl ether into a solution of the complex in CD_3CN. The structure of the $[Ag_2L^4]^{2+}$ dication is shown in Figure 5 with atomic co-ordinates in Table 9 and bond lengths and angles in Table 10. The asymmetric unit also contains two perchlorate anions, one of which is rotationally disordered with occupancies 0.631:0.369, and with fairly adjacent (0.74 Å) chlorine sites. The macrocycle co-ordinates to two silver atoms which are in very similar and well separated environments (Ag · · · Ag 5.828 Å). Each silver is linked to a pyridyl nitrogen, to the two adjacent imino nitrogens, and to a tertiary amino nitrogen. Each set of four nitrogens is approximately coplanar (r.m.s. deviations 0.051 and 0.058 Å) and the silvers deviate by 0.034 and 0.019 Å respectively in directions towards the oxygen atoms of the adjacent pendant methyl aryl ether fragments to which they are weakly bonded [2.82(3) and 2.77(3) Å]. The cleft in the molecule between the planes of the pyridyl rings has 'hinged' open such that the angle between their planes is 44°. This may be compared to the complex dications $[Ag_2L^2]^{2+}$ and $[Ag_2L^3]^{2+}$ where, for the same macrocyclic framework, the pyridyl groups are approximately parallel. In the latter they give a narrow cleft with a short silver–silver distance, whereas in the former the macrocycles had suffered a 'concertina' expansion. Presumably this is attributable to the greater donor capacity of the methyl aryl ether as compared with its alkyl counterpart, thus permitting the silver to achieve full co-ordination without

Table 5. Atom co-ordinates (× 10⁴) for $[Ag_2L^2][ClO_4]_2{\cdot}0.5H_2O$

Atom	*x*	*y*	*z*
Ag(1)	2 667(2)	4 883(2)	2 987(1)
Ag(2)	7 618(2)	943(2)	1 558(1)
Cl(1)	1 444(11)	137(9)	3 086(7)
O(1)	1 568(11)	433(9)	3 821(7)
O(2)	2 524(11)	−150(9)	2 448(7)
O(3)	914(11)	−634(9)	3 371(7)
O(4)	746(11)	955(9)	2 678(7)
Cl(2)	7 268(7)	6 236(5)	2 210(4)
O(5)	8 439(21)	5 764(25)	2 215(16)
O(6)	6 627(32)	6 758(24)	2 940(19)
O(7)	7 196(27)	6 879(20)	1 364(14)
O(8)	6 681(25)	5 496(21)	2 358(21)
O(9)	1 348(85)	−1 213(47)	5 247(68)
N(1)	6 087(18)	152(14)	1 511(13)
N(2)	8 541(22)	783(17)	−61(17)
N(3)	8 615(13)	2 166(13)	852(11)
N(4)	7 029(15)	2 525(12)	2 561(12)
N(5)	3 325(15)	4 661(13)	4 376(12)
N(6)	3 234(17)	6 433(17)	2 476(15)
N(7)	3 218(16)	5 169(15)	1 383(12)
N(8)	3 416(20)	3 130(18)	2 079(15)
N(9)	1 395(15)	4 121(15)	4 136(11)
N(10)	7 287(18)	−127(15)	2 924(13)
C(1)	6 439(22)	−190(18)	560(18)
C(2)	7 720(27)	−696(18)	185(18)
C(3)	8 473(29)	−27(21)	−495(21)
C(4)	9 616(25)	1 500(23)	−1 602(20)
C(5)	9 017(22)	1 429(21)	−536(17)
C(6)	9 173(19)	2 230(17)	−83(15)
C(7)	9 777(21)	2 962(17)	−560(18)
C(8)	9 843(22)	3 636(20)	−43(18)
C(9)	9 257(20)	3 580(18)	905(16)
C(10)	8 664(18)	2 818(14)	1 334(15)
C(11)	7 972(18)	2 789(15)	2 316(14)
C(12)	8 430(19)	3 088(16)	3 020(14)
C(13)	6 217(19)	2 602(16)	3 491(13)
C(14)	5 260(19)	3 589(18)	3 498(15)
C(15)	4 246(18)	3 709(19)	4 405(15)
C(16)	2 209(18)	4 604(18)	5 144(14)
C(17)	1 534(18)	3 970(14)	5 020(16)
C(18)	1 115(22)	3 261(19)	5 734(15)
C(19)	466(23)	2 696(23)	5 656(21)
C(20)	278(21)	2 838(22)	4 760(22)
C(21)	766(18)	3 531(19)	4 044(18)
C(22)	3 744(21)	5 518(18)	4 405(17)
C(23)	2 998(26)	6 545(24)	4 132(21)
C(24)	3 426(24)	7 017(18)	3 068(19)
C(25)	4 208(36)	7 533(23)	1 130(26)
C(26)	3 607(23)	6 687(20)	1 594(18)
C(27)	3 501(20)	6 044(23)	971(18)
C(28)	3 731(21)	6 280(26)	−34(20)
C(29)	3 609(23)	5 634(32)	−525(21)
C(30)	3 341(29)	4 746(30)	−111(19)
C(31)	3 202(18)	4 499(23)	868(15)
C(32)	2 979(21)	3 551(25)	1 366(17)
C(33)	2 394(31)	2 964(31)	1 014(24)
C(34)	3 295(24)	2 152(20)	2 655(17)
C(35)	4 492(25)	1 349(20)	2 517(20)
C(36)	4 915(27)	890(22)	1 677(18)
C(37)	6 128(29)	−707(20)	2 223(20)
C(38)	6 441(24)	−600(17)	3 089(15)
C(39)	5 941(23)	−1 035(19)	3 945(21)
C(40)	6 271(25)	−961(22)	4 706(14)
C(41)	7 132(17)	−542(18)	4 543(15)
C(42)	7 622(30)	−102(23)	3 648(19)

Atom O(9) is the oxygen atom of a 50% occupancy water molecule.

recourse to imine bridging and a consequently shorter silver–silver distance. The co-ordination geometry of each silver is very 'one-sided,' but there are no further ligands *trans* to the ether oxygen atoms: this site in Ag(2) is blocked at 3.14 Å by a hydrogen atom, H(23), of a glide-related molecule. In view of the constraints applied to bond lengths during refinement, it is not possible to discuss details of the molecular geometry. The silver atoms deviate from the planes of the pyridyl rings by 0.074 and 0.715 Å respectively. In the absence of protonated oxygen or nitrogen atoms, the perchlorate anions do not participate in hydrogen bonding.

The use of two imino residues as bridging or semi-bridging groups, and the consequent silver–silver distances that ensue, seems likely to be related to the donor capacity of the pendant groups, and the need to achieve adequate co-ordination of the silver ions.

Conclusion

We have previously reported that in the structures of the molecules $[BaL^n(H_2O)_2][ClO_4]_2$ (n = 7 or 8) the macrocyclic ligands are substantially folded about the alcoholic carbon atoms with angles of 137.2° between the pyridyl fragments and 129.2° between the furanyl ring planes.[19] Introduction of the diethylenetriamine lateral units gives a larger macrocyclic ring size and a more exaggerated folding in the corresponding $Ba(ClO_4)_2$ complex leading to a molecular cleft with the pyridinyl fragments approximately parallel to each other. On forming the binuclear silver(I) complexes the 'cleft-like' appearance of the macrocyclic ligand is retained but the Ag ··· Ag separation and the configuration of the ligand change with both ring expansion and the introduction of pendant groups of varying donor strength. The Ag ··· Ag separation ranges from 2.91 to 6.82 Å.

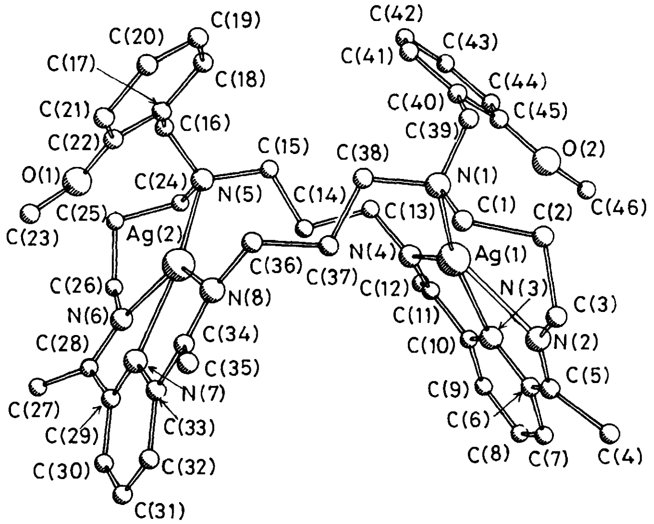


Figure 5. The molecular structure with atom labelling of the cation $[Ag_2L^4]^{2+}$

It has been noted that in certain co-ordination compounds of copper(I), silver(I), and gold(I) in which the d^{10} atoms are held together in pairs by rigid 1,3-bifunctional bidentate ligands[1–4] there is a $M^+ \cdots M^+$ contact similar to, and often shorter than, the intermetallic distances of the elements themselves.[20] In the

Table 6. Selected bond lengths (Å) and angles (°) for $[Ag_2L^2][ClO_4]_2 \cdot 0.5H_2O$

Ag(1)–N(5)	2.440(22)	Ag(1)–N(6)	2.364(25)
Ag(1)–N(7)	2.286(18)	Ag(1)–N(9)	2.241(18)
Ag(1) ··· N(8)	2.807(20)	Ag(2)–N(1)	2.491(25)
Ag(2)–N(2)	2.371(24)	Ag(2)–N(3)	2.276(18)
Ag(2) ··· N(4)	2.721(20)	Ag(2)–N(10)	2.274(19)
N(1)–C(1)	1.504(35)	N(1)–C(36)	1.451(32)
N(1)–C(37)	1.427(31)	N(2)–C(3)	1.463(47)
N(2)–C(5)	1.198(36)	N(4)–C(11)	1.239(30)
N(4)–C(13)	1.435(23)	N(5)–C(15)	1.442(26)
N(5)–C(16)	1.482(25)	N(5)–C(22)	1.455(37)
N(6)–C(24)	1.456(44)	N(6)–C(26)	1.273(32)
N(8)–C(32)	1.315(36)	N(8)–C(34)	1.470(34)
O(9) ··· O(1)	2.802		
N(5)–Ag(1)–N(6)	89.2(8)	N(5)–Ag(1)–N(7)	144.9(7)
N(6)–Ag(1)–N(7)	70.5(8)	N(5)–Ag(1)–N(9)	75.1(7)
N(6)–Ag(1)–N(9)	142.7(7)	N(7)–Ag(1)–N(9)	137.5(8)
N(8)–Ag(1)–N(5)	115.3(9)	N(8)–Ag(1)–N(6)	129.8(9)
N(8)–Ag(1)–N(7)	64.7(9)	N(8)–Ag(1)–N(9)	87.4(9)
N(1)–Ag(2)–N(2)	88.3(8)	N(1)–Ag(2)–N(3)	145.2(6)
N(2)–Ag(2)–N(3)	69.5(8)	N(1)–Ag(2)–N(4)	122.1(6)
N(2)–Ag(2)–N(4)	131.9(7)	N(3)–Ag(2)–N(4)	65.0(5)
N(1)–Ag(2)–N(10)	74.7(8)	N(2)–Ag(2)–N(10)	137.0(8)
N(3)–Ag(2)–N(10)	139.4(8)	N(4)–Ag(2)–N(10)	89.5(7)
Ag(2)–N(1)–C(1)	109.0(15)	Ag(2)–N(1)–C(36)	110.1(19)
Ag(2)–N(1)–C(37)	104.7(20)	Ag(2)–N(2)–C(3)	122.2(17)
Ag(2)–N(2)–C(5)	117.7(23)	C(3)–N(2)–C(5)	120.0(25)
Ag(2)–N(3)–C(6)	120.0(17)	Ag(2)–N(3)–C(10)	121.3(12)
Ag(2)–N(4)–C(11)	103.2(13)	Ag(2)–N(4)–C(13)	125.3(14)
C(11)–N(4)–C(13)	121.7(22)	Ag(1)–N(5)–C(15)	109.4(15)
Ag(1)–N(5)–C(16)	101.8(15)	Ag(1)–N(5)–C(22)	112.0(13)
Ag(1)–N(6)–C(24)	125.4(15)	Ag(1)–N(6)–C(26)	117.4(22)
C(24)–N(6)–C(26)	116.0(25)	Ag(1)–N(7)–C(27)	117.9(19)
Ag(1)–N(7)–C(31)	121.2(15)	Ag(1)–N(8)–C(32)	97.8(16)
Ag(1)–N(8)–C(34)	118.4(16)	C(32)–N(8)–C(34)	125.9(30)
Ag(1)–N(9)–C(17)	116.1(16)	Ag(1)–N(9)–C(21)	127.4(15)
Ag(2)–N(10)–C(38)	116.7(17)	Ag(2)–N(10)–C(42)	124.1(21)
N(3)–C(6)–C(5)	112.0(20)	C(5)–C(6)–C(7)	124.9(21)
N(3)–C(10)–C(11)	117.5(19)	C(9)–C(10)–C(11)	120.5(22)
N(9)–C(17)–C(16)	114.8(18)	C(16)–C(17)–C(18)	121.5(24)
N(7)–C(27)–C(26)	116.6(23)	C(26)–C(27)–C(28)	125.0(28)
N(7)–C(31)–C(32)	116.7(21)	C(30)–C(31)–C(32)	121.6(32)
N(10)–C(38)–C(37)	116.4(20)	C(37)–C(38)–C(39)	120.8(29)

$[Ag_2L^3]^{2+}$ cation there is an intermetallic contact of 2.907(4) Å as compared with *ca.* 2.89 Å in silver metal, even in the presence of a flexible ligand.

There is an ongoing discussion as to whether such close approaches are dictated by the steric requirements of the ligand or through the formation of a silver–silver bond. In the disilver(I) complex of macrocycle L^6 the silver atoms are retained by the pyridinyl head-units and each is four-co-ordinated by three imino and one secondary amino nitrogen atoms; the silver ··· silver separation is 6.0 Å.[13] If introduction of a pendant arm reduces the conformational mobility of the secondary amino nitrogen atom then this could force the present situation by placing the d^{10} cations in mutual proximity. An ion–dipolar interaction between the silver(I) cation and the ligand donor atoms is expected, but purely coulombic forces are unlikely because of the 'soft' nature of silver(I). No significant directional influence is anticipated for the d^{10} cation and so it is possible that in $[Ag_2L^3][ClO_4]_2$ the weaker donating capability of the alkoxy-arms relative to the pyridinyl arms in the corresponding 28-membered ring complex prejudices the metals towards an association similar to that found in the dimeric complex $[AgL^9][ClO_4]$.[21] In this complex, as in the present case, there is an apparent involvement of the imine nitrogen atoms in bridges between the silver atoms. There is no obvious residual σ-co-ordinating capacity at the imine nitrogens, nor does the possibility of π involvement of the imine seem likely. The imine nitrogens may simply be involved in ion–dipole derived bridges between the proximal d^{10} cations. The Ag ··· Ag contact in $[Ag_2L^1]^{2+}$ is slightly longer at 3.068(6) Å. Both pyridinyl arms co-ordinate to the metal ions and there are imine bridges. The macrocyclic ring size has been contracted to 23 members and so it is possible that the closeness of the silver atoms in this case is imposed by ring-size constraints. The differences in the structures, albeit with different pendant arms present, suggest that there might be considerable mobility in the complexes in solution related to the concertina movement in the lateral aliphatic units on ring expansion and the on–off movement of the pendant arms on changing the strength of the donor atoms.

The ^1H n.m.r. spectra of the disilver complexes of macrocycles L^6 gave readily interpretable spectra as expected for normal, fully extended 28-membered macrocycles.[14] When the spectrum of the $[Ag_2L^2][ClO_4]_2$ complex is recorded at ambient temperature in CD_2Cl_2 at 250 MHz, the only resolved signals present are attributable to the aromatic component of the macrocycle. The aliphatic signals are now only detected as a series of broadened lines suggesting that there is some fluxional behaviour of the type hinted at in the structural studies. As the temperature is lowered to 273 K, the spectrum becomes fully resolved for the aromatic signals. The aliphatic signals also start to be resolved, with two methyl singlets being observed, and the remaining aliphatic signals appearing as partially resolved multiplets. A further reduction in the temperature to 193 K does not serve further to clarify the spectrum. This behaviour pattern is similar for all of the silver complexes and in-depth studies which might help to determine the nature of these fluxional processes have been hindered by the low solubility of the complexes in the requisite solvents. A similar pattern was previously reported for the barium complex.[5] Although these solubility difficulties have prevented such studies which might help rationalise the nature of these fluxional mechanisms, it is nevertheless plausible to consider the structures as photographic stills representing steps in the actual molecular motions available to the general ligand framework and to propose that both the concertina-like flexing of the ligand and the on–off movement of the pendant arms would contribute significantly to the fluxional behaviour in solution.

Experimental

I.r. spectra were measured using a Perkin-Elmer 297 i.r. spectrometer, as either KBr discs or a liquid film between NaCl plates, in the region 4,000—600 cm^{-1}. Elemental analyses were carried out by the University of Sheffield microanalytical service. Electron-impact (e.i.) and chemical ionisation (c.i.) (NH_3) mass spectra were recorded with a Kratos MS25 spectrometer operating at low resolution. Positive-ion f.a.b. mass spectra were recorded with a Kratos MS80 spectrometer. Proton n.m.r. spectra were recorded at 220 MHz on a Perkin-Elmer R34 spectrometer and at 250 MHz on a Bruker AM-250 spectrometer.

Crystal Structure Data and Determination.—Three-dimensional, room-temperature *X*-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω scan method. Scans were performed at a variable rate, to a maximum of 29.3° min^{-1}: background counts were taken for a total period of 50% of the scan time. Azimuthal scans were all performed on reflections with $50 < \chi < 90°$. In general the quality of the diffraction data was only moderate, notwithstanding the reasonable size of some of the crystalline samples. Where refinement

Table 7. Atom co-ordinates (× 10^4) for $[Ag_2L^3][ClO_4]_2{\cdot}0.5H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	680(1)	2 601(1)	2 218(1)	C(22)	2 300(11)	1 326(7)	4 968(10)
Ag(2)	−921(1)	2 044(1)	3 139(1)	C(23)	1 757(8)	1 827(6)	4 354(8)
O(1)	−3 605(5)	1 369(4)	1 607(6)	C(24)	2 658(8)	2 854(6)	5 272(8)
O(2)	2 026(6)	1 143(4)	1 303(7)	C(25)	3 530(9)	3 282(7)	6 735(9)
N(1)	418(7)	2 270(4)	153(6)	C(26)	4 301(9)	4 227(7)	7 501(9)
N(2)	−1 442(6)	2 430(4)	966(6)	C(27)	4 248(8)	4 747(6)	6 813(8)
N(3)	−63(6)	3 602(4)	3 769(6)	C(28)	3 399(7)	4 287(5)	5 346(7)
N(4)	446(7)	2 967(4)	5 627(6)	C(29)	3 358(7)	4 785(5)	4 510(8)
N(5)	−2 111(6)	666(4)	3 178(6)	C(30)	4 409(8)	5 823(5)	5 311(9)
N(6)	620(7)	1 454(4)	3 147(6)	C(31)	2 409(8)	4 679(5)	2 241(9)
N(7)	2 593(6)	3 352(4)	4 601(6)	C(32)	1 276(9)	3 921(6)	696(9)
N(8)	2 451(6)	4 271(4)	3 165(6)	C(33)	1 376(9)	3 136(6)	293(9)
C(1)	−1 028(8)	1 795(6)	−1 118(8)	C(34)	748(9)	1 613(6)	−13(8)
C(2)	−2 074(8)	1 179(5)	−987(8)	C(35)	2 070(8)	1 905(6)	1 329(9)
C(3)	−2 530(8)	1 643(6)	−467(8)	C(36)	3 296(10)	1 393(7)	2 489(11)
C(4)	−2 176(9)	3 377(7)	255(9)	Cl(1)	4 218(2)	3 026(2)	−68(2)
C(5)	−1 307(7)	3 178(6)	1 309(8)	O(3)	4 053(8)	3 721(5)	−135(7)
C(6)	−255(7)	3 906(5)	2 834(8)	O(4)	2 920(8)	2 175(5)	−1 080(8)
C(7)	474(8)	4 858(5)	3 260(9)	O(5)	4 837(7)	3 125(5)	1 304(6)
C(8)	1 441(9)	5 488(6)	4 679(11)	O(6)	5 004(10)	3 059(8)	−403(9)
C(9)	1 656(8)	5 197(5)	5 640(9)	Cl(2)	7 044(11)	2 534(6)	6 231(8)
C(10)	880(8)	4 236(5)	5 161(8)	O(7)	6 669(11)	1 673(6)	6 202(8)
C(11)	993(7)	3 809(6)	6 108(7)	O(8)	6 292(11)	2 778(6)	6 391(8)
C(12)	1 823(10)	4 488(6)	7 678(8)	O(9)	8 484(11)	3 228(6)	7 338(8)
C(13)	533(8)	2 575(6)	6 547(8)	O(10)	6 717(11)	2 433(6)	4 918(8)
C(14)	−128(9)	1 539(6)	5 808(9)	Cl(3)	7 173(12)	2 610(10)	6 356(12)
C(15)	−1 681(9)	905(6)	4 611(8)	O(11)	8 200(12)	3 449(10)	7 685(12)
C(16)	−3 616(8)	206(6)	2 150(9)	O(12)	6 357(12)	1 939(10)	6 543(12)
C(17)	−4 008(9)	845(6)	2 183(9)	O(13)	6 369(12)	2 749(10)	5 298(12)
C(18)	−3 887(9)	2 017(6)	1 654(10)	O(14)	7 793(12)	2 313(10)	6 013(12)
C(19)	−1 869(10)	14(6)	2 744(9)	O(15)	3 947(30)	148(20)	4 886(31)
C(20)	−1 782(9)	10(5)	1 596(8)	O(16)	4 668(48)	18(32)	5 711(50)
C(21)	−337(10)	438(5)	2 113(9)				

Atoms Cl(2) and O(7)–O(10) constitute the 52.4% occupancy component, Cl(3) and O(11)–O(14) the 47.6% occupancy component of the disordered perchlorate. Atoms O(15) and O(16) are the adjacent sites for the oxygen atom of a disordered water molecule (occupancies fixed at 0.333 and 0.167 respectively) which are situated adjacent to crystallographic inversion centres.

became ill determined as a result of limitations in quality or quantity of data, or of disorder, geometric constraints were applied and, if necessary, were retained until completion of the refinement. Complex scattering factors were taken from ref. 22 and from the program package SHELXTL[23] as implemented on a Data General Nova 3 computer which was used throughout all refinements. Unless otherwise stated, unit weights were used. Throughout the following, *R* is defined as $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

Crystal data for $[BaL^1][ClO_4]_2$. $C_{38}H_{46}BaCl_2N_{10}O_8$, $M = 979.05$, crystallises from hexane–methanol by liquid–liquid diffusion as colourless needles, crystal dimensions 0.425 × 0.20 × 0.15 mm, monoclinic, space group *C*2/*c* (C^6_{2h}, no. 15), $a = 20.310(38)$, $b = 14.453(41)$, $c = 15.137(29)$ Å, $\beta = 104.84(15)^\circ$, $U = 4295(17)$ Å^3, $D_c = 1.514$ g cm^{-3}, $Z = 4$, Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 11.08 cm^{-1}, $F(000) = 1983.66$.

The 1900 independent reflections (of 4068 measured) for which $|F|/\sigma(|F|) > 5.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of five azimuthal scans (minimum and maximum transmission coefficients 0.535 and 0.700 respectively). The structure was solved by conventional Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The perchlorate anion was refined with constrained T_d symmetry, and both pyridyl groups with constrained D_{6h} symmetry. Further constraints were also applied to the macrocycle in order to maintain similar lengths for chemically equivalent bonds [with the exception of N(2)–C(19a)], although the lengths themselves were not constrained. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms. Refinement converged (250 parameters) at a final *R* 0.0923 with allowance for the thermal anisotropy of all non-hydrogen atoms.

Crystal data for $[Ag_2L^1][ClO_4]_2$. $C_{38}H_{46}Ag_2Cl_2N_{10}O_8$, $M = 1057.49$, crystallises from CD_3CN–diethyl ether by liquid–liquid diffusion as orange blocks, crystal dimensions 0.50 × 0.25 × 0.20 mm, tetragonal, space group *I*4$_1$*cd* (C^{12}_{4v}, no. 110), $a = 28.11(4)$, $c = 21.618(16)$ Å, $U = 17\,084(38)$ Å^3, $D_c = 1.645$ g cm^{-3}, $Z = 16$, Mo-K_α radiation, μ(Mo-K_α) = 10.94 cm^{-1}, $F(000) = 8574.51$.

The 1916 independent reflections (of 4 180 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected (minimum and maximum transmission coefficients 0.408 and 0.432 respectively), and the structure was solved and refined, as above. One of the two perchlorate anions was refined with constrained T_d geometry. Constraints were also applied to the macrocycle in order to maintain similar lengths for chemically equivalent bonds, although the lengths themselves were not constrained. Hydrogen atoms were placed in calculated positions as above. Refinement converged (308 parameters) at a final *R* 0.1092 with allowance for the thermal anisotropy of silver, chlorine, and oxygen only.

Crystal data for $[Ag_2L^2][ClO_4]_2{\cdot}0.5H_2O$. $C_{42}H_{55}Ag_2Cl_2N_{10}O_{8.5}$, $M = 1122.60$, crystallises from CD_3CN–diethyl ether by liquid–liquid diffusion as yellow blocks; crystal

Table 8. Selected bond lengths (Å) and angles (°) for $[Ag_2L^3][ClO_4]_2 \cdot 0.5H_2O$

Ag(1) · · · Ag(2)	2.907(4)	Ag(1)–N(1)	2.346(9)	N(2)–C(5)	1.263(14)	N(4)–C(11)	1.232(12)
Ag(1)–N(2)	2.424(9)	Ag(1)–N(6)	2.549(9)	N(4)–C(13)	1.434(14)	N(5)–C(15)	1.478(14)
Ag(1)–N(7)	2.320(6)	Ag(1)–N(8)	2.471(7)	N(5)–C(16)	1.489(11)	N(5)–C(19)	1.477(18)
Ag(2) · · · O(1)	2.724(8)	Ag(2) · · · N(2)	2.735(9)	N(6)–C(21)	1.484(10)	N(6)–C(23)	1.261(9)
Ag(2)–N(3)	2.343(7)	Ag(2)–N(4)	2.376(7)	N(8)–C(29)	1.270(9)	N(8)–C(31)	1.463(14)
Ag(2)–N(5)	2.358(8)	Ag(2) · · · N(6)	2.830(9)	O(15) · · · O(7)	2.826	O(15) · · · O(12)	2.739
O(1)–C(17)	1.383(15)	O(1)–C(18)	1.413(16)	O(16) · · · O(7)	2.763	O(16) · · · O(12)	2.838
O(2)–C(35)	1.364(14)	O(2)–C(36)	1.421(13)	O(15) · · · O(7^{I})	2.919	O(15) · · · O(15^{I})	3.150
N(1)–C(1)	1.479(10)	N(1)–C(33)	1.467(13)	O(16) · · · O(7^{I})	2.604	O(16) · · · O(12^{I})	3.308
N(1)–C(34)	1.493(17)	N(2)–C(3)	1.446(8)				

Ag(2)–Ag(1)–N(1)	141.3(2)	Ag(2)–Ag(1)–N(2)	60.9(2)	Ag(1)–N(1)–C(1)	110.7(8)	Ag(1)–N(1)–C(33)	109.9(5)
N(1)–Ag(1)–N(2)	89.9(3)	Ag(2)–Ag(1)–N(6)	62.1(3)	Ag(1)–N(1)–C(34)	107.8(6)	Ag(1)–N(2)–Ag(2)	68.3(2)
N(1)–Ag(1)–N(6)	116.9(3)	N(2)–Ag(1)–N(6)	113.9(3)	Ag(1)–N(2)–C(3)	113.3(7)	Ag(2)–N(2)–C(3)	117.2(6)
Ag(2)–Ag(1)–N(7)	85.4(2)	N(1)–Ag(1)–N(7)	132.1(3)	Ag(1)–N(2)–C(5)	116.0(4)	Ag(2)–N(2)–C(5)	107.2(7)
N(2)–Ag(1)–N(7)	134.1(3)	N(6)–Ag(1)–N(7)	68.1(2)	C(3)–N(2)–C(5)	122.5(8)	Ag(2)–N(3)–C(6)	122.4(5)
Ag(2)–Ag(1)–N(8)	121.1(2)	N(1)–Ag(1)–N(8)	88.2(3)	Ag(2)–N(3)–C(10)	117.7(6)	Ag(2)–N(4)–C(11)	117.5(7)
N(2)–Ag(1)–N(8)	103.0(3)	N(6)–Ag(1)–N(8)	134.3(2)	Ag(2)–N(4)–C(13)	123.1(5)	C(11)–N(4)–C(13)	119.0(8)
N(7)–Ag(1)–N(8)	66.9(2)	Ag(1)–Ag(2)–O(1)	126.0(2)	Ag(2)–N(5)–C(15)	109.9(4)	Ag(2)–N(5)–C(16)	108.2(6)
Ag(1)–Ag(2)–N(2)	50.8(2)	O(1)–Ag(2)–N(2)	76.7(2)	Ag(2)–N(5)–C(19)	110.5(7)	Ag(1)–N(6)–C(21)	119.1(6)
Ag(1)–Ag(2)–N(3)	76.9(3)	O(1)–Ag(2)–N(3)	94.3(2)	Ag(1)–N(6)–C(23)	112.1(6)	C(21)–N(6)–C(23)	122.4(9)
N(2)–Ag(2)–N(3)	65.7(2)	Ag(1)–Ag(2)–N(4)	112.6(2)	Ag(2)–N(6)–Ag(1)	65.2(2)	Ag(2)–N(6)–C(21)	109.3(6)
O(1)–Ag(2)–N(4)	113.3(3)	N(2)–Ag(2)–N(4)	134.5(2)	Ag(2)–N(6)–C(23)	114.9(6)	Ag(1)–N(7)–C(24)	119.0(4)
N(3)–Ag(2)–N(4)	69.3(3)	Ag(1)–Ag(2)–N(5)	132.8(3)	Ag(1)–N(7)–C(28)	118.3(6)	Ag(1)–N(8)–C(29)	116.9(7)
O(1)–Ag(2)–N(5)	72.2(3)	N(2)–Ag(2)–N(5)	132.4(2)	Ag(1)–N(8)–C(31)	122.3(3)	C(29)–N(8)–C(31)	120.6(7)
N(3)–Ag(2)–N(5)	150.0(4)	N(4)–Ag(2)–N(5)	91.3(3)	N(3)–C(6)–C(5)	116.5(7)	C(5)–C(6)–C(7)	121.6(9)
Ag(1)–Ag(2)–N(6)	52.7(3)	O(1)–Ag(2)–N(6)	139.1(3)	N(3)–C(10)–C(11)	113.6(7)	C(9)–C(10)–C(11)	124.8(7)
N(2)–Ag(2)–N(6)	97.0(3)	N(3)–Ag(2)–N(6)	120.3(3)	N(7)–C(24)–C(23)	116.2(7)	C(23)–C(24)–C(25)	122.5(10)
N(4)–Ag(2)–N(6)	99.9(3)	N(5)–Ag(2)–N(6)	84.4(3)	N(7)–C(28)–C(29)	116.3(7)	C(27)–C(28)–C(29)	123.1(7)
Ag(2)–O(1)–C(17)	101.1(6)	Ag(2)–O(1)–C(18)	118.4(4)				

Symmetry operation: I $\frac{1}{2} - x, -y, \frac{1}{2} - z$.

dimensions 0.30 × 0.40 × 0.30 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 12.277(16)$, $b = 13.899(14)$, $c = 15.260(50)$ Å, $\alpha = 77.30(20)$, $\beta = 70.17(20)$, $\gamma = 71.27(9)°$, $U = 2302(9)$ Å^3, $D_c = 1.620$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, μ(Mo-K_α) = 10.21 cm^{-1}, $F(000) = 1145.81$.

The 4 097 independent reflections (of 8 155 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of seven azimuthal scans (minimum and maximum transmission coefficients 0.582 and 0.605 respectively). The structure was solved and refined as above. One of the two perchlorate anions was refined with constrained T_d geometry. Hydrogen atoms were placed in calculated positions as above. Refinement converged (547 parameters) at a final R 0.1323 with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of those of C(12) and C(18) which remained isotropic, and the oxygen atoms of the perchlorate based on Cl(1), which were given a common isotropic thermal parameter.

Crystal data for $[Ag_2L^3][ClO_4]_2 \cdot 0.5H_2O$. $C_{36}H_{57}Ag_2Cl_2N_8O_{10.5}$, $M = 1056.54$, crystallises from methanol as pale yellow prisms, crystal dimensions 0.25 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 14.171(14)$, $b = 18.323(16)$, $c = 12.495(23)$ Å, $\alpha = 99.20(12)$, $\beta = 120.13(11)$, $\gamma = 116.35(7)°$, $U = 2187(6)$ Å^3, $D_c = 1.605$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, μ(Mo-K_α) = 10.71 cm^{-1}, $F(000) = 1081.84$.

The 4 818 independent reflections (of 7 760 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by the analysis of seven azimuthal scans (minimum and maximum transmission coefficients 0.869 and 0.944 respectively). The structure was solved and refined as above. Of the two perchlorate anions, one was found to be disordered approximately equally (refined 0.524 : 0.476) in two interpenetrating sites, and both components of this latter were refined with constrained geometries (T_d symmetry, Cl–O 1.411 Å). Two possible, but mutually exclusive, sites were found for a water molecule adjacent to an inversion centre, and they were included with occupancies of 0.333 and 0.167, which best reflected their refined electron densities. Hydrogen atoms (with the exception of those of the disordered water molecule) were placed in calculated positions with isotropic thermal parameters related to those of the supporting atom. Convergence was reached (558 parameters) at a final R of 0.0661, with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of the disordered water oxygen atoms. A weighting scheme $w^{-1} = [\sigma^2(F) + gF^2]$ with $g = 0.000\,20$ was used in the later stages of refinement.

Crystal data for $[Ag_2L^4][ClO_4]_2$. $C_{46}H_{60}Ag_2Cl_2N_8O_{10}$, $M = 1171.67$, crystallises from CD_3CN–diethyl ether by liquid–liquid diffusion as pale yellow plates, crystal dimensions 0.05 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/a$ (a non-standard setting of $P2_1/c$, C_{2h}^5, no. 14), $a = 16.595(16)$, $b = 13.363(11)$, $c = 23.951(25)$ Å, $\beta = 105.43(8)°$, $U = 5120(8)$ Å^3, $D_c = 1.520$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, μ(Mo-K_α) = 9.22 cm^{-1}, $F(000) = 2399.64$.

The 1 528 independent reflections (of 5 323 measured) for which $|F|/\sigma(|F|) > 4.5$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.689 and 0.794 respectively). The structure was solved and refined as above. One of the two perchlorate anions was found to be disordered (refined occupancies 0.631 : 0.369 in two interpenetrating sites, and both these components and the ordered perchlorate were refined with constrained T_d geometries. All four six-membered rings were given D_{6h} constrained geometries. In addition, all chemically equivalent skeletal bond lengths were constrained to be approximately equal, although actual values were not imposed. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms. Refinement converged (239

Table 9. Atom co-ordinates (× 10^4) for $[Ag_2L^4][ClO_4]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	−1 490(3)	−1 162(3)	1 325(2)	C(12)	−319(26)	−4 188(28)	2 017(18)
Ag(2)	1 021(2)	−228(3)	3 472(2)	C(13)	−964(20)	−2 461(32)	2 526(7)
Cl(1)	−885(11)	3 253(15)	1 002(7)	C(14)	−186(19)	−2 010(30)	2 924(10)
O(3)	−1 094(11)	3 197(15)	1 530(7)	C(15)	−428(18)	−1 678(30)	3 460(10)
O(4)	− 1 574(11)	3 588(15)	572(7)	C(16)	−66(27)	−634(23)	4 333(12)
O(5)	−658(11)	2 295(15)	858(7)	C(17)	−403(18)	344(20)	4 139(12)
O(6)	−203(11)	3 891(15)	1 053(7)	C(18)	−1 273(18)	405(20)	3 952(12)
Cl(2)	1 090(9)	4 944(12)	3 827(6)	C(19)	−1 660(18)	1 333(20)	3 813(12)
O(7)	487(9)	5 628(11)	3 532(6)	C(20)	−1 177(18)	2 199(20)	3 861(12)
O(8)	1 264(9)	4 258(11)	3 434(6)	C(21)	−308(18)	2 138(20)	4 048(12)
O(9)	1 820(9)	5 452(11)	4 106(6)	C(22)	79(18)	1 210(20)	4 187(12)
O(10)	783(9)	4 432(11)	4 237(6)	C(23)	1 480(39)	1 707(48)	4 464(30)
Cl(3)	−1 253(20)	3 449(25)	1 043(13)	C(24)	842(15)	−1 976(13)	4 209(16)
O(11)	−1 499(20)	3 073(24)	1 517(13)	C(25)	1 660(13)	−1 711(36)	4 639(13)
O(12)	−1 637(20)	2 897(24)	548(13)	C(26)	2 419(25)	−1 729(32)	4 404(17)
O(13)	−384(20)	3 371(24)	1 152(13)	C(27)	3 901(23)	−713(38)	4 334(18)
O(14)	−1 487(20)	4 454(24)	955(13)	C(28)	3 053(24)	−602(31)	3 914(15)
O(1)	877(19)	949(27)	4 393(14)	N(7)	2 169(9)	479(19)	3 252(10)
O(2)	−3 139(20)	−1 895(26)	1 096(12)	C(29)	2 969(9)	67(19)	3 429(10)
N(1)	−2 210(10)	190(18)	1 518(9)	C(30)	3 564(9)	306(19)	3 135(10)
N(2)	−1 552(19)	−614(21)	336(12)	C(31)	3 360(9)	958(19)	2 663(10)
N(4)	−849(20)	−2 485(25)	1 943(7)	C(32)	2 560(9)	1 370(19)	2 486(10)
N(5)	240(14)	−1 222(16)	3 915(7)	C(33)	1 965(9)	1 131(19)	2 780(10)
N(6)	2 378(19)	−994(26)	3 945(14)	C(34)	1 134(18)	1 547(26)	2 633(16)
N(8)	594(19)	999(26)	2 765(14)	C(35)	982(33)	2 521(31)	2 304(21)
C(1)	−2 353(26)	938(21)	1 057(11)	C(36)	−285(19)	1 283(32)	2 586(15)
C(2)	−2 648(20)	487(42)	461(15)	C(37)	−808(9)	704(32)	2 076(16)
C(3)	−2 046(23)	269(30)	104(16)	C(38)	−1 729(8)	701(36)	2 041(16)
C(4)	−1 253(39)	−946(50)	−600(17)	C(39)	−3 022(10)	−134(22)	1 585(15)
C(5)	−1 226(28)	−1 149(29)	23(15)	C(40)	−3 082(18)	−990(18)	1 943(11)
N(3)	−873(17)	−2 272(20)	850(11)	C(41)	−3 050(18)	−974(18)	2 531(11)
C(6)	−829(17)	−2 056(20)	289(11)	C(42)	−3 058(18)	−1 870(18)	2 828(11)
C(7)	−427(17)	−2 717(20)	1(11)	C(43)	−3 098(18)	−2 781(18)	2 538(11)
C(8)	−69(17)	−3 594(20)	274(11)	C(44)	−3 130(18)	−2 797(18)	1 950(11)
C(9)	−114(17)	−3 810(20)	835(11)	C(45)	−3 122(18)	−1 901(18)	1 653(11)
C(10)	−516(17)	−3 149(20)	1 123(11)	C(46)	−3 153(32)	−2 797(35)	793(21)
C(11)	−605(28)	−3 221(28)	1 704(15)				

Atoms Cl(1) and O(3)–O(6) comprise the component of occupancy 0.631 of the disordered perchlorate, Cl(3) and O(11)–O(14) the component of occupancy 0.369.

parameters) at a final *R* 0.0997 with allowance for the thermal anisotropy of silver and chlorine only: the oxygen atoms of the disordered perchlorate were given a common isotropic thermal parameter.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

*Preparations.—*N,N-*Bis(*n*-phthalimidoalkyl)amines* (n = 2 *or* 3, *alkyl = ethyl or propyl*). These were prepared using the method of Ng *et al.*[9]

N,*N*-Bis(2-phthalimidoethyl)amine (75.0%), m.p. 180—182 °C (Found: C, 65.9; H, 4.8; N, 11.4. Calc. for $C_{20}H_{17}N_3O_4$: C, 66.1; H, 4.7; N, 11.6%). $\nu_{max.}$ 3 340 (NH), 1 780, 1 770, and 1 730—1 710 cm^{-1} (CO) (KBr disc); δ_H(CDCl$_3$) 2.60 (1 H, s, NH), 3.00 (4 H, t, CH$_2$NCH$_2$), 3.80 (4 H, t, 2 phthalimide NCH$_2$), and 7.70 (8 H, m, 8 aryl H); *m*/*z* (e.i.) 363 (M^+, 23%).

N,*N*-Bis(3-phthalimidopropyl)amine (79.1%), m.p. 120 °C (Found: C, 67.6; H, 5.4; N, 10.9. Calc. for $C_{22}H_{21}N_3O_4$: C, 67.5; H, 5.4; N, 10.7%); $\nu_{max.}$ 3 350 and 3 335 (NH), 1 775 and 1 730—1 710 cm^{-1} (CO) (KBr disc); δ_H(CDCl$_3$) 1.52 (1 H, s, NH), 1.81 (4 H, qnt, 2 CH$_2$), 2.61 (4 H, t, CH$_2$NCH$_2$), 3.75 (4 H, t, phthalimide NCH$_2$), 7.71 (4 H, m, 4 aryl H), and 7.83 (4 H, m, 4 aryl H); *m*/*z* (e.i.) 391 (M^+, 13%).

Centrally substituted N,N-*bis(*n*-phthalimidoalkyl)amines* (n = 2 *or* 3, *alkyl = ethyl or propyl*). The substitution of the *N*,*N*-bis(*n*-phthalimidoalkyl)amines was effected using the general method outlined below.

The bromoalkane (0.05 mol) was added dropwise to a suspension of the *N*,*N*-bis(*n*-phthalimidoalkyl)amine (0.04 mol) and anhydrous Na_2CO_3 (0.04 mol) in ethanol (absolute, 600 cm^3) under N_2. The suspension dissolved after *ca.* 30 min to form a pale yellow solution. This was heated at reflux temperature for *ca.* 18 h. The inorganic solid present in the hot solution at the end of the reflux was removed by filtration and the product crystallised from the hot filtrate as it cooled to ambient temperature. It was collected by filtration and may be recrystallised from absolute ethanol.

N,*N*-Bis(2-phthalimidoethyl)-2-(aminomethyl)pyridine (80.0%), m.p. 99—100 °C (Found: C, 68.5; H, 4.9; N, 12.4. $C_{26}H_{22}N_4O_4$ requires C, 68.7; H, 4.9; N, 12.3%); $\nu_{max.}$ 1 770 and 1 715 cm^{-1} (CO) (KBr disc); δ_H(CDCl$_3$) 2.87 (4 H, t, CH$_2$NCH$_2$), 3.79 (4 H, t, 2 phthalimide NCH$_2$), 3.89 (2 H, s, NCH$_2$C$_5$H$_4$N), 7.00 (1 H, t, pyridine H), 7.10 (2 H, m, 2 pyridine H), 7.70 (8 H, m, 8 aryl H), and 8.40 (1 H, d, pyridine H); *m*/*z* (e.i.) 453 (M^+, 2%).

N,*N*-Bis(3-phthalimidopropyl)-2-(aminomethyl)pyridine hemihydrate (78.0%), m.p. 105 °C (Found: C, 68.1; H, 5.4; N, 11.3. $C_{20}H_{27}N_4O_{4.5}$ requires C, 68.4; H, 5.5; N, 11.4%); $\nu_{max.}$ 1 770 and 1 710 cm^{-1} (CO) (KBr disc); δ_H 1.82 (4 H, qnt, 2 CH$_2$), 2.55 (4 H, t, CH$_2$NCH$_2$), 3.70 (6 H, s + t, NCH$_2$C$_5$H$_4$N + 2 phthalimide NCH$_2$), 7.08 (1 H, t, pyridine H), 7.58 (2 H, m, 2

Table 10. Selected bond lengths (Å) and angles (°) for $[Ag_2L^4][ClO_4]_2$

Ag(1)–N(1)	2.281(23)	Ag(1)–N(2)	2.455(29)
Ag(1)–N(4)	2.368(29)	Ag(1)–N(3)	2.271(29)
Ag(1) · · · O(2)	2.819(25)	Ag(2)–N(5)	2.303(23)
Ag(2)–N(6)	2.459(30)	Ag(2)–N(8)	2.326(33)
Ag(2)–N(7)	2.310(21)	Ag(2) · · · O(1)	2.771(28)
O(1)–C(22)	1.330(41)	O(1)–C(23)	1.403(72)
O(2)–C(45)	1.325(41)	O(2)–C(46)	1.404(59)
N(1)–C(1)	1.461(35)	N(1)–C(38)	1.463(40)
N(1)–C(39)	1.464(28)	N(2)–C(3)	1.460(47)
N(2)–C(5)	1.258(53)	N(4)–C(11)	1.258(51)
N(4)–C(13)	1.459(30)	N(5)–C(15)	1.464(33)
N(5)–C(16)	1.465(42)	N(5)–C(24)	1.463(29)
N(6)–C(26)	1.460(54)	N(6)–C(28)	1.257(54)
N(8)–C(34)	1.262(49)	N(8)–C(36)	1.458(44)
N(1)–Ag(1)–N(2)	94.0(9)	N(1)–Ag(1)–N(4)	129.6(9)
N(2)–Ag(1)–N(4)	136.2(10)	N(1)–Ag(1)–N(3)	161.7(9)
N(2)–Ag(1)–N(3)	67.7(9)	N(4)–Ag(1)–N(3)	68.8(9)
O(2)–Ag(1)–N(1)	77.3(8)	O(2)–Ag(1)–N(2)	97.3(8)
O(2)–Ag(1)–N(3)	102.7(8)	O(2)–Ag(1)–N(4)	96.5(8)
N(5)–Ag(2)–N(6)	96.1(10)	N(5)–Ag(2)–N(8)	129.9(10)
N(6)–Ag(2)–N(8)	133.9(12)	N(5)–Ag(2)–N(7)	160.2(7)
N(6)–Ag(2)–N(7)	64.3(10)	N(8)–Ag(2)–N(7)	69.9(10)
O(1)–Ag(2)–N(5)	77.4(10)	O(1)–Ag(2)–N(6)	97.6(9)
O(1)–Ag(2)–N(7)	101.6(10)	O(1)–Ag(2)–N(8)	96.0(9)
Ag(2)–O(1)–C(22)	98.2(18)	Ag(2)–O(1)–C(23)	107.2(19)
Ag(1)–O(2)–C(45)	92.7(17)	Ag(1)–O(2)–C(46)	106.3(18)
Ag(1)–N(1)–C(1)	112.2(19)	Ag(1)–N(1)–C(38)	110.3(16)
Ag(1)–N(1)–C(39)	109.6(17)	Ag(1)–N(2)–C(3)	118.9(24)
Ag(1)–N(2)–C(5)	119.4(23)	C(3)–N(2)–C(5)	121.3(30)
Ag(1)–N(3)–C(6)	119.5(7)	Ag(1)–N(3)–C(10)	120.4(7)
Ag(1)–N(4)–C(11)	116.4(19)	Ag(1)–N(4)–C(13)	115.5(24)
C(11)–N(4)–C(13)	126.3(32)	Ag(2)–N(5)–C(15)	107.8(15)
Ag(2)–N(5)–C(16)	110.2(18)	Ag(2)–N(5)–C(24)	102.9(17)
Ag(2)–N(6)–C(26)	118.7(25)	Ag(2)–N(6)–C(28)	121.3(27)
C(26)–N(6)–C(28)	117.5(30)	Ag(2)–N(7)–C(29)	123.0(6)
Ag(2)–N(7)–C(33)	113.7(5)	Ag(2)–N(8)–C(34)	119.5(22)
Ag(2)–N(8)–C(36)	119.0(26)	C(34)–N(8)–C(36)	119.8(32)
C(5)–C(6)–N(3)	117.7(20)	C(5)–C(6)–C(7)	122.4(20)
N(3)–C(10)–C(11)	111.6(19)	C(9)–C(10)–C(11)	128.4(19)
C(16)–C(17)–C(18)	115.8(20)	C(16)–C(17)–C(22)	123.9(20)
O(1)–C(22)–C(17)	107.8(19)	O(1)–C(22)–C(21)	132.1(19)
C(28)–C(29)–N(7)	111.8(17)	C(28)–C(29)–C(30)	128.2(18)
N(7)–C(33)–C(34)	116.7(19)	C(32)–C(33)–C(34)	123.3(19)
C(39)–C(40)–C(41)	126.5(17)	C(39)–C(40)–C(45)	113.4(17)
O(2)–C(45)–C(40)	118.7(18)	O(2)–C(45)–C(44)	121.2(18)

pyridine H), 7.69 (4 H, m, 4 aryl H), 7.80 (4 H, m, 4 aryl H), and 8.43 (1 H, d, pyridine H); *m/z* (e.i.) 483 $[M + H]^+$, 1%).

Cleavage of the phthalimido systems to their corresponding primary amine derivatives. The cleavage may be effected by refluxing the phthalimido systems in hydrochloric acid as described by Casella and Ghelli.[10]

N,N-Bis(2-aminoethyl)-2-(aminomethyl)pyridine trihydrochloride (95%), m.p. 196 °C (Found: C, 39.3; H, 7.2; Cl, 33.5; N, 18.6. $C_{10}H_{21}Cl_3N_4$ requires C, 39.5; H, 7.0; Cl, 35.0; N, 18.5%); $\nu_{max.}$ 3 100—2 700, 1 615, and 1 595 cm^{-1} (NH_3^+) (KBr disc); $\delta_H(D_2O)$ 2.98 (4 H, t, CH_2NCH_2), 3.23 (4 H, t, 2 CH_2N), 4.28 (2 H, s, $NCH_2C_5H_4N$), 8.02 (1 H, t, pyridine H), 8.10 (1 H, d, pyridine H), 8.60 (1 H, t, pyridine H), and 8.77 (1 H, d, pyridine H); *m/z* (f.a.b.) 195 ($[M + H - 3HCl]^+$, 100%).

N,N-Bis(3-aminopropyl)-2-(aminomethyl)pyridine tetrahydrochloride monohydrate (93.0%), m.p. 194 °C (Found: C, 37.1; H, 6.8; N, 14.4. $C_{12}H_{28}Cl_4N_4O$ requires C, 37.3; H, 7.3; N, 14.5%); $\nu_{max.}$ 3 100—2 900 and 1 620 cm^{-1} (NH_3^+) (KBr disc); $\delta_H(D_2O)$ 2.30 (4 H, qnt, 2 CH_2), 3.15 (4 H, t, CH_2NCH_2), 3.50 (4 H, t, 2 CH_2N), 4.91 (2 H, s, $NCH_2C_5H_4N$), 8.13 (1 H, t, pyridine H), 8.25 (1 H, d, pyridine H), 8.62 (1 H, t, pyridine H), and 8.94 (1 H, d, pyridine H); *m/z* (f.a.b.) 224 ($[M + H + 3HCl - H_2O]^+$, 100%).

N,N-*Bis*(2-*cyanoethyl*)*alkylamines*. These were prepared by a modification of the route described by Whitmore *et al.*[24]

Acrylonitrile (0.15 mol) was added dropwise to a solution of the primary amine (0.05 mol) in methanol (8 cm^3) at 0 °C (ice-bath) over a period of *ca.* 60 min. When the exothermic reaction had subsided the solution was heated at reflux temperature (48 h). On cooling, the excess of acrylonitrile and methanol solvents were removed *in vacuo* to allow isolation of the product as a pale yellow liquid. Some of the products were purified by distillation under reduced pressure in a nitrogen atmosphere.

N,N-Bis(2-cyanoethyl)-2-methoxyethylamine (100%), b.p. 216—218 °C (20 mmHg); $\nu_{max.}$ 2 250 cm^{-1} (CN) (liquid film between NaCl plates); $\delta_H(CDCl_3)$ 2.47 (4 H, t, CH_2NCH_2), 2.77 (2 H, t, NCH_2), 2.94 (4 H, t, 2 CH_2CN), 3.32 (3 H, s, OCH_3), and 3.46 (2 H, t, CH_2O); *m/z* (e.i.) 181 (M^+, 3%), (c.i.) 182 ($[M + H]^+$, 63%).

N,N-Bis(2-cyanoethyl)-2-methoxybenzylamine (100%), $\nu_{max.}$ 2 250 cm^{-1} (CN) (liquid film between NaCl plates); $\delta_H(CDCl_3)$ 2.48 (4 H, t, CH_2NCH_2), 2.88 (4 H, t, 2 CH_2CN), 3.71 (2 H, s, aryl NCH_2), 3.83 (3 H, s, OCH_3), 6.95 (2 H, d + t, 2 aryl H), and 7.30 (2 H, d + t, 2 aryl H); *m/z* (e.i.) 243 (M^+, 29%).

N,N-*Bis*(3-*aminopropyl*)*alkylamines*. These were prepared by the reduction of the *N,N*-bis(2-cyanoethyl)alkylamines using sodium metal dissolved in dry ethanol according to the method of Alcock *et al.*[12] They were purified by distillation under reduced pressure in a nitrogen atmosphere.

N,N-Bis(3-aminopropyl)-2-methoxyethylamine (87.0%), b.p. 130—134 °C (1 mmHg); $\nu_{max.}$ 3 365, 3 300, and 1 600 cm^{-1} (NH_2) (liquid between NaCl plates); $\delta_H(CDCl_3)$ 1.16 (4 H, s, 2 NH_2), 1.54 (4 H, qnt, 2 CH_2), 2.49 (4 H, t, CH_2NCH_2), 2.59 (2 H, t, NCH_2), 2.69 (4 H, t, 2 CH_2N), 3.31 (3 H, s, OCH_3), and 3.43 (2 H, t, CH_2O); *m/z* (e.i.) 190 ($[M + H]^+$, 16%), (c.i.) 190 ($[M + H]^+$, 100%).

N,N-Bis(3-aminopropyl)-2-methoxybenzylamine (81.0%), b.p. 171-175 °C (1 mmHg); $\nu_{max.}$ 3 370 and 3 290 cm^{-1} (NH_2) (liquid between NaCl plates); $\delta_H(CDCl_3)$, 1.09 (4 H, s, 2NH_2), 1.57 (4 H, qnt, 2 CH_2), 2.44 (4 H, t, CH_2NCH_2), 2.65 (4 H, t, 2 CH_2N), 3.52 (2 H, s, aryl NCH_2), 3.75 (3 H, s, OCH_3), 6.81 (1 H, d, aryl H), 6.90 (1 H, t, aryl H), 7.19 (1 H, t, 1 H), and 7.38 (1 H, d, aryl H); *m/z* (e.i.) 252 ($[M + H]^+$, 17%), (c.i.) 252 ($[M + H]^+$, 93%).

Template formation of [2 + 2] *tetraimine Schiff bases on barium*(II) *perchlorate*. The *N,N*-bis(*n*-aminoalkyl)-2-(aminomethyl)pyridine hydrochloride salt (1 mmol) was neutralised by heating at reflux temperature (30 min) with the appropriate amount of NaOH in ethanol (absolute, 15 cm^3). The reaction mixture was filtered to remove the inorganic solid and the solvent removed from the filtrate *in vacuo*. The pale yellow oil was dissolved in methanol (10 cm^3) and added dropwise to a solution of $Ba(ClO_4)_2$ (0.5 mmol) and 2,6-diacetylpyridine in methanol (30 cm^3). The solution was heated at reflux temperature for *ca.* 22 h. The product deposited from the hot solution at the end of the reflux period as it cooled to ambient temperature: $[BaL^1][ClO_4]_2$ (78.0%) (Found: C, 46.8; H, 4.8; Cl, 7.1; N, 14.2. $C_{38}H_{46}BaCl_2N_{10}O_8$ requires C, 46.6; H, 4.7; Cl, 7.2; N, 14.3%); $\nu_{max.}$ 1 635 (C=N), 1 110—1 080, and 624 cm^{-1} (ClO_4) (KBr disc); *m/z* 879 ($[M - ClO_4]^+$, 100%).

Template formation of [2 + 2] *tetraimine Schiff-base macrocycles on silver*(I) *salts*. The *N,N*-bis(*n*-aminoalkyl)alkylamine hydrochloride salt (3 mmol) was neutralised using the method described for the barium(II) templating reaction. The free amine was dissolved in methanol (15 cm^3) and added dropwise to a suspension of $AgNO_3$ (3 mmol) and 2,6-diacetylpyridine (3 mmol) in methanol (75 cm^3). The reaction mixture was heated at reflux temperature for *ca.* 20 h and filtered through Hyflosupercel (to remove solid silver metal present) into a solution of $NaClO_4$ (8 mmol) in methanol (10 cm^3). The product precipitated as the filtrate cooled to ambient temperature. It was collected by filtration and washed with methanol (2 × 10 cm^3).

$[Ag_2L^1][ClO_4]_2$ (72.0%) (Found: C, 43.5; H, 4.4; Cl, 6.4; N, 13.1. $C_{38}H_{46}Ag_2Cl_2N_{10}O_8$ requires C, 43.2; H, 4.4; Cl, 6.7; N, 13.2%; $\nu_{max.}$ 1 645 and 1 630 (C=N), 1 120—1 070 and 624 cm^{-1} (ClO_4) (KBr disc); *m*/*z* 957 ($[M - ClO_4]^+$, 100%).

$[Ag_2L^2][ClO_4]_2$ (74.0%) (Found: C, 45.2; H, 4.8; Cl, 6.0; N, 12.3. $C_{42}H_{54}Ag_2Cl_2N_{10}O_8$ requires C, 45.3; H, 4.9; Cl 6.4; N, 12.6%; $\nu_{max.}$ 1 640 (C=N), 1 120—1 070 and 624 cm^{-1} (ClO_4) (KBr disc); *m*/*z* 1 013 ($[M - ClO_4]^+$, 85%).

$[Ag_2L^3][ClO_4]_2 \cdot H_2O$ (80.0%) (Found: C, 40.4; H, 5.3; Cl, 6.5; N, 10.1. $C_{36}H_{58}Ag_2Cl_2N_8O_{11}$ requires C, 40.6; H, 5.5; Cl, 6.6; N, 10.5%; $\nu_{max.}$ 1 635 (C=N), 1 100–1 080 and 624 cm^{-1} (ClO_4) (KBr disc); *m*/*z* (f.a.b.) 948 ($[M - ClO_4]^+$, 80%).

$[Ag_2L^4][ClO_4]_2$ (74.0%) (Found: C, 47.2; H, 5.2; Cl, 6.4; N, 9.2. $C_{46}H_{60}Ag_2Cl_2N_8O_{10}$ requires C, 47.2; H, 5.2; Cl, 6.1; N, 9.6%; $\nu_{max.}$ 1 640 (C=N), 1 110—1 080 and 624 cm^{-1} (ClO_4) (KBr disc); *m*/*z* (f.a.b.) 1 071 ($[M - ClO_4]^+$, 100%).

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