DALTON
FULL PAPER

Dinuclear silver(I) complexes of bibracchial tetraimine Schiff base macrocycles derived from pyrrole-2,5-dicarbaldehyde

Harry Adams,[a] Mark R. J. Elsegood,[b] David E. Fenton,*[a] Sarah L. Heath[a] and Sara J. Ryan[a]

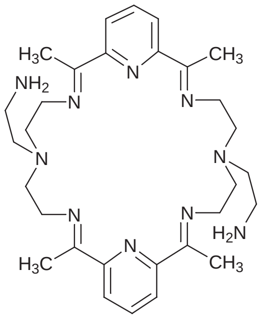
[a] *Department of Chemistry, Dainton Building, The University of Sheffield, Sheffield, UK S3 7HF*
[b] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*

Received 15th March 1999, Accepted 26th April 1999

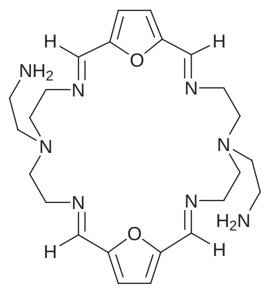
The cyclocondensation of pyrrole-2,5-dicarbaldehyde and the amines *N*,*N*-bis(2-aminoethyl)- and *N*,*N*-bis-(3-aminopropyl)-2-(aminomethyl)pyridine in the presence of silver(I) nitrate yielded homodinuclear bibracchial tetraimine Schiff base macrocyclic complexes $[Ag_2(L^3)]$ **1** and $[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ **2**. In **1** the Ag···Ag separation is 2.748 Å. In **2** the silver atoms Ag(1) and Ag(2) are disordered over two sites with refined occupancies of 94.12 and 97.22% respectively. They are three-co-ordinate in the molecule having higher silver site occupancy and four-co-ordinate in that molecule having lower occupancy; the Ag···Ag separations are 5.881 and 7.224 Å respectively. There are protonated imine nitrogen atoms present in both molecules and the structure contains a disordered acetonitrile of crystallisation.

Introduction

Mono- or homodi-nuclear metal-containing molecular clefts can be synthesized from the cyclocondensation of functionalised triamines with 2,6-diacetylpyridine, pyridine-2,6-dicarbaldehyde, thiophene-2,5-dicarbaldehyde and furan-2,5-dicarbaldehyde in the presence of appropriate metal templates such as barium and silver(I).[1–13] The clefts are derived from bibracchial tetraimine Schiff base macrocycles such as L^1 and L^2 and have been used, *via* transmetallation reactions, to complex copper(II) and manganese(II). The incorporation of a range of functionalised triamines has provided the conformational flexibility to vary the homodinuclear intermetallic separation from *ca.* 3.0 Å to in excess of 6 Å,[2,5,7] and also to incorporate anions as intermetallic spacers.[6,9–11]

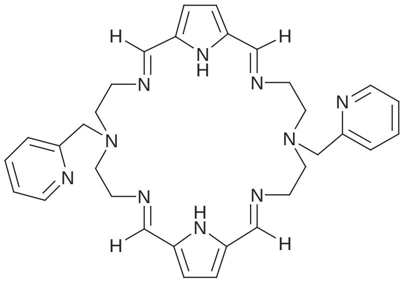


L^1

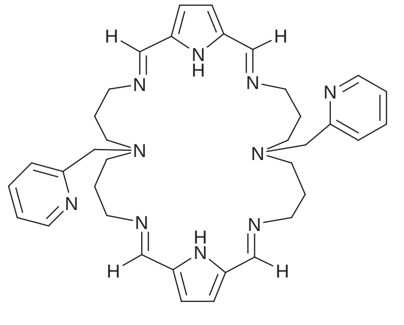


L^2

In furtherance of our programme concerned with the generation of such macrocycles we have now investigated the reaction between pyrrole-2,5-dicarbaldehyde and the amines *N*,*N*-bis(2-aminoethyl)-2-(aminomethyl)pyridine and *N*,*N*-bis-(3-aminopropyl)-2-(aminomethyl)pyridine in the presence of silver(I) nitrate. Herein we report the synthesis of the homodinuclear silver(I) complexes $[Ag_2(L^3)]$ **1** and $[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ **2**, of the bibracchial tetraimine Schiff base macrocycles, H_2L^3 and H_2L^4, so formed together with their crystal structures.



H_2L^3



H_2L^4

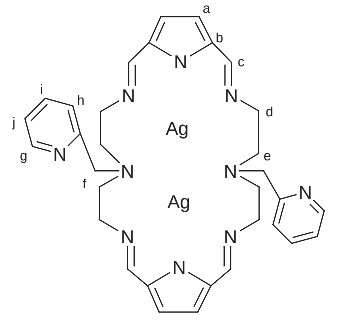
Experimental

Elemental analyses were carried out by the University of Sheffield microanalytical service. Infrared spectra were recorded as KBr discs or as liquid films between NaCl plates, using a Perkin-Elmer 297 (4000–600 cm^{-1}) or 1600 (4000–400 cm^{-1}) spectrophotometer, ^{13}C NMR spectra using either a Bruker ACF-250, AM-250 or WH-400 spectrometer and positive ion fast atom bombardment (FAB) mass spectra using a Kratos MS80 or a VG PROSPEC spectrometer (the matrix was 4-nitrobenzyl alcohol).

Synthetic procedures

N,*N*-Bis(2-aminoethyl)-2-(aminomethyl)pyridine and *N*,*N*-bis-

Table 1 NMR data for $[Ag_2(L^3)]$



	δH ($CDCl_3$)	δC ($CDCl_3$)
a	6.50 (s, 4 H)	136.7
b		160.0
c	7.99 (s, 4 H)	148.8
d	3.54 (t, 8 H)	61.0
e	2.90 (t, 8 H)	58.7
f	3.78 (s, 4 H)	141.0
g	8.39 (d, 2 H)	158.6
h	7.50 (d, 2 H)	123.5
i	7.28 (t, 2 H)	122.0
j	7.01 (t, 2 H)	118.9

(3-aminopropyl)-2-(amino methyl)pyridine were prepared as previously reported[2] and pyrrole-2,5-dicarbaldehyde by the method of Miller and Olsson.[14] **CAUTION**: perchlorate salts of silver complexes with organic ligands are potentially explosive and so should be prepared in small quantities and handled with extreme caution.

Reaction of 2,5-diformylpyrrole and *N*,*N*-bis(*n*-aminoalkyl)-2-(aminomethyl)pyridine in the presence of silver(I) ions. The *N*,*N*-bis(*n*-aminoalkyl)-2-(aminomethyl)pyridine hydrochloride salt (3 mmol) was neutralised by heating at reflux temperature for 30 min with the appropriate quantity of NaOH in absolute ethanol (15 cm^3). The reaction mixture was filtered to remove the inorganic solid produced and the solvent removed from the filtrate *in vacuo*. A solution of the neutralised amine (1 mmol) in methanol (20 cm^3) was added dropwise to a solution of 2,5-diformylpyrrole (1 mmol) and silver(I) nitrate (4 mmol) in methanol (50 cm^3). The solution was heated at reflux temperature under nitrogen and in the absence of light for ≈3 h.

Complex **1** was obtained by reduction of the solvent volume under reduced pressure followed by cooling to give a yellow precipitate of the product. For complex **2** hot filtration of the reaction solution through hyflo supercel into a methanolic solution of sodium perchlorate (2.5 mmol in 10 cm^3) produced a yellow filtrate which on reduction of the solvent volume under reduced pressure and cooling produced a yellow precipitate of the product.

Complex $[Ag_2(L^3)]$ **1** [Found (Required for $C_{16}H_{18}AgN_5$): C, 49.07(49.60); H, 4.68(4.69); N, 17.84(18.09)%]: IR (KBr disc) 1610($\nu_{C=N}$), 1426, 1316, 1071, 1041 and 756 cm^{-1}; MS (FAB^+) *m*/*z* 671(100), $[Ag(H_2L^3)]^+$; 777(87), $[Ag_2(HL^3)]^+$; and 885(74%), $[Ag_3(L^3)]^+$. The ^1H and ^{13}C NMR spectra were run in $CDCl_3$ and the assignments are listed in Table 1. Recrystallisation of the yellow precipitate from methanol gave pale yellow block crystals suitable for X-ray analysis.

Complex $[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ **2** [Found for bulk sample (required for $C_{36}H_{46}Ag_2Cl_2N_{10}O_8\cdot AgClO_4$): C, 35.10(34.85); H, 3.91(3.74); N, 11.65(11.29)%]: IR (KBr disc) 1646, 1616($\nu_{C=N}$), 1294, 1090(br), 623(ν_{ClO4}) cm^{-1}; MS (FAB^+) *m*/*z* 725(30), $[Ag(H_2L^4)]^+$, 833(100), $[Ag_2(HL^4)]^+$; and 933(44%), $[Ag_2(H_2L^4)(ClO_4)]^+$. Recrystallisation of the yellow bulk sample from slow diffusion of diethyl ether into a solution of the complex dissolved in CD_3CN gave small yellow block crystals suitable for X-ray analysis.

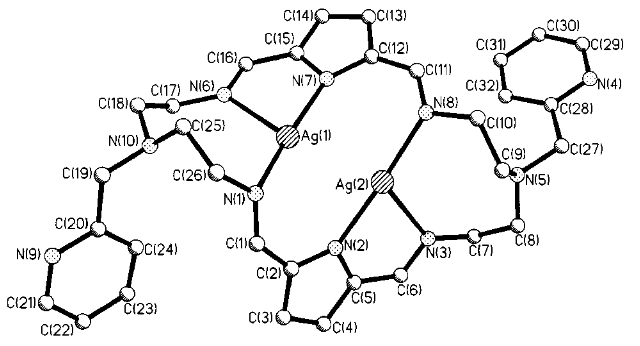


Fig. 1 The molecular structure of complex $[Ag_2(L^3)]$.

X-Ray crystallography

Details of the X-ray crystal data, and of the structure solution and refinement, are given in Table 3. In the solution of the structure of compound **2** the two silver atoms, Ag(1) and Ag(2), are disordered over two sites and were refined to have occupancies of 94.12 and 97.22% respectively. The structure contains an acetonitrile of crystallisation which is disordered about an inversion centre. This was refined anisotropically with the occupancy fixed at 50%, no hydrogen atoms were modelled for the solvent.

The programs used were Siemens SMART and SAINT for control and integration software and SHELXL 93[15a] together with local programs.[15b]

CCDC reference number 186/1443.

See http://www.rsc.org/suppdata/dt/1999/2031/ for crystallographic files in .cif format.

Results and discussion

The complex $[Ag_2(L^3)]$ 1

The generality of using Schiff base procedures for the synthesis of macrocyclic ligands has enabled, through the seminal studies of Sessler *et al.*,[16,17] a systematic investigation of a wide range of expanded porphyrin ligands. Non-aromatic pyrrole-containing macrocycles have also been synthesized and their copper(II) and dioxouranium(VI) complexes studied.[18–22] Throughout this work complexation has been accompanied by deprotonation of the pyrrole (it has been noted that rings such as pyrrole are only important in complexation after deprotonation) and without protonation of the imine bonds present in the ligands.

The cyclocondensation of pyrrole-2,5-dicarbaldehyde and the appropriate *N*,*N*-bis(2-aminoalkyl)-2-(aminomethyl)pyridine was carried out in methanol in the presence of silver nitrate; for the aminopropyl-derived complex sodium perchlorate was added to effect anion exchange and promote crystallisation.

Complex **1** was recovered as a yellow precipitate the IR spectrum of which gave a single sharp imine band at 1610 cm^{-1} indicating that the imine macrocycle had been formed. No bands were found corresponding to an accompanying anion. The MS showed peaks at $m/z = 671$ (100), 777 (87) and 885 (74%) corresponding to $[Ag(H_2L^3)]^+$, $[Ag_2(HL^3)]^+$, and $[Ag_3(L^3)]^+$ respectively. The observation of the peak assigned to $[Ag_3(L^3)]^+$ is intriguing as it implies that there is an opportunity for the co-ordination of a third silver atom, possibly through use of the pendant pyridinyl arms.

Slow evaporation of a methanolic solution of complex **1** afforded yellow crystalline blocks suitable for study by X-ray crystallography. The molecular structure of the cation is depicted in Fig. 1; selected bond lengths and angles at the silver atoms are listed in Table 2. It can be seen that each silver(I) ion is in a T-shaped three-co-ordinate environment composed of two imine nitrogen atoms and one nitrogen atom from a depro-

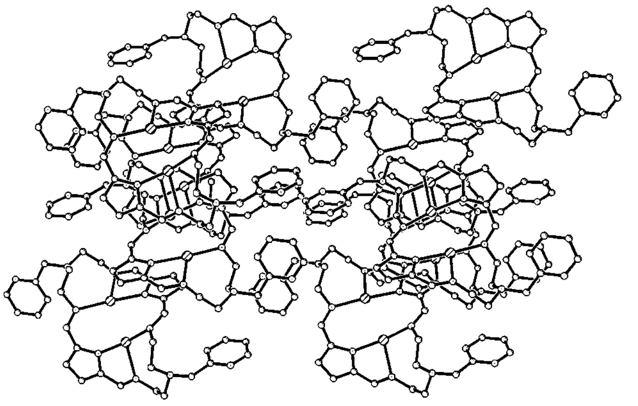
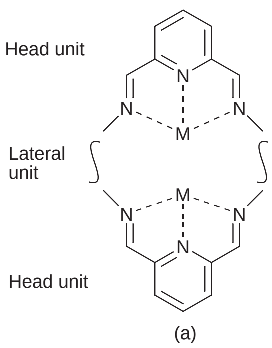
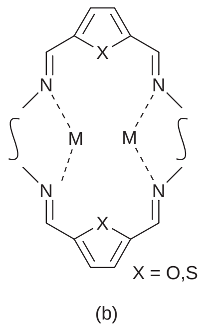


Fig. 2 The crystal packing of $[Ag_2(L^3)]$ viewed along the *b* axis.

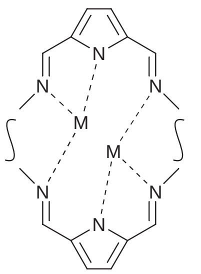
tonated pyrrolic head group. This leads to an interesting juxtaposition of a five-membered chelate ring [*i.e.* C(15), N(7), Ag(1), N(6), C(16)] with an eight-membered chelate ring [*i.e.* C(18), C(17), N(6), Ag(1), N(1), C(26), C(25), N(10)]. A pyrrolic N atom and one imine N atom comprise a chelating unit with the non-chelating imine N atom of the second head-unit providing the third interaction. One set of $Ag–N_{imine}$ distances, those from the chelating N atoms, are significantly longer (*ca.* 2.45 Å) than those for the second $Ag–N_{imine}$ and $Ag–N_{pyrrole}$ distances which are both *ca.* 2.15 Å. The silver atoms lie slightly above the planes constituted by the three donor atoms: Ag(1) is 0.1363 Å above the plane derived by N(1), N(6) and N(7) and Ag(2) is 0.0263 Å above the plane derived by N(2), N(3) and N(8); the two planes of donor atoms lie at an angle of 106.3° to each other. The *cis*-imines and pyrrole of each head group are close to coplanar and the silver atoms are diagonally disposed within the macrocyclic framework being involved with donor atoms derived from both the head and lateral units (**c**). This may be compared with the propensity for head–head co-ordination in the analogous pyridine-derived species (**a**)[2] and lateral–lateral co-ordination in the furan-[10] and thiophene-derived[11,13,23] species (**b**) where the head-unit serves as an inert spacer.



(a)



(b)



(c)

In complex **1**, unlike the disilver complexes of L^6 and L^8, the 2-(aminomethyl)pyridine pendant arms are not coordinated to the metals either intra- or inter-molecularly; this is clearly evidenced in the packing diagram (Fig. 2). Furthermore there is no evidence for the incorporation of a third silver atom as hinted at by the FAB MS and so it is probable that $[Ag_3(L^3)]^+$ arises as an artefact of the mass spectral experiment. The pendant pyridine rings are situated 3.615 Å apart so providing opportunity for π–π stacking and the two pendant pyridines within a single macrocyclic unit are angled at 95.9° to each other.

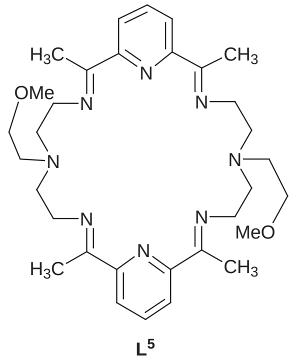
The relative planarity of the structure and non-involvement of the pyridine arms in the intermolecular structure can be contrasted with that found for the analogous pyridine-derived complex $[Ag_2L^6][ClO_4]_2$ in which the two metal ions reside within a clearly defined molecular cleft.[2] The Ag···Ag separation is 3.068 Å and each Ag^I has its shortest interactions with a pyridine N atom (*ca.* 2.38 Å) and the primary pendant pyridinyl N atom (*ca.* 2.40 Å), an intermediate interaction with one imine N atom (*ca.* 2.43 Å) and longer range interactions with the tertiary amine N atom (*ca.* 2.57 Å) and the remaining imine N atom (*ca.* 2.60 Å). One of the imine N atoms also provides a symmetric bridge between the two silver atoms and this bridge together with weak interactions between the close to parallel pyridine head-units helps maintain the integrity of the cleft-like structure. Further comparison can be made of the structure of complex **1** with that of $[Ag_2L^8(NO_3)(ClO_4)]$ in which the two silver(I) ions were found to be laterally co-ordinated and separated by 4.56 Å within a much diminished molecular cleft. One silver atom, Ag(1), lies in a four-co-ordinate environment formed by the nitrogen atoms of a pendant pyridine group, two imino N atoms and a tertiary amino nitrogen. The second silver atom, Ag(2), has this environment augmented by an interaction with a nitrate anion, or a methanol molecule of solvation; the structure is complicated by a disorder problem.[24] This comparison of the disilver complexes of L^3, L^6 and L^8 clearly shows the differences in co-ordination which can be induced by simply changing the nature of the head group of the macrocycle.

It has been shown that in certain compounds of Cu^I, Ag^I and Au^I the d^{10} atoms are held together in pairs by rigid 1,3-bifunctional bidentate ligands with a $M^+\cdots M^+$ separation similar to, or shorter than, the intermetallic distances in the metals themselves.[25] This has also been noted for disilver(I) and dicopper(I) complexes of Schiff base derived cryptands[26–28] and we have previously reported close approaches of silver in metal complexes of molecular clefts derived from bibracchial tetraimine Schiff base macrocycles, the shortest being 2.907 Å for the complex $[Ag_2L^5][ClO_4]_2\cdot0.5H_2O$.[2] In complex **1** the $Ag^I\cdots Ag^I$ separation is 2.748 Å which is the shortest so far recorded for such an interaction sustained by a macrocyclic ligand.

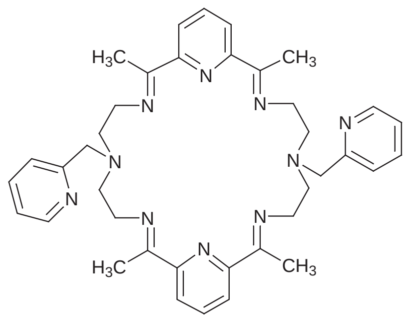
There has been an ongoing debate as to whether such close approaches arise as a consequence of the steric requirements of the ligand or *via* a metal–metal bond. The reason for close approach of d^{10} cations remains an enigma as the metals have filled shells although it has been suggested that hybridisation of 4d orbitals with higher energy 5s and 5p orbitals could convert the closed shell repulsions into weak attractive forces.[29] In the present case it is tempting to emphasise the likelihood of metal–metal interaction as the ligands are not rigid and so should not impose any severe constraint.

The complex $[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ 2

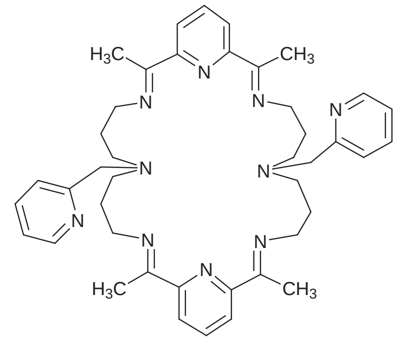
Complex **2** was recovered as a yellow precipitate the IR spectrum of which gave two sharp imine bands at 1646 and 1616 cm^{-1} indicating that the imine macrocycle had been formed but that there was a dissimilarity in the imine environment. A sharp band at 623 cm^{-1} evidenced the presence of anionic perchlorate. The presence of the perchlorate anions suggested that either the pyrroles in the macrocyclic ligand had not deprotonated (**2a**), which would have been unusual in the light of the observation that rings such as pyrrole are only important in complex form-



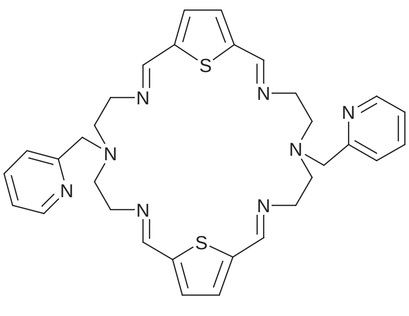
L^5



L^6



L^7



L^8

ation after deprotonation, or that the macrocyclic ligand itself had been protonated (**2b**) in order to maintain the overall charge balance. Although the bulk sample analysis indicated that a trinuclear silver complex might have been formed the mass spectrum only showed peaks at *m*/*z* = 933 (44), 833 (100) and 725 (30%) corresponding to $[Ag_2(H_2L^4)(ClO_4)]^+$, $[Ag_2(HL^4)]^+$ and $[Ag(H_2L^4)]^+$ respectively. The solubility of **2** in $CDCl_3$ was poor and so an attempt was made to run the ^1H NMR spectrum in CD_3CN . This gave only a weak and poorly resolved spectrum. The broadness suggested that exchange processes were occurring but the complex was not soluble enough for this to be verified by low temperature studies in an appropriate solvent.

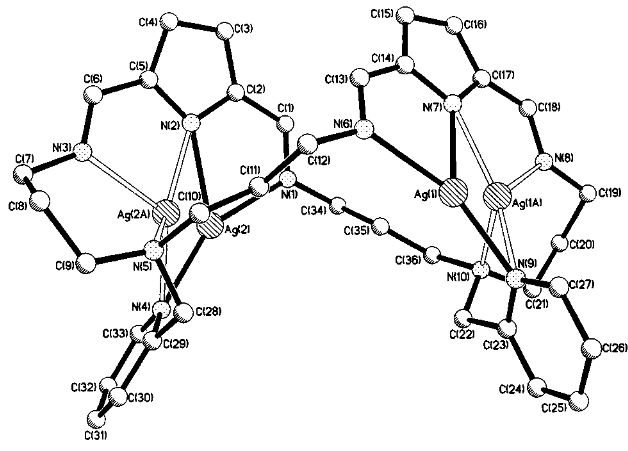
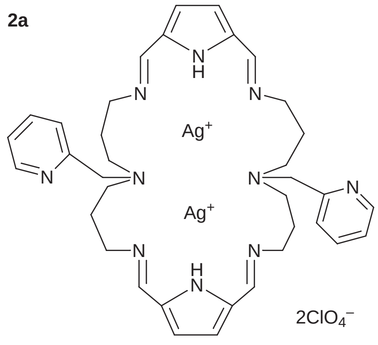
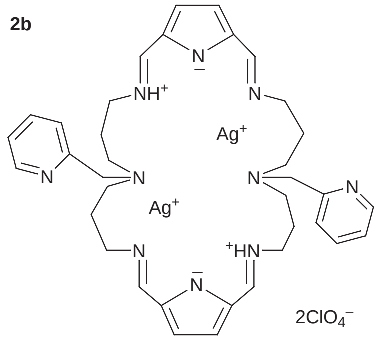


Fig. 3 The molecular structure of the cation $[Ag_2(H_2L^4)]^{2+}$.

2a



2b



Slow diffusion of diethyl ether into a d_3-acetonitrile solution of the bulk sample afforded yellow crystalline blocks of complex **2** suitable for study by X-ray crystallography. The structure was solved by direct methods confirming its homodinuclear nature and that the protonated form of the ligand was present thus giving complex **2b**. The molecular structure of the cation is depicted in Fig. 3; selected bond lengths and angles at the silver atoms are listed in Table 2. It can be seen that expansion of the ligand from a 24- to a 28-membered ring has allowed the generation of a more cleft-like conformation.

Significant peaks very close to the silver atoms were revealed inside the macrocyclic framework in complex **2**; these were too close to the metal to represent donor atoms and so it was likely that they arose from disorder involving the silver atom as had been earlier reported for a related disilver azacryptate structure.[30] Refinement as described below using a disorder model converged with the major component (**2b**^{a}) having *ca.* 95% occupancy [Ag(1), 94.12%; Ag(2), 97.22%] and the minor component (**2b**^{b}) having *ca.* 5% occupancy.

A related disorder problem concerning alternative positions for cationic guest occupancy in cryptates has been reported by Nelson and co-workers.[30] The structure of the disilver cryptate complex $[Ag_2(L^9)(ClO_4)_2]$ showed that one silver atom occupied

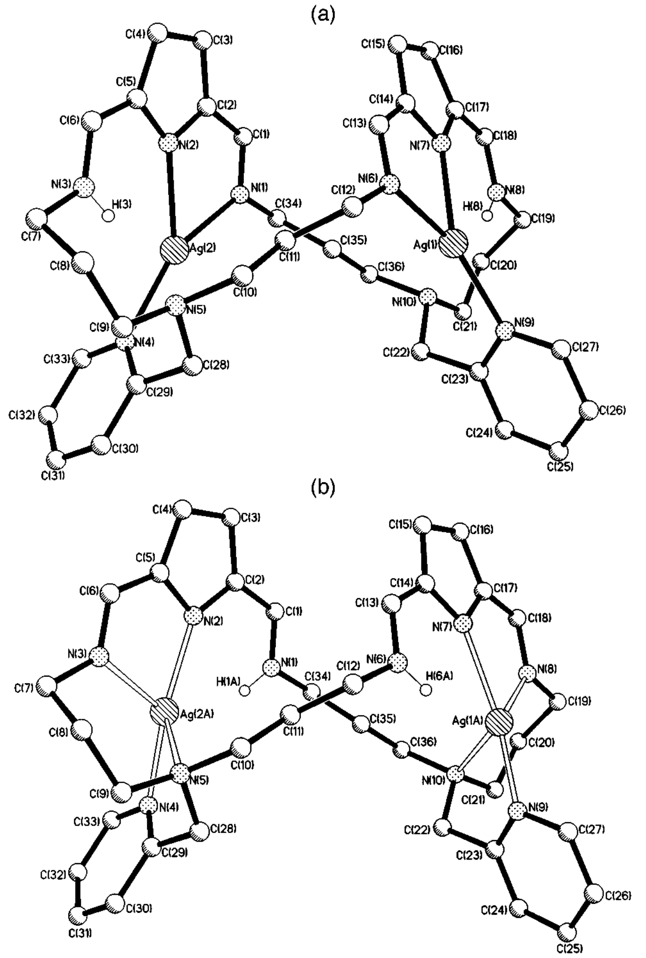
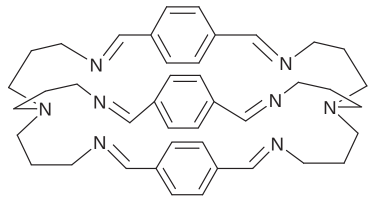


Fig. 4 Perspective views of the (a) the major component and (b) the minor component of the cation $[Ag_2(H_2L^4)]^{2+}$.



L^9

a disordered site with 78% occupancy at the major three-co-ordinate site and 22% occupancy at the minor four-co-ordinate site; both sites exhibited irregular geometry.

The silver atoms in the major occupancy site are three-co-ordinated in a distorted trigonal planar geometry composed of an imine nitrogen atom, a nitrogen atom from a deprotonated pyrrolic head group and a pendant pyridinyl nitrogen atom [Fig. 4(a)]. The silver atoms lie slightly out the planes constituted by the three donor atoms: Ag(1) is 0.0687 Å below the plane derived by N(6), N(7) and N(9) and Ag(2) is 0.0683 Å above the plane derived by N(1), N(2) and N(4); the two planes of donor atoms are at an angle of 30.9° to each other. The silver to pyridinyl-N distances are shorter (2.203, 2.181 Å) than the remaining silver to nitrogen distances (mean 2.319 Å). The two silver atoms are 5.881 Å apart in this configuration and move to 7.224 Å apart in the minor occupancy configuration. In this latter configuration each silver atom is four-co-ordinated in a distorted tetrahedral geometry composed of an imine nitrogen atom, a nitrogen atom from a deprotonated pyrrolic head group, a pendant pyridinyl nitrogen atom and a tertiary amino nitrogen atom [Fig. 4(b)]. The pendant pyridine nitrogen atoms are strongly co-ordinated (2.021, 2.162 Å) with the pyrrolic nitrogen atoms also held tightly (2.274, 2.126 Å). The remaining nitrogen atoms are less strongly held at mean distances of 2.440 (-imine) and 2.556 Å (-tertiary-N). The macrocycle is folded such that the pendant pyridine arms approach the silver atoms from opposing sides of the macrocyclic ring as has been noted for related bibracchial macrocyclic complexes. The relative site occupancy by the silver atoms is viewed as indicating a preference of the metal for three- over four-co-ordination. The perchlorate anions and the acetonitrile of solvation are not involved in bonding to the silver atoms.

Table 2 Bond lengths (Å) and angles (°) at the silver atoms in complexes **1** and **2**

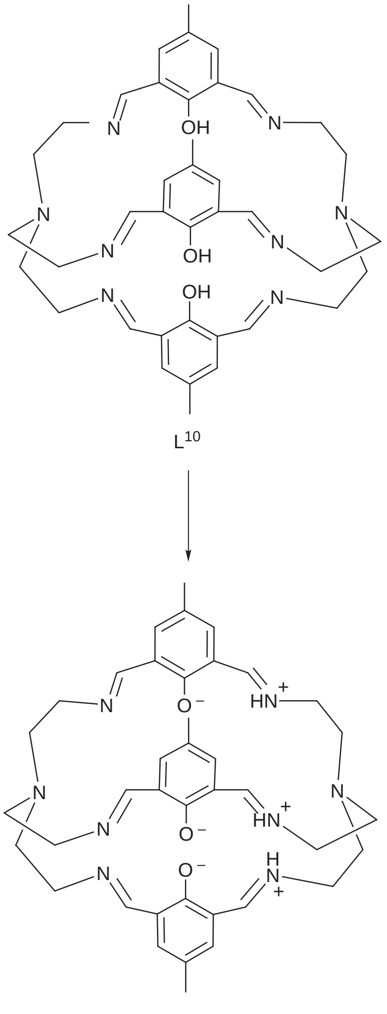
$[Ag_2L^3]$ **1**			
Ag(1)–N(1)	2.139(2)	Ag(2)–N(2)	2.159(2)
Ag(1)–N(6)	2.425(2)	Ag(2)–N(3)	2.513(2)
Ag(1)–N(7)	2.164(2)	Ag(2)–N(8)	2.154(2)
Ag(1) ··· Ag(2)	2.7484(3)		
N(6)–Ag(1)–N(1)	112.36(7)	N(8)–Ag(2)–N(3)	109.18(7)
N(6)–Ag(1)–N(7)	75.30(7)	N(3)–Ag(2)–N(2)	74.14(7)
N(1)–Ag(1)–Ag(2)	92.75(5)	N(2)–Ag(2)–N(1)	80.46(5)
N(7)–Ag(1)–Ag(2)	83.09(5)	N(8)–Ag(2)–Ag(1)	95.96(5)
N(6)–Ag(1)–Ag(2)	147.93(5)	N(3)–Ag(2)–Ag(1)	138.98(5)
N(7)–Ag(1)–N(1)	169.11(7)	N(8)–Ag(2)–N(2)	176.38(7)
$[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ **2**			
Ag(1)–N(6)	2.352(2)	Ag(2)–N(1)	2.273(2)
Ag(1)–N(7)	2.303(2)	Ag(2)–N(2)	2.349(2)
Ag(1)–N(9)	2.213(2)	Ag(2)–N(4)	2.181(2)
Ag(1) ··· Ag(2)	5.881		
Ag(1A)–N(7)	2.274(5)	Ag(2A)–N(2)	2.126(11)
Ag(1A)–N(8)	2.425(5)	Ag(2A)–N(3)	2.455(11)
Ag(1A)–N(9)	2.021(5)	Ag(2A)–N(4)	2.162(11)
Ag(1A)–N(10)	2.534(4)	Ag(2A)–N(5)	2.579(12)
Ag(1A) ··· Ag(2A)	7.224		
N(6)–Ag(1)–N(9)	148.24(8)	N(1)–Ag(2)–N(4)	148.61(8)
N(6)–Ag(1)–N(7)	73.85(8)	N(2)–Ag(2)–N(1)	74.00(8)
N(7)–Ag(1)–N(9)	137.55(8)	N(2)–Ag(2)–N(4)	137.03(8)
N(7)–Ag(1A)–N(8)	74.5(2)	N(2)–Ag(2A)–N(3)	76.0(4)
N(7)–Ag(1A)–N(10)	112.4(2)	N(2)–Ag(2A)–N(5)	117.3(5)
N(8)–Ag(1A)–N(9)	128.4(2)	N(3)–Ag(2A)–N(4)	123.4(5)
N(8)–Ag(1A)–N(10)	69.92(13)	N(5)–Ag(2A)–N(34)	69.3(3)
N(9)–Ag(1A)–N(10)	81.4(2)	N(4)–Ag(2A)–N(5)	80.3(4)
N(9)–Ag(1A)–N(7)	157.0(2)	N(4)–Ag(2A)–N(2)	159.0(6)

Both isomers display a diagonal disposition of the silver atoms as found in complex **1**. A more general comparison can be made with the corresponding pyridine-derived complex, $[Ag_2L^7][ClO_4]_2$, in which the macrocyclic ring also is 28-membered.[2] In this complex the conformation of the macrocycle has undergone a concertina-like expansion opening the features of the molecular cleft derived from the smaller 24-membered macrocycle L^6. The two silver atoms are separated by 6.824 Å and are now four-co-ordinated to the ring pyridine N atom (*ca.* 2.28 Å), the pendant pyridinyl N atom (*ca.* 2.26Å), the tertiary N atom (*ca.* 2.46 Å) and a single imine N atom (*ca.* 2.36 Å). There is a weaker interaction with the second imine N atom (*ca.* 2.76 Å) and the pyridine head-units are not close enough to interact with each other.

An unusual feature of complex **2b** is the presence of the iminium groups which are formed by prototropic shift of the pyrrolic proton to the adjacent imine nitrogen atom *i.e.* N(3)–H(3), N(8)–H(8) in **2b**[a] and N(1)–H(1), N(6)–H(6) in **2b**[b]. Proton NMR spectroscopic studies have shown that proton transfer occurs in the phenol-based compartmental cryptate L^{10} with three protons being transferred from the phenol to imino nitrogen atoms giving L^{10a},[31,32] but we are unaware of a similar process having been observed in pyrrole-derived Schiff base macrocycles or macrobicycles.

Table 3 Crystal data, structure solution and refinement for complexes **1** and **2**

	$[Ag_2L^3]$ **1**	$[Ag_2(H_2L^4)(ClO_4)_2]\cdot CH_3CN$ **2**
Chemical formula	$C_{32}H_{36}Ag_2N_{10}$	$C_{38}H_{49}Ag_2Cl_2N_{11}O_8$
Formula weight	776.45	1074.52
T/K	160(2)	160(2)
Radiation and wavelength (λ/Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a/Å	9.9470(10)	10.0484(2)
b/Å	12.2896(3)	12.2896(3)
c/Å	15.541(2)	18.0780(4)
α/°	106.560(3)	90.352(2)
β/°	92.882(3)	97.606(2)
γ/°	108.241(2)	102.199(2)
V/Å^3	1501.2(3)	2161.52(8)
Z	2	2
D_c/Mg cm^{-3}	1.718	1.651
μ/mm^{-1}	1.346	1.094
F(000)	784	1092
Crystal colour	Yellow	Yellow
Crystal size/mm	0.52 × 0.29 × 0.16	0.30 × 0.20 × 0.06
Reflections collected	11031	15636
Independent reflections	6560 (R_{int} = 0.0173)	9400 (R_{int} = 0.0238)
Reflections with $[I > 2\sigma(I)]$	5304	7343
Absorption correction	Semiempirical from ψ scans	Semiempirical from ψ scans
Maximum and minimum transmission	0.801, 0.664	0.862, 0.741
Structure solution	Patterson synthesis	Direct methods
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	6558/0/398	9399/55/595
Goodness of fit on F^2	0.981	1.022
Final $R1$, $WR2$ indices $[I > 2\sigma(I)]$	0.0243, 0.0560	0.0346, 0.0698
(all data)	0.0356, 0.0696	0.0536, 0.0858
Extinction coefficient	0.0018(3)	0.0014(2)
Largest difference peak, hole/e Å^{-3}	0.498, −0.499	0.561, −0.469



L^{10}

L^{10a}

Acknowledgements

We thank the EPSRC for a studentship (to S. J. R.), the Royal Society for a University Fellowship (to S. L. H.) and the EPSRC for funds towards the purchase of the diffractometer.

References

1 D. E. Fenton and G. Rossi, *Inorg. Chim. Acta*, 1985, **98**, L29.
2 H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton and G. Rossi, *J. Chem. Soc., Dalton Trans.*, 1990, 1271.
3 H. Adams, N. A. Bailey, D. E. Fenton, C. Fukuhara, P. C. Hellier and P. D. Hempstead, *J. Chem. Soc., Dalton Trans.*, 1992, 729.
4 D. E. Fenton and P. C. Hellier, *Inorg. Chim. Acta.*, 1992, **198–200**, (1992), 577.
5 N. A. Bailey, D. E. Fenton, P. C. Hellier, P. D. Hempstead, U. Casellato and P. A. Vigato, *J. Chem. Soc., Dalton Trans.*, 1992, 2809.
6 H. Adams, N. A. Bailey, M. J. S. Dwyer, D. E. Fenton, P. C. Hellier, P. D. Hempstead and J.-M. Latour, *J. Chem. Soc., Dalton Trans.*, 1993, 1207.
7 N. A. Bailey, C. O. Rodriguez de Barbarin, D. E. Fenton, P. C. Hellier, P. D. Hempstead, M. Kanesato and P. B. Leeson, *J. Chem. Soc., Dalton Trans.*, 1995, 765.
8 S. R. Collinson and D. E. Fenton, *Coord. Chem. Rev.*, 1996, **48**, 19.
9 H. Adams, N. A. Bailey, N. Debaecker, D. E. Fenton, W. Kanda, J.-M. Latour, H. Okawa and H. Sakiyama, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2535.
10 H. Adams, N. A. Bailey, S. R. Collinson, D. E. Fenton, C. J. Harding and S. J. Kitchen, *Inorg. Chim. Acta*, 1996, **246**, 81.
11 H. Adams, N. A. Bailey, P. Bertrand, S. R. Collinson, D. E. Fenton and S. J. Kitchen, *Inorg. Chim. Acta*, 1996, **250**, 139.
12 H. Adams, N. A. Bailey, D. E. Fenton, W. Kanda, M. Kanesato, M. B. Hursthouse, K. M. A. Malik and E. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1997, 921.
13 H. Adams, N. A. Bailey, S. R. Collinson, D. E. Fenton and S. J. Kitchen, *J. Organomet. Chem.*, 1998, **550**, 5.
14 R. Miller and K. Olsson, *Acta Chem. Scand., Ser. B*, 1981, **35**, 303.
15 (*a*) G. M. Sheldrick, SHELXL 93, An integrated system for solving and refining crystal structures from diffraction data, University of Göttingen, 1993; (*b*) W. Clegg, University of Newcastle-upon-Tyne.
16 J. L. Sessler, G. Hemmi, T. D. Mody, T. Murai, A. Burrell and S. W. Young, *Acc. Chem. Res.*, 1994, **27**, 43.

17 J. L. Sessler, V. Kral, M. C. Hoehnes, K. O. A. Chin and R. M. Davila, *Pure Appl. Chem.*, 1996, **68**, 1291.

18 H. Adams, N. A. Bailey, D. E. Fenton, S. Moss and G. Jones, *Inorg. Chim. Acta.*, 1984, **83**, L79.

19 H. Adams, N. A. Bailey, D. E. Fenton, S. Moss and C. O. Rodriguez de Barbarin, *J. Chem. Soc.*, *Dalton Trans*, 1986, 693.

20 D. E. Fenton and R. Moody, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 219; D. E. Fenton, in *Copper Coordination Chemistry*: *Biochemical and Inorganic Perspectives*, eds. K. D. Karlin and J. Zubieta, Adenine Press Inc., New York, 1986, 179.

21 J. L. Sessler, T. D. Mody, M. T. Dulay, R. Espinoza and V. Lynch, *Inorg. Chim. Acta*, 1996, **246**, 23.

22 J. L. Sessler, T. D. Mody and V. Lynch, *Inorg. Chem.*, 1992, **31**, 531; J. Reedijk, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 13.2.

23 N. A. Bailey, M. Eddy, D. E. Fenton, S. Moss, A. Mukhopadhyay and G. Jones, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2281.

24 S. J. Ryan, Ph.D. Thesis, University of Sheffield, 1998.

25 M. Jensen, *Angew. Chem.*, *Int. Edn. Engl.*, 1987, **99**, 1136.

26 G. G. Morgan, *Abstr. Annu. Meet. RSC Macrocyclic Supramolecular Chem. Group*, Nottingham, 1998, L13.

27 C. Harding, V. McKee and J. Nelson, *J. Am. Chem. Soc*, 1991, **113**, 9684.

28 J. A. Farrar, V. McKee, A. H. R. Alobaidi, J. J. McGarvey, J. Nelson and A. J. Thomson, *Inorg. Chem.*, 1995, **34**, 1302.

29 P. K. Mehrotra and R. Hoffman, *Inorg. Chem.*, 1978, **17**, 2187.

30 G. Morgan, V. McKee and J. Nelson, *Inorg.Chem.*, 1994, **33**, 4427.

31 M. G. B. Drew, O. W. Howarth, G. G. Morgan and J. Nelson, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3149.

32 M. G. B. Drew, O. W. Howarth, C. J. Harding, N. Martin and J. Nelson, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 903.

Paper 9/01992H