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Synthesis and Crystal Structure of a Disilver(I) Complex of a Tetraimine Schiff-base Macrocycle Having *N*-Isopropylidene-bearing Pendant Arms

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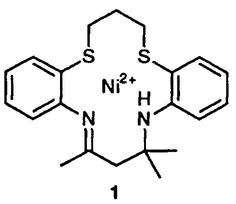
A disilver(I) complex of a tetraimine Schiff-base macrocycle with stabilised *N*-isopropylidene-bearing pendant arms has been synthesised and its crystal structure shows that the molecule does not possess the cleft-like appearance previously noted for related disilver(I) complexes.

Since the early observation of Curtis and House[1] that two molecules of acetone will condense with two primary amines, in the presence of a templating cation, to give a macrocyclic ligand, this reaction has seen wide application.[2,3] A representative example is the preparation of the macrocyclic complex **1** by reaction of Ni^{2+} with 1,5-bis(2-aminophenylthio)pentane and acetone in methanol.[4] Although in general terms the reaction sequence to macrocyclic formation in such reactions remains uncertain, in this case it was proposed that the mechanism involves the formation of *N*-isopropylidene intermediates.



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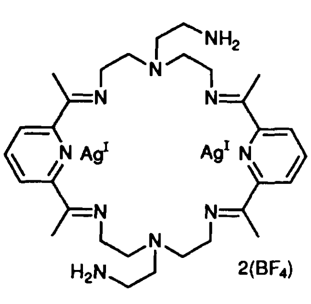
We have recently developed synthetic routes to mononuclear barium and dinuclear silver(I) complexes of a series of bibracchial tetraimine Schiff-base macrocycles.[5] Structural studies on these complexes showed that the macrocycles fold to present molecular clefts into which the metal ions co-ordinate and it was noted that application of the Curtis reaction to complex **2** could lead to macrobicyclisation with the molecular cleft being converted into an unsymmetric cryptand, **3**.

The reaction of complex **2**, which is synthesised by the silver(I)-templated cyclocondensation of tris(2-aminoethyl)amine and 2,6-diacetylpyridine using the procedure of Adams *et al.*,[5] with acetone in methanol gave a yellow crystalline product analysis of which showed that two molecules of acetone had indeed condensed with **2**. The IR spectrum showed imine bands at 1645 and 1630 cm^{-1}, with an absence of bands corresponding to primary amine functions, and the fast atom bombardment mass spectra gave a parent ion peak at *m*/*z* 929 corresponding to $\{[\mathbf{2} + 2(CH_3)_2CO - 2H_2O] - BF_4\}^+$. The ^{13}C NMR spectrum, run in CD_3CN, showed only two additional methyl-carbon signals relative to the spectrum of **2** and an imino-carbon signal at δ 207; this suggested that macrobicyclisation had not occurred and that a bis(*N*-isopropylidene) compound **4** had been synthesised. In order to verify this the crystal structure of the compound was determined.*



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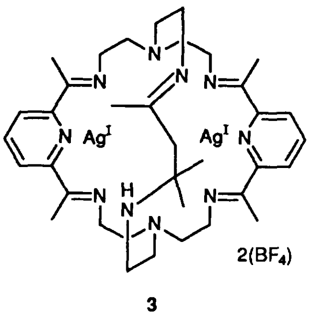

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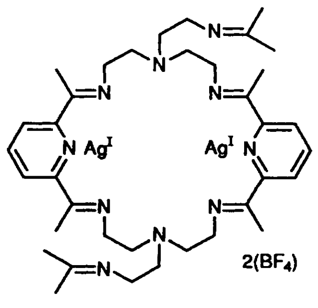
* *Crystal data for* **4**: $C_{36}H_{54}Ag_2B_2F_8N_{10}$, $M = 1016.24$, crystallises from methanol–acetone as orange, elongated blocks; crystal dimensions 0.50 × 0.25 × 0.25 mm, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 26.206(24)$, $b = 8.025(7)$, $c = 21.672(24)$ Å, $\beta = 110.07(8)°$, $U = 4281(6)$ $Å^3$, $Z = 4$, $D_c = 1.577$ g cm^{-3}, $F(000) = 2063.62$, Mo-Kα X-radiation (λ = 0.710 69 Å) with graphite monochromator, μ(Mo-Kα) = 9.78 cm^{-1}, R, $R' = 0.0759$, 0.0747 respectively $[w^{-1} = \sigma^2(F) + 0.0014(F)^2]$ for 2597 independent reflections [of 4152 measured for which $|F|/\sigma(|F|) > 3.0$], collected on a Nicolet R3 diffractometer. The minimum and maximum residuals in the final difference electron-density synthesis were −1.27 and +1.18 e $Å^{-3}$ and the maximum in the region of the BF_4^- was approximately +0.68 e $Å^{-3}$. The anisotropic thermal vibrations of the BF_4^- anion were analysed for rigid-body libration and translation, and the fit found to be extremely close (about 8%); the large thermal parameters therefore correspond to a real concerted motion.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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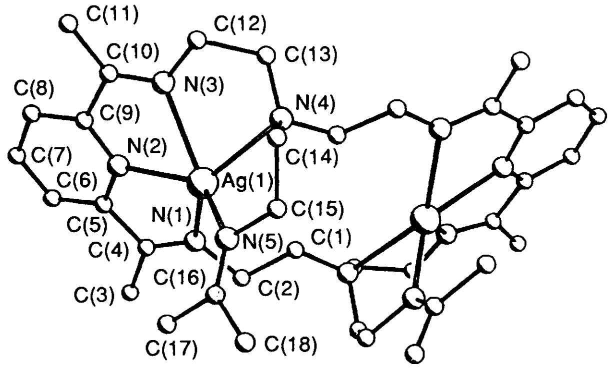
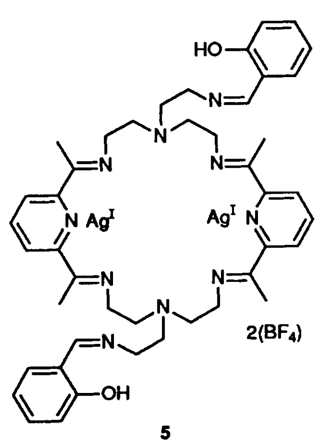


Fig. 1 The molecular geometry of the cation of complex **4** [Ag(1)–N(1) 2.447, Ag(1)–N(2) 2.352, Ag(1)–N(3) 2.461, Ag(1)–N(4) 2.528, Ag(1)–N(5) 2.270, and N(5)–C(16) 1.257 Å; Ag(1)–N(5)–C(16) 126.0°].



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The structure of the dication, with atom labelling, is illustrated in Fig. 1; the crystal also contains two symmetry-related tetrafluoroborate anions per dication. The presence of stabilised *N*-isopropylidene-bearing pendant arms is confirmed. The structure of the dication shows crystallographically imposed C_2 symmetry, with each silver atom forming five interactions with nitrogen atoms of the macrocycle (Ag–N 2.27–2.53 Å); there is no silver–silver bond (Ag ··· Ag 5.378 Å). The shortest interactions shown by the silver are to the imino nitrogen on the pendant chain, and to the pyridyl nitrogen (2.27, 2.35 Å).

The overall conformation of the macrocyclic dication is open and although somewhat folded no cleft is formed; none of the nitrogen atoms forms bridges between the silver atoms. In this respect the structure is remarkably different both from that of the precursor molecule **2**, in which there is a silver–silver separation of 3.17 Å and the conformation of the macrocycle forms a deep cleft with two bridging macrocyclic imino nitrogen atoms,[6] and from those of related disilver(I) complexes derived from bibracchial tetraimine Schiff-base macrocycles.[5]

The angle between the mean planes through the pyridyl fragments of complex **4** (root mean square deviation 0.017 Å) is 54°: the silver atom lies 0.292 Å from the pyridyl plane. The two macrocyclic imino nitrogen atoms are twisted by 11 and 10° respectively out of the pyridyl plane in the same direction [deviations 0.367 and 0.319 Å, torsional angles N(1)–C(4)–C(5)–N(2) −9 and N(2)–C(9)–C(10)–N(3) +7°] so that the diiminopyridyl head-unit does not adopt the usual meridional conformation. Indeed, the co-ordination geometry of the silver atom does not resemble any simple shape; the most coplanar set of atoms are N(1),N(3),N(5) with the silver [deviation of silver from the plane through three nitrogens +0.212 Å; displacements of N(2) and N(4), −1.286 and +2.015 Å respectively]. All three imino nitrogens are imperfectly planar with deviations from the planes of their immediate neighbours of 0.147, 0.166 and 0.126 Å for N(1), N(3) and N(5) respectively. Bond lengths in the macrocycle are all unexceptionable and there are no noteworthy intermolecular contacts.

Complexes containing *N*-isopropylidene groups have been isolated from the reactions of tris(propane-1,3-diamine)nickel(II) perchlorate,[7] and bis(dipropylenetriamine)nickel(II) perchlorate with acetone;[8] they were spectroscopically identified but not proven structurally. A limited number of *N*-isopropylidene complexes have been characterised by X-ray crystallography[9–12] and of these only one is directly related to **4** in that it is the product of a single condensation of a platinum(II)-co-ordinated, and hence polarised, acetone molecule with one end only of a molecule of 1,2-diaminoethane.[12] The IR spectrum for the latter complex shows a band for the co-ordinated imine at 1649 cm^{-1} and the dimensions and geometry of the co-ordinated *N*-isopropylidene group are directly comparable to those found in **4**.

We have recently reported that in the structure of a *triangulo*-Cu_3 complex of a tetraimine Schiff-base macrocycle derived from **2** and bearing salicylideneimino-arms the cleft-like nature of **2** is lost.[13] The nature of **4** gives an opportunity to propose that this change in molecular geometry occurs during the formation of the disilver intermediate **5** prior to the trans-metallation reaction leading to the *triangulo*-Cu_3 complex.

Acknowledgements

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