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Dinuclear copper-(I) and -(II) complexes derived from a diprotonated Schiff-base cryptand

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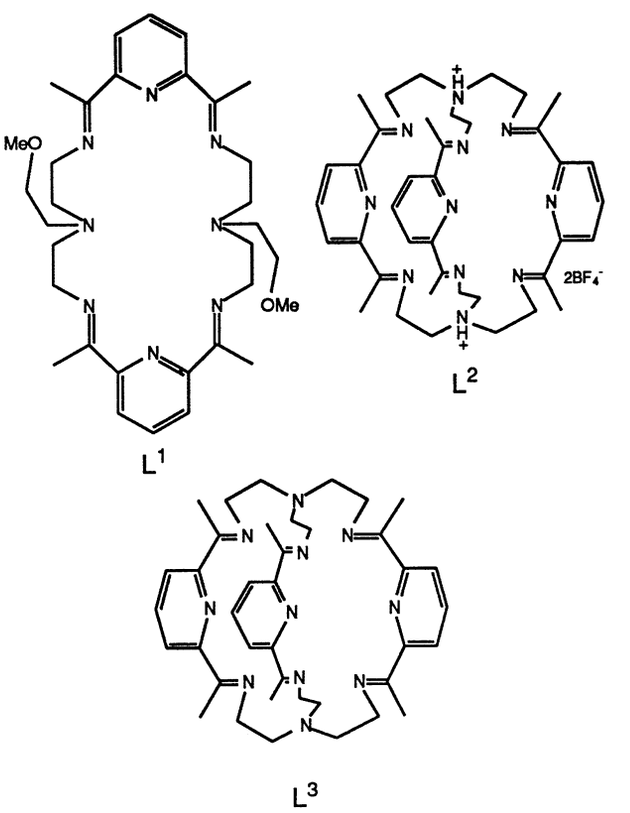
The reactions of the diprotonated Schiff-base cryptand derived from the bicyclocondensation of tris(2-aminoethyl)amine with 2,6-diacetylpyridine in the presence of acid and copper-(I) and -(II) tetrafluoroborates have been studied. In the former reaction a homodinuclear copper(I) complex of the neutral cryptand was recovered whereas in the latter a homodinuclear copper(II) complex of the bibracchial tetraimine Schiff-base macrocycle in which one pyridinyl unit has been eliminated was the product. The crystal structures of the two dinuclear complexes were determined. The $Cu^{I} \cdots Cu^{I}$ separation in the cryptate complex is 6.25 Å and the $Cu^{II} \cdots Cu^{II}$ separation in the macrocyclic complex is *ca.* 4.6 Å.

The cations in mononuclear barium and dinuclear silver(I) complexes of [2 + 2] tetraimine Schiff-base macrocycles derived from the metal-templated cyclocondensation of 2,6-diacetylpyridine ('head' units) and N-functionalised triamines in which the central nitrogen atom bears a functionalised pendant arm ('lateral' units) have been shown to be encapsulated within the macrocycle.[1,2] The aromatic 'head' units lie almost parallel with each other and the macrocycle folds about the central atoms of the 'lateral' spacers to provide the metal-binding cleft. The barium complex of L^1, $[BaL^1][ClO_4]_2$ **1**, has the barium atom completely encapsulated within the macrocyclic cavity with additional donors being provided by the pendant arms such that the cation is ten-co-ordinate. On transmetallation of this barium complex with copper(II) a dinuclear copper(II) complex results having a completely different topography. The macrocycle is now open and rather flat as opposed to cleft-like and each copper(II) is bound within a pyridine diimine 'head' unit. The metals are separated by 5.56 Å and so the donor atoms constitute two identical isolated co-ordination sites. The co-ordination geometry around each copper(II) ion is close to square pyramidal [trigonality index (see Scheme 3), $\tau = 0.075$] and the apical site is occupied by the ether O-donor atom and the pendant arms approach the copper(II) atoms from opposite sides of the macrocyclic ring ('*trans*').[1]

In the present work a different approach to the synthesis of a dinuclear coppper(II) complex of a bibracchial tetraimine Schiff base commencing from a diprotonated Schiff-base cryptand[3] (L^2) is presented together with the crystal structure of the complex. The synthesis and crystal structure of a dicopper(I) complex of the deprotonated cryptand (L^3) is also reported.



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, ^1H and ^{13}C NMR spectra using a Bruker ACF-250 (250), AM-250 (250) or WH-400 (400 MHz) spectrometer and positive-ion fast atom bombardment (FAB) mass spectra using a Kratos MS80 or VG PROSPEC spectrometer (the matrix used was 4-nitrobenzyl alcohol).

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The diprotonated cryptand $[L^2][BF_4]_2 \cdot H_2O$ was prepared by the literature method.[3]

Preparations

$[Cu_2L^3][BF_4]_2$ 2. To absolute methanol (80 cm^3) was added $[L^2][BF_4]_2 \cdot H_2O$ (1.10 g, 1.25 mmol) and $[Cu(MeCN)_4]BF_4$ (0.79 g, 2.5 mmol) under a nitrogen atmosphere. The resulting solution was stirred for 3 h at room temperature, then filtered and concentrated. An orange-yellow product was obtained which was recrystallised from methanol–ethanol to give orange crystals suitable for X-ray analysis [Found (bulk sample): C, 45.7; H, 5.25; N, 15.1. Calc. for $C_{39}H_{51}B_2Cu_2F_8N_{11} \cdot 2.5H_2O$: C, 45.9; H, 5.5; N, 15.1%]. FAB mass spectrum: *m/z* 888, $[Cu_2L(BF_4)]^+$.

IR 1626 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (CD_3CN): δ 2.41 (s, 12 H, CH_3), 3.15 (m, 12 H, CH_2), 3.73 (m, 12 H, CH_2), 6.94 (d, 6 H, CH_{py}) and 7.55 (t, 3 H, CH_{py}).

$[Cu_2L^6][BF_4]_4\cdot 3H_2O$ 3. A solution of hydrated $Cu(BF_4)_2$ (0.255 g, 1 mmol) in methanol (5 cm^3) was added to a refluxing solution of $[L^2][BF_4]_2\cdot H_2O$ (0.434 g, 0.5 mmol) in methanol–acetonitrile (4:1, 50 cm^3). The resulting solution was refluxed for 5 min and filtered hot. A dark turquoise product was obtained which was recrystallised from acetonitrile–ethanol to give crystals (**4**) suitable for X-ray analysis [Found (bulk sample of **3**): C, 33.7; H, 4.9; N, 12.9. Calc. for $C_{30}H_{46}Cu_2B_4F_{16}N_{10}\cdot 3H_2O$: C, 33.5; H, 4.9; N, 13.0%]. FAB mass spectrum: *m/z* 934, $[Cu_2L(BF_4)_3]^+$. IR 1645 cm^{-1} ($\nu_{C=N}$).

Crystallography

Crystal data for $[Cu_2L^3][BF_4]_2$. $C_{39}H_{51}B_2Cu_2F_8N_{11}$, M = 974.62, crystallises from methanol–ethanol as orange asymmetrically truncated hexagonal bipyramids, crystal dimensions 0.65 × 0.56 × 0.48 mm, hexagonal, space group $P6_3/m$ (C^2_{6h}, no. 176), a = 10.148(10), c = 24.925(31) Å, U = 2223(4) Å^3, D_c = 1.456 g cm^{-3}, Z = 2, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 10.32 cm^{-1}, $F(000)$ = 1003.74.

Three-dimensional, room-temperature X-ray data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 two-circle diffractometer by the ω-scan method. The 1151 independent reflections (of 4022 measured as a centred, monoclinic data set with an orthogonal unit cell of twice the volume) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz-polarisation effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.63 and 0.68). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods on F. Two sites were found for the single tetrafluoroborate anion per asymmetric unit, one ordered on the C_3 axis at 0.33333, 0.66667, z in line with the cation and one on the C_3 axis at 0, 0, z disordered across an inversion centre. Optimum refinement was achieved with the latter site carrying full occupancy (50:50 disordered) and the former carrying 50% occupancy. The geometries at both anion sites were constrained (B–F 1.35 Å, T_d symmetry). Attempts at refinement in the lower-symmetry space group $P6_3$ failed to achieve convergence, indicating high correlation coefficients and were abandoned. Hydrogen atoms were included in calculated positions and were refined in riding mode with isotropic thermal vibrational parameters related to those of the supporting atom. Refinement converged at a final R 0.0530 (115 parameters, mean and maximum final δ/σ 0.001 and 0.012 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minima and maxima of −0.46 and +0.44 e Å^{-3}. Complex scattering factors were taken from the program package SHELXTL,[4] as implemented on a Data General DG30 computer, which was used for structure solution and refinement. Unit weights were used throughout the refinement, as they were found to achieve more satisfactory convergence than other weighting schemes and gave satisfactory analyses. Table 1 lists selected bond lengths and angles.

Crystal data for $[Cu_2L^6][BF_4]_4\cdot 0.33MeCN\cdot 0.25H_2O$. $C_{30.67}H_{47.50}B_4Cu_2F_{16}N_{10.33}O_{0.25}$, M = 1039.28, tetragonal, space group $P4_2$ (no. 77), $a = b$ = 18.385(7), c = 12.5556(8) Å, U = 4244(2) Å^3 (by least-squares refinement of diffractometer angles for 250 reflections within θ = 1.96–27.20°, λ = 0.710 69 Å, D_c = 1.627 g cm^{-3}, Z = 4, $F(000)$ = 2111, μ = 11.13 cm^{-1}, T = 150 K.

All crystallographic measurements were made on a crystal measuring 0.35 × 0.20 × 0.15 mm using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator and Mo-Kα radiation by following previously described procedures.[5] 22 344 Reflections were measured (1.96 < θ < 27.20°; −23 < h < 23, −20 < k < 22, −16 < l < 13) and processed to yield 8294 unique reflections (R_{int} = 0.0644) with intensities greater than zero. Absorption effects were ignored.

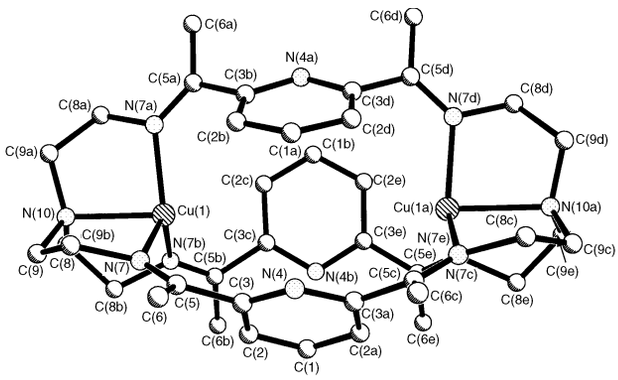


Fig. 1 Crystal structure of the cation in complex **2**

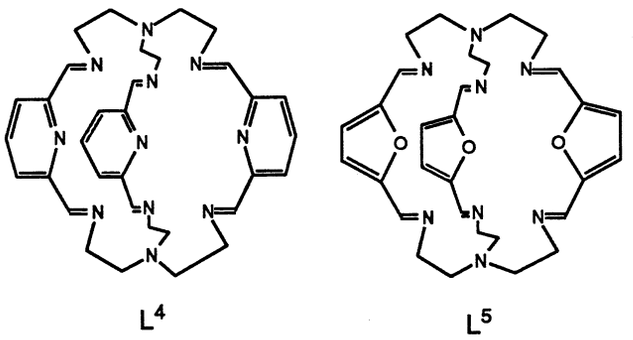
Table 1 Bond lengths (Å) and angles (°) with estimated standard deviations for $[Cu_2L^3][BF_4]_2$

Cu(1)–N(7)	2.012(4)	Cu(1)–N(10)	2.215(7)
C(1)–C(2)	1.371(7)	C(2)–C(3)	1.394(8)
C(3)–N(4)	1.353(6)	C(3)–C(5)	1.470(7)
C(5)–C(6)	1.504(6)	C(5)–N(7)	1.273(6)
N(7)–C(8)	1.487(7)	C(8)–C(9)	1.521(7)
C(9)–N(10)	1.456(6)	Cu(1)···Cu(1)[a]	6.250
N(7)–Cu(1)–N(10)	84.7(1)	N(7)–Cu(1)–N(7)[b]	119.2(1)
C(2)–C(1)–C(2)[a]	121.0(8)	C(1)–C(2)–C(3)	117.9(5)
C(2)–C(3)–N(4)	122.6(5)	C(2)–C(3)–C(5)	120.3(5)
N(4)–C(3)–C(5)	117.0(5)	C(3)–N(4)–C(3)[a]	117.5(6)
C(3)–C(5)–C(6)	117.2(4)	C(3)–C(5)–N(7)	117.0(4)
C(6)–C(5)–N(7)	125.8(5)	Cu(1)–N(7)–C(5)	129.3(3)
Cu(1)–N(7)–C(8)	106.7(3)	C(5)–N(7)–C(8)	121.3(4)
N(7)–C(8)–C(9)	108.6(4)	C(8)–C(9)–N(10)	112.1(5)
Cu(1)–N(10)–C(9)	103.3(3)	C(9)–N(10)–C(9)[b]	114.9(3)

Symmetry operations: [a] $x, y, \frac{1}{2} - z$; [b] $1 - y, 1 + x - y, z$.

The structure was solved in the non-symmetric space group $P4_2$ *via* direct methods (SHELXS 86)[6] and difference syntheses, and refined on F^2 using full-matrix least squares (SHELXL 93).[7] The asymmetric unit comprised one dinuclear complex cation, four BF_4^- anions and some fractionally occupied solvate species (acetonitrile and water). All non-hydrogen atoms were anisotropic. The hydrogen atoms of the cationic complex were all included in calculated positions (riding model) with $U_{iso} = xU_{eq}$ of the parents (x = 1.2 for the CH_2/NH_2 and 1.5 for the CH_3 groups); those on the solvent molecules were ignored. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0509P)^2]$ where $P = [\max(F_o)^2 + 2F_c^2]/3$ which gave satisfactory agreement analyses. Final $wR2 = |\Sigma w[\Delta(F^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ and $R1 = \Sigma(\Delta F)/\Sigma(F_o)$ values were 0.1021 and 0.0568 respectively for 583 parameters and all 8294 data [ρ_{min}, ρ_{max} −0.253, 0.696 e Å^{-3}; $(\Delta/\sigma)_{max}$ 0.001]. The corresponding R indices for 6261 observed data [$I > 2\sigma(I)$] were 0.0997 and 0.0444 respectively. The Flack parameter calculated during refinement [−0.036(12)] was very close to zero, which indicated that the structure determined was the correct enantiomorph. All calculations were done on a Pentium P90 personal computer. Sources of scattering factor data are given in ref. 7. Selected bond lengths and angles are given in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the



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Results and Discussion

Previously dinuclear copper complexes of bibracchial tetraimine Schiff-base macrocycles have been prepared by transmetallation of mononuclear barium, dilead or disilver complexes of the required macrocycle.[8] The precursor complexes were synthesized by metal-templated cyclocondensation reactions of heterocyclic dicarbonyls and the requisite 1,*n*-diamines. The availability of the diprotonated cryptand, L^2, prepared by [2 + 3] cyclocondensation of 2,6-diacetylpyridine and tris(2-aminoethyl)amine in the presence of hydrochloric acid followed by filtration into a solution of sodium tetrafluoroborate in methanol,[3] suggested that it might serve as a useful precursor for metal complexes if it would engage in 'transmetallation' reaction in which the protons were exchanged for a metal cation. The reaction of L^2 with $[Cu(MeCN)_4]BF_4$ in methanol gave a dinuclear copper(I) complex, $[Cu_2L^3][BF_4]_2$ **2**, of the neutral cryptand, exchange of proton for copper(I) having occurred.

The molecular structure of the dication from complex **2** is illustrated in Fig. 1; bond lengths and angles with estimated standard deviations are given in Table 1. The structure shows that both the integrity of the cryptand and the unusual *trans-trans* conformations of the dicarbimine functions found in the protonated cryptand[3] are retained in the structure of the complex. The dimetallic cryptand possesses crystallographically imposed C_{3h} symmetry, with each copper(I) and each tertiary amine nitrogen lying on the C_3 axis and the pyridyl nitrogens and their *para*-C–H groups lying on the mirror plane: thus, the remainder of each asymmetric unit comprises only half of one of the 'arms' of the cryptand and a single tetrafluoroborate anion. This latter is disordered over two sites, one of which lies on the same C_3 axis as the cation (refined with overall 50% occupancy); the other site lies adjacent to inversion centres across which the anion is disordered 50 : 50, resulting in a set of three such sites which surround the end of the cryptand. The copper(I) is co-ordinatively saturated being bonded to four nitrogen atoms in an approximately trigonal-pyramidal geometry with the unique axial bond to the bridgehead tertiary amine much the longer at 2.215 Å as compared to the three symmetry equivalent bonds to the imines at 2.012 Å: the copper is displaced by 0.185 Å from the plane through the imino nitrogen atoms in a direction away from the bridgehead tertiary nitrogen. The copper–copper separation is 6.250 Å but there is no evidence for any electron density lying between the metals within the cavity. Each symmetry-equivalent pyridyl ring is planar [root mean square (r.m.s.) deviation 0.021 Å] and the set of three such rings form a barrel or 'corset' around the cryptand: the angle between the normal to the pyridyl ring and the line joining its centroid to the centre of the cryptand is only 0.9°. When viewed along the N (bridgehead)···N (bridgehead) vector (Fig. 2) the ligand shows a predominantly eclipsed arrangement as has been reported for the free cryptands L^4 and L^5.[9,10]

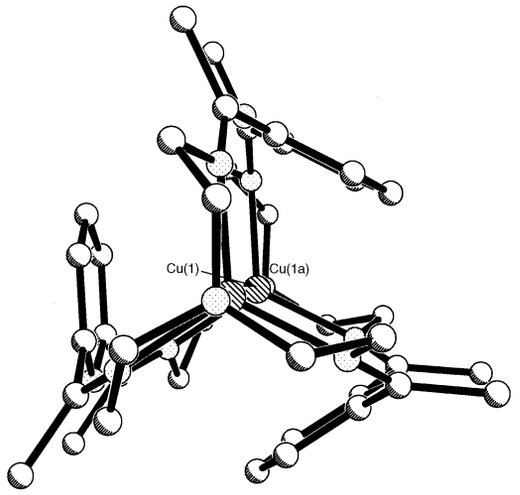
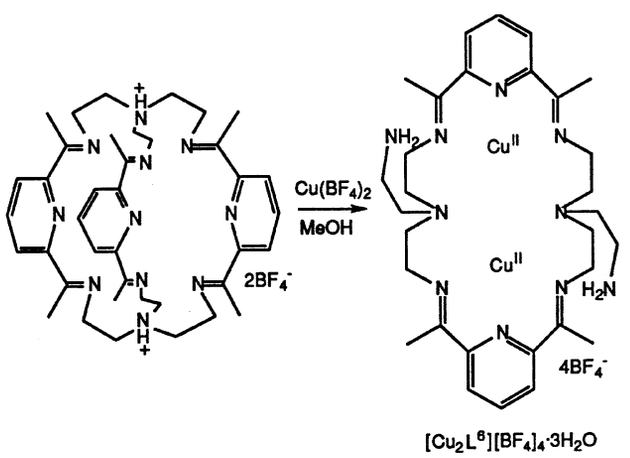


Fig. 2 The cation in complex **2** viewed along the N (bridgehead)···N (bridgehead) vector



Scheme 1

The copper separation is well in excess of that reported, 3.04 Å, for the dicopper(I) complex, $[Cu_2L^4][ClO_4]_2$, in which L^4 is the [3 + 2] Schiff-base cryptand derived from pyridine-2,6-dicarbaldehyde and tris(2-aminoethyl)amine.[11] The structures of the complexes differ significantly and in $[Cu_2L^4][ClO_4]_2$ each copper is co-ordinated to three imino N atoms with Cu–N ≈ 2.02 Å; the bridgehead N atom is more distant, Cu–N ≈ 2.75 Å and at best weakly interacting. There is a further weak interaction with a pyridine N atom, Cu–N ≈ 2.64 Å. The copper(I) is described as being three-co-ordinate and the dicarbimine functions in this complex are in *cis-cis* conformations.

Further comparison may be made with the structure of $[Cu_2L^5][BF_4]_2$ in which the cryptand is derived from furan-2,5-dicarbaldehyde and tris(2-aminoethyl)amine.[12] Here the copper atoms are 4.2 Å apart; each is four-co-ordinate interacting with the bridgehead N atom (Cu–N 2.379 Å) and three imine N atoms (2.388, 1.986 and 1.981 Å). The conformations of the dicarbimine functions are again *cis-cis* and the furan oxygen atom is non-co-ordinating.

The reaction of $Cu(BF_4)_2$ with the diprotonated cryptand L^2 in methanol (Scheme 1) gave a dinuclear complex, $[Cu_2L^6][BF_4]_4{\cdot}3H_2O$ **3**. Hydrolytic cleavage of one dicarbimine bridge of the cryptand has occurred to give a bibracchial tetraimine Schiff-base macrocyclic ligand. Such behaviour has been noted in the reactivity of an isophthaldehyde-derived cryptand with copper(II)[13] and in the reaction of L^2 with manganese(II).[14]

Recrystallisation of complex **3** from ethanol–acetonitrile gave crystals of $[Cu_2L^6][BF_4]_4{\cdot}0.33MeCN{\cdot}0.25H_2O$ **4** suitable

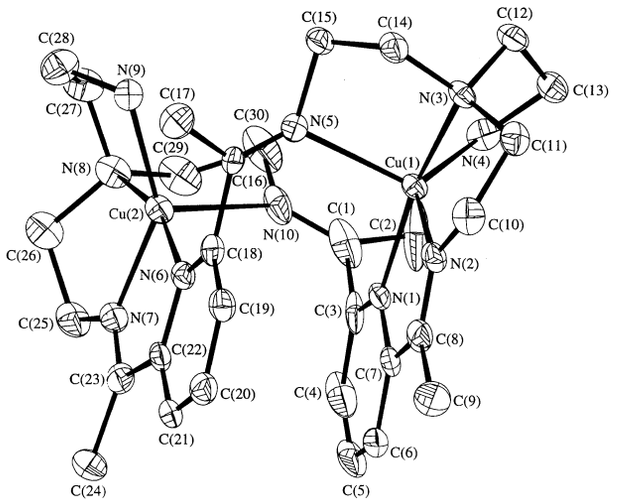


Fig. 3 General view of the cation in complex **4** showing the atom numbering scheme used. The ellipsoids are drawn at 35% probability

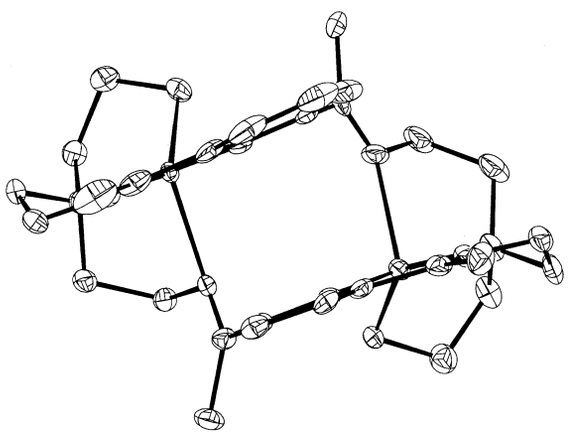
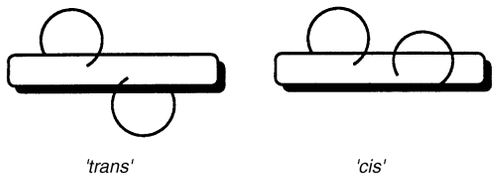


Fig. 4 View of the cation in complex **4** showing the presence of an approximate two-fold axis

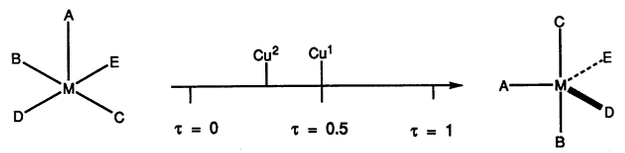
Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations for $[Cu_2L^6][BF_4]_4\cdot 0.33MeCN\cdot 0.25H_2O$

Cu(1)–N(2)	1.963(4)	Cu(1)–N(4)	2.013(4)
Cu(1)–N(1)	2.010(4)	Cu(1)–N(3)	2.043(3)
Cu(1)–N(5)	2.243(4)	Cu(2)–N(7)	1.963(4)
Cu(2)–N(6)	2.053(4)	Cu(2)–N(8)	2.055(4)
Cu(2)–N(9)	1.996(4)	Cu(2)–N(10)	2.213(4)
Cu(1)···Cu(2)	4.577(1)		
N(2)–Cu(1)–N(4)	137.0(2)	N(2)–Cu(1)–N(1)	81.8(2)
N(1)–Cu(1)–N(4)	103.3(2)	N(2)–Cu(1)–N(3)	83.4(2)
N(4)–Cu(1)–N(3)	85.6(2)	N(1)–Cu(1)–N(3)	164.9(2)
N(2)–Cu(1)–N(5)	99.6(2)	N(4)–Cu(1)–N(5)	119.9(2)
N(1)–Cu(1)–N(5)	102.98(13)	N(3)–Cu(1)–N(5)	82.42(14)
N(7)–Cu(2)–N(6)	81.1(2)	N(7)–Cu(2)–N(8)	83.0(2)
N(6)–Cu(2)–N(8)	163.4(2)	N(7)–Cu(2)–N(9)	143.6(2)
N(6)–Cu(2)–N(9)	104.59(14)	N(8)–Cu(2)–N(9)	85.6(2)
N(7)–Cu(2)–N(10)	101.8(2)	N(6)–Cu(2)–N(10)	106.7(2)
N(8)–Cu(2)–N(10)	81.2(2)	N(9)–Cu(2)–N(10)	110.4(2)

for X-ray crystallography. The results of X-ray analysis confirm the ring opening of the Schiff-base cryptand, caused by scission of one pyridinyl diimine unit, has occurred such that the dicopper(II) moiety is held inside a cleft. A general view of the $[Cu_2L^6]^{4+}$ cation is shown in Fig. 3 and selected geometric parameters are presented in Table 2. The cation possesses an approximate two-fold axis of symmetry as shown in Fig. 4, and as a result of co-ordination the organic ligand is folded in such a way that the two pyridinyl units are nearly parallel [within



Scheme 2 Representation of '*cis*' and '*trans*' isomers found in the bibracchial tetraimine Schiff bases



Scheme 3 For perfect square-pyramidal and trigonal-bipyramidal geometries the values of τ are zero and unity respectively, τ being an index of the degree of trigonality within the structural continuum between square-pyramidal and trigonal-bipyramidal geometries:[15] A is the apical donor atom of a square-based pyramid and should not be any of the atoms B–E which define the largest two angles (α,β) at the metal centre; B and C are associated with the larger basal angle β, D and E with the smaller basal angle α. $\tau = (\beta - \alpha)/60$

7.4(4)°] with stacking distances of 3.23 Å. Each copper environment is best described as distorted trigonal bipyramidal; for Cu(1), the N(2), N(4) and N(5) atoms define the equatorial triangle with N(1) and N(3) in axial positions and for Cu(2) the N(7), N(9) and N(10) atoms define the equatorial triangle with N(6) and N(8) axial. The distortions from more regular geometry can be seen from the sum of the three equatorial interbond angles at each copper, 356.5(2) and 356.8(2)°.

If the donor-atom difference in the pendant arms is disregarded then the behaviour of the bibracchial macrocyclic framework towards copper(II) may be regarded as an example of polytopal isomerism. The N-donor atoms of the pendant arms in the dicopper(II) complex **4** approach the metal atoms from the same side of the macrocyclic ring ('*cis*') consistent with the clipping out of one bridge from the cryptate precursor (Scheme 2). This process has also been demonstrated in a dimanganese(II) complex,[14] $[Mn_2L^6(O_2CMe)][BF_4]_3$, and may be contrasted with the approach of the methoxyethyl pendant arms from opposing side ('*trans*') found in $[Cu_2L^1][ClO_4]_4$ formed by transmetallation of the mononuclear barium precursor complex **1**.[2] Furthermore the co-ordination geometries at the metal atoms differ; those at the copper atoms in the $[Cu_2L^1]^{4+}$ cation are very close to square pyramidal (the index of trigonality τ being 0.075 based on the pendant-arm donor atom being the axial donor atom, Scheme 3), whereas each copper atom in **4** is five-co-ordinate with a distorted trigonal-bipyramidal geometry (τ lies between 0.33 and 0.47).[15]

The Cu–N bond distances in complex **4** vary from 1.963(4) to 2.243(4) Å around Cu(1) and 1.963(4) to 2.213(4) Å around Cu(2) (average 2.055 Å). These distances are generally comparable with those found in **2** described earlier, but in the present case the longest bond around each copper is associated not with any tertiary nitrogen but with the imino nitrogen involved in bridge formation. It is interesting that for each copper the differences in the two Cu–N (imino) bonds [1.963(4), 2.243(4) for Cu(1); 1.963(4), 2.213(4) Å for Cu(2)] appear to be of little importance at first but a closer examination of the geometry parameters reveals that the C=N distances for the imino nitrogens are also different [1.252(8), 1.290(6) for Cu(1); 1.263(6), 1.280(6) Å for Cu(2)] and that the shorter of these bonds involves the nitrogen atoms having the longer Cu–N bonds. It is also observed that the shorter C=N bonds are nearly perpendicular to the respective pyridine rings whilst the longer ones are nearly coplanar, as shown

by the dihedral angles N(10)–C(1)–C(3)–N(1) −87.3(6), N(5)–C(16)–C(18)–N(6) −69.1(6), N(1)–C(7)–C(8)–N(2) −2.6(6) and N(6)–C(22)–C(23)–N(7) 0.3(6)°. These observations are consistent with the suggestion that the differences in the C=N bonds involving the imino nitrogens, although small, are significant and reflect the different degrees of conjugation with the pyridine ring. The pyridine rings are both planar [r.m.s. deviations 0.011(8) and 0.015(8) Å] and there is clear evidence of reduced delocalisation within these rings are shown by the bond-length data.

In the crystal the complex $[Cu_2L^6]^{4+}$ cations and BF_4^- anions are held together by several C–H · · · F hydrogen bonds and electrostatic interactions; the partially occupied solvate species MeCN and H_2O are all sited on crystallographic symmetry axes and appear to have no significant short contacts.

The dicopper(I) separation found in deoxygenated haemocyanin from *Limulus polyphemus*[16] is 4.6 Å. This suggests that if, as the $Cu^{II} \cdots Cu^{II}$ separation in complex **4** is 4.577(1) Å, the complex could be reduced to the dicopper(I) species then it would be available as a model for Type 3 copper sites. Although the separation is comparable we have not yet been able to synthesize a dicopper(I) complex of L^6.

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