Mononuclear Barium and Dinuclear Copper(II) Complexes of a 24-Membered Bibracchial Tetraimine Schiff-base Macrocycle derived from *N,N*-Bis(2-aminoethyl)-2-methoxyethylamine†

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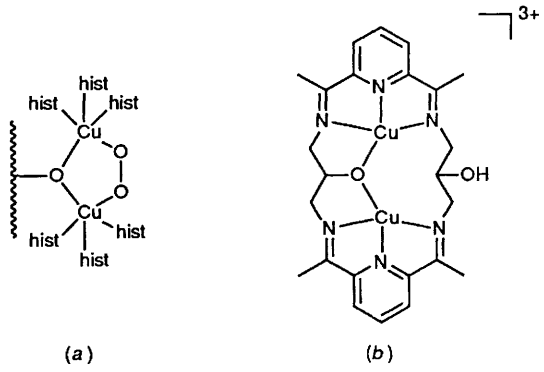
The X-ray structure of a mononuclear barium complex of the bibracchial tetraimine Schiff-base macrocycle derived from the cyclocondensation of 2,6-diacetylpyridine and *N,N*-bis(2-aminoethyl)-2-methoxyethylamine [monoclinic, space group $P2/n$ (no. 13), a = 27.494(20), b = 14.120(13), c = 21.024(14) Å, β = 91.68(57)°, Z = 8] confirms that the macrocycle folds to present a molecular cleft within which the metal is co-ordinated. Transmetallation with Cu^{II} gives a homodinuclear copper(II) complex the crystal structure of which [monoclinic, space group $P2_1/c$, a = 14.807(6), b = 9.558(4), c = 17.432(8) Å, β = 113.89(5)°, Z = 2] shows that the copper(II) atoms are held by the 'head' units of the macrocycle, an opening of the cleft having occurred.

Structural studies on barium complexes of [2 + 2] tetraimine Schiff-base macrocycles derived from the metal-templated cyclocondensation of heterocyclic, or phenolic, dicarbonyl derivatives ('head' units) and 1,*n*-diaminoalcohols ('lateral' units) showed that the macrocycles encapsulated the cation.[1,2] The aromatic 'head' units lie almost parallel with each other and the macrocycle folds about the central atoms of the 'lateral' bridges to provide the metal-binding pocket. When *N*-functionalised triamines, in which the central nitrogen atom bears a functionalised pendant arm, are used in the cyclocondensation reactions then *N,N'*-bibracchial macrocyclic complexes of the templating cation are prepared.[3,4] Mononuclear complexes result from using barium as a template whereas dinuclear complexes are derived from the use of silver(I) as the template and structural studies have shown that the macrocycles again fold to present a topography which has been termed a molecular cleft, by analogy with the metal-binding clefts found in metalloproteins and -enzymes, and into which the metal ions co-ordinate.

Collective evidence from vibrational, magnetic, chemical and electronic data have suggested that the metallo-biosite in oxyhaemocyanin requires a Type 3 dinuclear copper(II) centre with both endogenous and exogenous bridges present in order to mediate the strong antiferromagnetic coupling which leads to diamagnetism [Fig. 1(*a*)].[5] The nature of the purported endogenous bridge is not yet established but extended X-ray absorption fine structure (EXAFS) data[6] and ligand-to-metal charge-transfer bands at 345 and 570 nm in the electronic spectrum[7] suggest that it arises from an oxygen atom. Hydroxide, alkoxide, phenoxide and carboxylate have all been listed as contenders for this bridging role however the absence of enhanced tyrosine vibrations in resonance Raman experiments indicate that there is no conserved tyrosine present and so a phenoxide bridge is unlikely.[8] EXAFS studies[6] show the presence of terminal N or O donor atoms of which two per Cu^{II} are imidazole N atoms and that the Cu · · · Cu separation is *ca.* 3.6 Å; the copper(II) atoms are in approximately tetragonal



(*a*) (*b*)

Fig. 1 (*a*) Spectroscopically derived dicopper(II) site in oxyhaemocyanin; (*b*) the homodinuclear copper(II) complex **1**

environments. Resonance Raman studies with isotopically substituted dioxygen have shown that it is bound symmetrically to the dinuclear centre through both oxygen atoms to provide the exogenous bridge.[9] The Cu · · · Cu separation of *ca.* 3.6 Å upon oxygenation suggested that this peroxide is probably bound in a *cis*-μ-1,2 mode. A more recent study of peroxobis[tris(3,5-diisopropylpyrazolyl)borate] copper(II), has revealed that the peroxide is bound in a μ-η^2:η^2 mode and that the Cu · · · Cu separation is 3.56 Å.[10] Close similarities in the physicochemical properties of this complex and those of oxyhaemocyanin suggest that the doubly bridged bonding mode of peroxide could also be available in the biomolecule.

Although the size of the protein has hampered attempts to elucidate its structure crystallographically, particularly in the oxy form, the structure of the colourless deoxy form from *Panulirus interruptus* (spiny lobster) has now been reported[11] and shows that each copper(I) ion is co-ordinated by three histidine residues with an inter-copper distance of *ca.* 3.7 Å. At a resolution of 3.2 Å there is no evidence for the presence of an endogenous bridging ligand and as the nearest tyrosine is > 10 Å away it is unlikely that tyrosyl bridge can be available. The presence of a bridging hydroxide has not yet been ruled out.[12]

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

The cleft-like nature of the barium complexes of [2 + 2] tetraimine Schiff-base macrocycles suggested that they might act as precursors for copper complexes which might in turn be viewed as speculative models for the above Type 3 copper biosites. Transmetallation of the barium complex of the tetraimine Schiff-base macrocycle derived from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane gave the dinuclear copper(II) complex **1** which provided the first example of a structurally characterised dinuclear complex having a single OR bridge and was thus related to oxyhaemocyanin [Fig. 1(*b*)].[13] Following the elucidation of the structure of deoxyhaemocyanin it was noted that the absence of an endogenously bridging hydroxyl atom within the ligand periphery of the [2 + 2] tetraimine Schiff-base macrocycles might provide closer but still speculative models for the Type 3 sites.

In this paper the synthesis, properties and crystal structures of a mononuclear barium complex and a dinuclear copper(II) complex of a bibracchial tetraimine Schiff-base macrocycle L derived from the cyclocondensation of 2,6-diacetylpyridine and *N*,*N*-bis(2-aminoethyl)-2-methoxyethylamine, and so not containing an endogenous bridge, are reported.

Experimental

Physical Measurements.—Elemental analyses were carried out by the Sheffield University microanalytical service. Infrared spectra were recorded as KBr discs or liquid films between NaCl plates, using a Perkin Elmer 297 infrared spectrophotometer (4000 to 600 cm^{-1}) or 1710 infrared Fourier transform spectrophotometer (4000–400 cm^{-1}). Proton NMR spectra were recorded using Perkin Elmer R34 (220 MHz) or Bruker AM-250 (250 MHz) spectrometers. Carbon-13 NMR spectra were obtained on a Bruker AM-250 (62.9 MHz) instrument. Electron impact (EI) and chemical impact (CI, ammonia) mass spectra were recorded with a Kratos MS25 spectrometer; positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS80 spectrometer with 3-nitrobenzyl alcohol (noba) as the matrix solvent. Electronic absorption spectra were recorded using a Phillips PU8720 UV/VIS scanning spectrophotometer operating in the range 280 to 900 nm.

N-(Toluene-*p*-sulfonyl)aziridine was prepared by the methods of Hope[14] and Bulkowski and their co-workers.[15]

2-*Methoxyethyl*-N,N-*bis*(2-*toluene*-p-*sulfonylaminoethyl*)-*amine*.—A solution of 2-methoxyethylamine (0.5 mol) in acetonitrile (40 cm^3) was added dropwise to a solution of *N*-(toluene-*p*-sulfonyl)aziridine (1 mol) in acetonitrile (100 cm^3). This was stirred at room temperature for 3 d. Cooling to 0 °C resulted in the precipitation of the analytically pure product as a white crystalline solid in 89% yield, m.p. 109 °C (Found: C, 53.65; H, 6.60; N, 9.00; S, 13.85. $C_{21}H_{31}N_3O_5S_2$ requires C, 53.70; H, 6.65; N, 8.95; S, 13.65%). IR (KBr disc): ν_{NH} 3212, ν_{SO_2} 1332 and 1156 cm^{-1}. Mass spectrum (CI), *m*/*z* 470 (M^+). NMR ($CDCl_3$): δ_H 7.76 (4 H, d), 7.29 (4 H, d), 5.80 (2 H, b), 3.48 (3 H, s), 3.41 (2 H, t), 2.83 (4 H, b), 2.53 (4 H, t), 2.47 (2 H, t) and 2.40 (6 H, s); δ_C 143.1, 136.9, 129.6, 127.0, 70.5, 58.7, 53.3, 52.5, 40.9 and 21.4.

N,N-*Bis*(2-*aminoethyl*)-2-*methoxyethylamine*.—This was prepared using an adaptation of the general procedure of Ji *et al.*[16] A sodium dihydronaphthylide solution (0.1 mol dm^{-3}) was prepared by dissolving sodium metal (0.5 mol) and naphthalene (0.5 mol) in tetrahydrofuran (500 cm^3) followed by stirring under a nitrogen atmosphere for 18 h, using a glass magnetic flea. To the resulting dark green solution was added a solution of ethyl-*N*,*N*-bis(2-toluene-*p*-sulfonylaminoethyl)amine (0.05 mol) in tetrahydrofuran (100 cm^3) using syringe techniques. A dark orange colouration rapidly developed and the reaction mixture was stirred at room temperature for 1 h. After careful addition of water (50 cm^3), to destroy any remaining radical, the tetrahydrofuran was removed under vacuum and the residue dissolved in dichloromethane (300 cm^3). The crude amine was then extracted using dilute hydrochloric acid (3 × 100 cm^3, 10 × dilution of commercial 11 mol dm^{-3} acid). The acidic aqueous layer was cooled to 0 °C, basified with aqueous potassium hydroxide (200 cm^3, 7 mol dm^{-3}), and extracted with dichloromethane (3 × 100 cm^3). The combined organic layers were dried over anhydrous magnesium(II) sulfate, and evaporated to yield the crude product. Purification by vacuum distillation in a nitrogen atmosphere resulted in the isolation of a colourless hygroscopic oil in 25% yield; b.p. 99–104 °C (0.2 mmHg, ≈ 26.6 Pa). IR (NaCl plates): ν_{NH_2} 3364 and 3293 cm^{-1}. Mass spectrum (CI), *m*/*z* 161 (M^+). NMR ($CDCl_3$): δ_H 3.40 (2 H, t), 3.29 (3 H, s), 2.69 (4 H, t), 2.61 (2 H, t), 2.50 (4 H, t) and 1.41 (4 H, br); δ_C 71.0, 58.3, 57.8, 53.5 and 39.6.

Precautions in the Handling of Perchlorates.—Although no problems were encountered during the course of this project, attention should be drawn to the potentially explosive nature of perchlorates as described in ref. 17.

'2 + 2' *Cyclisation of* N,N-*Bis*(2-*aminoethyl*)-2-*methoxyethylamine with* 2,6-*Diacetylpyridine in the Presence of Barium*(II) *Perchlorate*.—A solution of *N*,*N*-bis(2-aminoethyl)-2-methoxyethylamine (2.5 mmol) in methanol (25 cm^3) was added dropwise to a refluxing solution of 2,6-diacetylpyridine (2.5 mmol) and barium(II) perchlorate (1.25 mmol) in methanol (50 cm^3). After heating at reflux temperature for 3 h, the reaction mixture was allowed to cool to room temperature resulting in the precipitation of the product. Recrystallisation from methanol gave beige crystals of $[BaL][ClO_4]_2$ in 21% yield (Found: C, 42.15; H, 5.10; Cl, 7.95; N, 12.00. $C_{32}H_{48}BaCl_2N_8O_{10}$ requires C, 42.10; H, 5.30; Cl, 7.75; N, 12.25%). IR (KBr disc): $\nu_{C=N}$ 1629 cm^{-1}. Mass spectrum (positive-ion FAB), *m*/*z* 814 $\{[BaL^1(ClO_4)]^+\}$. ^{13}C NMR (CD_3CN): δ 169.3, 154.9, 142.1, 125.7, 70.8, 60.4, 57.3, 55.5, 52.7 and 14.1.

Transmetallation of $[BaL][ClO_4]_2$ *with Copper*(II) *Perchlorate*.—A methanolic solution (20 cm^3) of copper(II) perchlorate hexahydrate (1 mmol) was added dropwise to a refluxing solution of the barium macrocyclic complex (0.5 mmol) in methanol (30 cm^3). After heating at reflux temperature for 1 h the resulting suspension was filtered hot to remove the pure product, $[Cu_2L][ClO_4]_4$, as a dark green powder in 72% yield (Found: C, 34.85; H, 4.30; Cl, 12.90; N, 9.75. $C_{32}H_{48}Cl_4Cu_2N_8O_{18}$ requires C, 34.90; H, 4.40; Cl, 12.85; N, 10.15%). IR (KBr disc): $\nu_{C=N}$ 1651 cm^{-1}. Mass spectrum (positive-ion FAB), *m*/*z* 1001 $\{[Cu_2L(ClO_4)_3]^+\}$.

X-Ray Structure Determinations.—The crystal parameters and the methods of data collection, solution and refinement for the X-ray crystal structure determinations are summarised in Table 1. Atomic coordinates with estimated standard deviations are given in Tables 2 and 3. Complex scattering factors were taken from ref. 18*b* and from the program package SHELXTL.[18c] Additional material available from the Cambridge Crystallographic Data centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

A useful synthon for the introduction of an ethylamine group into a molecule is the three-membered heterocycle *N*-(toluene-*p*-sulfonyl)aziridine (*N*-tosylaziridine).[19–21] Murase *et al.*[22,23] have reported that the addition of *N*-tosylaziridine to 1,4,8,11-tetraazacyclotetradecane (cyclam) followed by detosylation with hydrobromic–acetic acid yielded the tetra(2-aminoethyl) pendant-armed derivative. Variations on this procedure have allowed not only the addition of pendant arms onto other

Table 1 Summary of crystallographic data[a]

(*a*) Crystal parameters		
Formula	$C_{32}H_{48}BaCl_2N_8O_{10}$	$C_{32}H_{48}Cl_4Cu_2N_8O_{18}$
M_r	913.02	1101.6
Crystal dimensions/mm	0.40 × 0.25 × 0.15	0.20 × 0.20 × 0.15
Crystal appearance	Pale yellow rectangular prism	Red transparent prisms
Unit cell:		
a/Å	27.494(20)	14.807(6)
b/Å	14.120(13)	9.558(4)
c/Å	21.024(14)	17.432(8)
β/°	91.68(57)	113.89(5)
U/Å^3	8159(11)	2256(3)
Space group	$P2/n$, no. 13	$P2_1/c$
Z, D_c/g cm^{-3}	8, 1.487	2, 1.622
μ/cm^{-1}	11.63	12.61
F(000)	3711.44	1131.78
(*b*) Data collection		
Diffractometer	Nicolet R3 4-circle	Siemens R3m/V
2θ range/°	3.5 ⩽ 2θ ⩽ 50.0	4.0 ⩽ 2θ ⩽ 50.0
h,k,l ranges	0–33, 0–17, −26 to 26	−17 to 16, 0–11, 0–20
No. unique reflections observed (measured)	2440 (14 292)	2003 (3990)
R_{int}	0.0604	0.0402
Absorption correction	9 ψ-scans	Empirical[18a]
Min., max. transmission coefficients	0.398, 0.436	0.0826, 0.1309
(*c*) Solution and refinement		
No. parameters refined	444	281
R	0.0807	0.0774
R' (g[b]), R_g	0.0721, 0.0005, 0.0798	Unit weights 0.0802
Maximum δ/σ	0.040	0.023
Data to parameter ratio	5.5:1	7.1:1
Largest difference peak/e Å^{-3}	0.88	1.38
Largest difference hole/e Å^{-3}	−1.01	−0.56
ClO_4 treatment	Ordered, constrained T_d	Each disordered (50:50%) about common Cl; constrained geometry
Anisotropy	Ba and Cl only	All ordered non-H

[a] Details in common: crystal system monoclinic; graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å); ω-scan mode; criterion for observation, $|F_o| > 6\sigma(F_o)$; Lorentz and polarization corrections applied; solution by Patterson synthesis; H-atom treatment riding mode. [b] A weighting scheme of the form $w^{-1} = \sigma^2(F) + g(F)^2$ was used, $R = \Sigma\Delta/\Sigma(F_o)$, $R' = \Sigma(w^{\frac{1}{2}}\Delta)/\Sigma(w^{\frac{1}{2}}F_o)$, $R_g = [\Sigma(w\Delta^2)/\Sigma(wF_o^2)]^{\frac{1}{2}}$ where $\Delta = |(F_o - F_c)|$.

macrocycles[24–27] but have also been of utility in the assembly of precursors for actual macrocyclic and macrobicyclic polyamine synthesis.[15,28–31] Thus the '2 + 1' addition of *N*-tosylaziridine to a primary amine followed by detosylation appeared to be a promising and versatile method for the synthesis of *N*,*N*-bis(2-aminoethyl)alkylamines.

N-(Toluene-*p*-sulfonyl)aziridine was prepared in good yield by two different synthetic routes.[14,15] The synthesis of 2-methoxyethyl-*N*,*N*-bis(2-toluene-*p*-sulfonylaminoethyl)amine *via* the addition of 2 equivalents of *N*-tosylaziridine to 1 equivalent of the corresponding primary alkylamine was readily effected by stirring the reactants together in acetonitrile at room temperature. The product was isolated direct from the reaction mixtures as a white crystalline solid in excellent yields (*ca.* 90%). Changes in the 3200 to 3400 cm^{-1} region of the IR spectrum indicated that addition of *N*-tosylaziridine to the primary alkylamines with concomitant ring opening had occurred. The two characteristic primary amine bands were replaced by a single absorption assigned to the sulfonamide N–H bond. The unsymmetric and symmetric stretching modes of the sulfone groups gave rise to two intense peaks around 1320 and 1160 cm^{-1}. The characterisation of the products was supported by elemental analysis, ^{13}C and ^1H NMR spectroscopy.

N,*N*-Bis(2-aminoethyl)-2-methoxyethylamine was prepared by detosylation of 2-methoxyethyl-*N*,*N*-bis(2-toluene-*p*-sulfonylaminoethyl)amine by reductive detosylation with sodium dihydronaphthyide generated in tetrahydrofuran[16] and was isolated as a viscous, hygroscopic oil which was purified by vacuum distillation in an inert atmosphere. The IR spectrum contained two peaks at around 3370 and 3290 cm^{-1} corresponding to the unsymmetric and symmetric primary amine NH_2 stretching frequencies with no bands attributable to the presence of sulfonamide groups. The nature of the product was confirmed by mass spectrometry and NMR spectroscopy.

Whilst copper(II) ions did not act as templates for the '2 + 2' cyclocondensation of *N*,*N*-bis(2-aminoethyl)-2-methoxyethylamine and 2,6-diacetylpyridine, the larger and less stereochemically demanding barium(II) ion was found to be successful. This reaction resulted in the formation of the mononuclear complex of the 24-membered macrocycle L (Scheme 1) in 21% yield.

In accordance with the proposed characterisation, the IR spectrum of $[BaL][ClO_4]_2$ did not contain any bands attributable to the presence of carbonyl or primary amine groups. A single absorption at the imino C=N stretching frequency of 1629 cm^{-1} indicated that cyclocondensation had occurred. The '2 + 2' nature of the macrocyclic Schiff-base complex was confirmed by positive-ion FAB mass spectrometry. The stepwise loss of the two perchlorate anions from the parent molecule accounted for the most intense mass spectral peaks at m/z 814 and 715. Vapour diffusion of diethyl ether into a solution of $[BaL][ClO_4]_2$ in acetonitrile resulted in the formation of crystals suitable for an X-ray crystallographic study. The molecular structure of the cation is shown in Fig. 2.

The asymmetric unit consists of two crystallographically independent molecules of the barium macrocyclic complex, and four perchlorate anions. An analytical comparison of the two independent molecules reveals that although as tabulated they

Table 2 Atomic coordinates ($\times 10^4$) for $[BaL][ClO_4]_2$

Atom	x	y	z	Atom	x	y	z
Ba(1)	4112(1)	2757(2)	177(1)	C(12)	5328(13)	4122(26)	507(17)
Ba(1A)	6454(1)	1085(2)	5002(1)	C(13)	4479(11)	1615(24)	−1303(16)
O(1)	5081(8)	3361(15)	131(10)	C(14)	3934(11)	1578(25)	−1517(15)
O(2)	4305(8)	751(16)	264(10)	C(15)	3186(12)	2123(26)	−1130(16)
O(1A)	5935(8)	−630(16)	4824(11)	C(16)	2943(14)	1842(27)	−1775(17)
O(2A)	7426(10)	469(19)	5010(12)	C(17)	2896(10)	2485(19)	−615(13)
Cl(1)	3941(1)	3238(1)	3645(1)	C(18)	2415(12)	2813(27)	−762(18)
Cl(2)	6466(1)	1765(4)	8404(1)	C(19)	2166(16)	3223(30)	−246(19)
Cl(3)	3881(1)	3535(1)	6810(1)	C(20)	2329(13)	3256(26)	374(17)
Cl(4)	6334(1)	2000(1)	1516(1)	C(21)	2813(13)	2844(29)	452(17)
O(3)	4207(6)	4099(7)	3620(8)	C(22)	3039(11)	2748(26)	1118(15)
O(4)	3828(6)	3037(12)	4287(3)	C(23)	2762(15)	3259(29)	1668(18)
O(5)	4225(5)	2489(8)	3399(8)	C(24)	3644(13)	2082(29)	1851(16)
O(6)	3502(3)	3328(13)	3275(7)	C(25)	4105(12)	1531(25)	1777(16)
O(7)	6106(1)	2286(3)	8055(2)	C(26)	4810(13)	1160(26)	1188(16)
O(8)	6472(5)	814(5)	8183(2)	C(27)	4608(13)	365(26)	785(16)
O(9)	6358(2)	1777(3)	9061(1)	C(28)	3974(12)	59(25)	−65(16)
O(10)	6930(1)	2184(11)	8318(3)	C(29)	4790(11)	2684(24)	1719(15)
O(11)	4094(1)	4419(2)	6985(2)	C(30)	4525(13)	3599(25)	1873(16)
O(12)	4178(4)	2786(2)	7054(7)	C(31)	3982(12)	4668(26)	1443(17)
O(13)	3845(6)	3468(6)	6136(1)	C(32)	3954(15)	5162(31)	2076(18)
O(14)	3410(3)	3468(6)	7066(7)	C(1A)	5426(11)	2242(26)	5854(15)
O(15)	6057(7)	2514(13)	1960(8)	C(2A)	5138(13)	3056(26)	5994(19)
O(16)	6121(7)	2109(16)	896(4)	C(3A)	5017(14)	3641(31)	5539(20)
O(17)	6339(8)	1025(4)	1684(10)	C(4A)	5124(13)	3471(26)	4904(19)
O(18)	6818(3)	2353(15)	1524(10)	C(5A)	5413(12)	2697(27)	4740(16)
N(1)	3730(8)	4661(17)	316(11)	C(6A)	5529(13)	2461(27)	4070(18)
N(2)	3980(9)	4134(18)	−879(11)	C(7A)	5443(13)	3201(25)	3562(16)
N(3)	4652(8)	2536(18)	−1002(11)	C(8A)	5808(14)	1363(25)	3319(16)
N(4)	3616(9)	1975(18)	−1009(12)	C(9A)	6031(13)	324(26)	3359(17)
N(5)	3086(8)	2507(17)	−19(11)	C(10A)	6453(16)	−890(30)	3963(21)
N(6)	3425(9)	2253(21)	1170(12)	C(11A)	6035(14)	−1245(29)	4300(17)
N(7)	4497(9)	1921(18)	1396(12)	C(12A)	5499(15)	−907(29)	5155(18)
N(8)	4222(10)	3984(21)	1336(12)	C(13A)	6910(14)	373(27)	3440(18)
N(1A)	5570(9)	2120(19)	5204(12)	C(14A)	6968(13)	1361(23)	3300(15)
N(2A)	5714(10)	1634(20)	3995(12)	C(15A)	6844(12)	2899(26)	3828(16)
N(3A)	6448(10)	129(20)	3734(13)	C(16A)	6990(13)	3452(26)	3237(16)
N(4A)	6864(8)	2013(18)	3841(11)	C(17A)	6711(11)	3458(22)	4369(14)
N(5A)	6776(9)	3052(18)	4942(11)	C(18A)	6506(13)	4321(26)	4331(18)
N(6A)	6827(9)	2159(20)	6094(12)	C(19A)	6331(11)	4839(23)	4825(14)
N(7A)	6859(9)	42(18)	6141(12)	C(20A)	6444(10)	4426(21)	5439(14)
N(8A)	5881(10)	866(21)	6130(13)	C(21A)	6678(11)	3540(22)	5504(15)
C(1)	3643(11)	5001(23)	911(15)	C(22A)	6763(11)	3010(24)	6105(16)
C(2)	3332(14)	5748(28)	979(19)	C(23A)	6758(15)	3651(30)	6705(18)
C(3)	3054(13)	6134(28)	497(15)	C(24A)	6912(12)	1653(19)	6700(13)
C(4)	3119(12)	5767(24)	−112(16)	C(25A)	7115(11)	650(21)	6619(14)
C(5)	3491(11)	5015(21)	−177(14)	C(26A)	7189(11)	−633(23)	5831(15)
C(6)	3578(11)	4688(23)	−836(14)	C(27A)	7590(12)	−152(24)	5476(15)
C(7)	3294(12)	4989(26)	−1427(16)	C(28A)	7781(14)	1007(29)	4722(17)
C(8)	4159(10)	3892(22)	−1489(13)	C(29A)	6421(12)	−444(25)	6366(16)
C(9)	4650(11)	3335(23)	−1425(15)	C(30A)	6028(14)	219(28)	6618(17)
C(10)	5123(11)	2289(26)	−767(15)	C(31A)	5573(11)	1510(23)	6308(15)
C(11)	5403(11)	3074(23)	−396(14)	C(32A)	5286(13)	1553(27)	6945(16)

are enantiomers they are otherwise almost identical [root mean square (r.m.s.) deviation 0.222 Å, maximum deviation 0.76 Å for C(23)–C(23A)]. The macrocycle adopts a conformation with approximate C_2 symmetry, defining a chiral molecular cleft between the pyridine diimine units. The chiral nature of the cleft extends to the different pairs of enantiomorphic conformations of the five-membered chelate rings formed by the pendant arms [N(3)–C(10)–C(11)–O(1) and N(7)–C(26)–C(27)–O(2)], resulting in the presence of both the Λ(δδ) and Δ(λλ) stereoisomers (Fig. 3) within the unit cell.

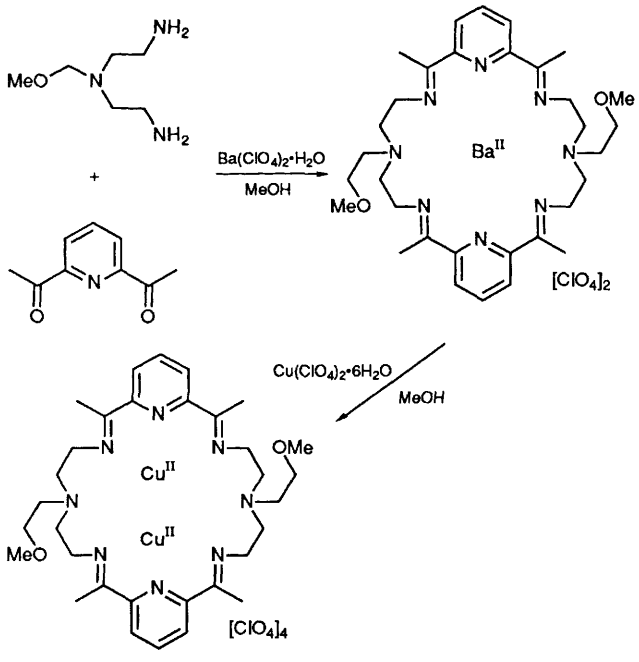
All ten donor atoms of the ligand interact with the barium ion, with bond lengths in the range 2.80–3.02 Å (Table 4). The pyridyl fragments are planar (r.m.s. deviations are 0.023 and 0.022 Å) and mutually inclined at 24°. The imine bonds are twisted out of the planes of the pyridyl rings, presumably to accommodate the interaction of the imino nitrogens with the metal ion. The space-filling diagram of the cation (Fig. 4) clearly shows the cleft-like structure of the molecule and the extent to which the barium ion is encapsulated within the macrocyclic ligand.

The ^1H NMR spectrum of $[BaL][ClO_4]_2$ indicates that the macrocyclic ligand L is maintained in a conformationally rigid state in solution. Rotation about the ring CH_2CH_2 groups is restricted and no inversion occurs at the tertiary amine nitrogen atoms. As a result the two hydrogen atoms constituting each macrocyclic methylene group are magnetically inequivalent. Thus the CH_2 group adjacent to the pendant-arm substituted amino nitrogens gives rise to two signals at δ_H 3.37 ($H_{g\beta}$) and 2.68 ($H_{g\alpha}$). The difference in the multiplet structures of these two resonances arises because the magnitude of the coupling constant $^3J(H_gH_f)$ with their vicinal counterparts $H_{f\alpha}$ and $H_{f\beta}$ is dependent on the dihedral angle between the two C–H bonds.[32,34] The hydrogen atom at δ_H 2.68 ($H_{g\alpha}$) is coupled strongly with the inequivalent geminal proton $H_{g\beta}$ [$^2J(H_{g\alpha}H_{g\beta})$

Table 3 Atomic coordinates ($\times 10^4$) for $[Cu_2L][ClO_4]_4$*

Atom	x	y	z
Cu(1)	1852(1)	1251(2)	817(1)
N(1)	2701(6)	1389(12)	1999(6)
N(2)	1370(6)	−430(10)	1292(5)
N(3)	1284(6)	1548(10)	−459(5)
N(4)	2457(8)	3058(11)	832(7)
C(1)	3261(9)	2520(15)	2243(8)
C(2)	3898(10)	2660(18)	3098(9)
C(3)	3884(10)	1607(20)	3618(8)
C(4)	3287(10)	466(17)	3356(8)
C(5)	2661(8)	366(15)	2498(7)
C(6)	1916(8)	−712(13)	2078(7)
C(7)	1839(10)	−1960(15)	2564(8)
C(8)	547(7)	−1372(13)	827(7)
C(9)	339(8)	931(14)	−1009(7)
C(10)	1250(10)	3125(14)	−569(8)
C(11)	2175(9)	3788(16)	48(8)
C(12)	3123(10)	3481(14)	1555(9)
C(13)	3679(12)	4836(16)	1715(11)
C(14)	2073(9)	991(16)	−720(7)
C(15)	2326(9)	−481(15)	−489(8)
C(16)	3118(15)	−1752(18)	732(12)
O(1)	2618(7)	−611(11)	391(6)
Cl(1)	395(3)	3590(4)	1529(2)
O(2)	347(14)	2455(14)	1009(10)
O(3)	−543(7)	3864(21)	1501(15)
O(4)	1042(15)	3277(22)	2351(5)
O(5)	739(17)	4766(13)	1252(14)
O(2A)	559(14)	3010(17)	861(8)
O(3A)	−579(6)	4059(20)	1244(11)
O(4A)	562(14)	2572(14)	2147(9)
O(5A)	1040(12)	4710(14)	1866(12)
Cl(2)	5245(3)	2059(5)	1117(3)
O(6)	4430(10)	2857(18)	612(9)
O(7)	5959(11)	2091(28)	785(12)
O(8)	4948(17)	680(10)	1143(14)
O(9)	5641(14)	2613(19)	1928(5)
O(6A)	5423(21)	3039(20)	601(16)
O(7A)	4266(6)	1607(24)	739(18)
O(8A)	5416(19)	2672(24)	1891(7)
O(9A)	5877(14)	917(16)	1239(13)

* All oxygen atoms, except O(1), are introduced with occupancy factor 0.5.



Scheme 1

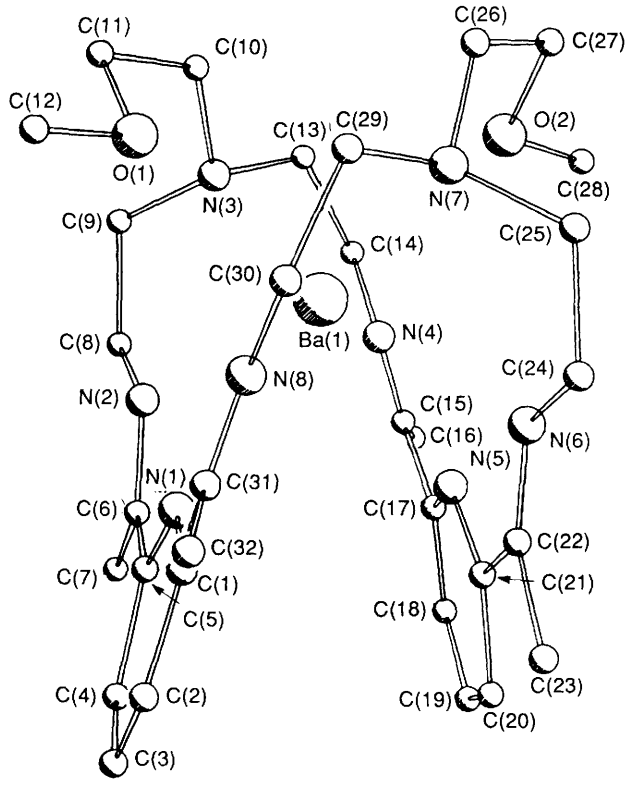


Fig. 2 The molecular structure of the $[BaL]^{2+}$ cation

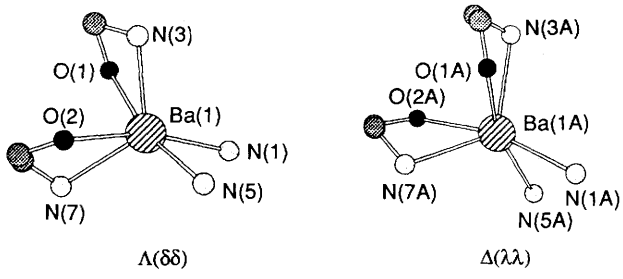


Fig. 3 Representation of the two enantiomeric forms of $[BaL]^{2+}$

Table 4 Barium–donor bond lengths in $[BaL][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

	Molecule 1	Molecule 2
Ba(1)–O(1)	2.800(21)	2.831(23)
Ba(1)–N(1)	2.904(25)	2.878(26)
Ba(1)–N(3)	2.943(24)	2.987(27)
Ba(1)–N(5)	2.861(23)	2.919(25)
Ba(1)–N(7)	2.988(25)	2.999(25)
Ba(1)–O(2)	2.886(22)	2.812(27)
Ba(1)–N(2)	2.964(25)	2.993(26)
Ba(1)–N(4)	3.016(25)	3.017(24)
Ba(1)–N(6)	2.945(27)	2.912(25)
Ba(1)–N(8)	2.998(27)	2.903(29)

13.5 Hz] resulting in the gross doublet character of the signal. The additional splitting originates from spin interactions with the two vicinal hydrogen atoms $H_{f\alpha}$ and $H_{f\beta}$ [$^3J(H_{g\alpha}H_{f\alpha})$ and $^3J(H_{g\alpha}H_{f\beta}) = 1$ and 4 Hz]. Similar considerations account for the coupling patterns of the $H_{g\beta}$ resonance at δ_H 3.37, although matters are slightly complicated by the occurrence of a second-order feature.[35]

The signals corresponding to the remaining aliphatic protons of the macrocyclic ring ($H_{f\alpha}$ at *ca.* δ_H 3.68 and $H_{f\beta}$ at *ca.* δ_H 3.52)

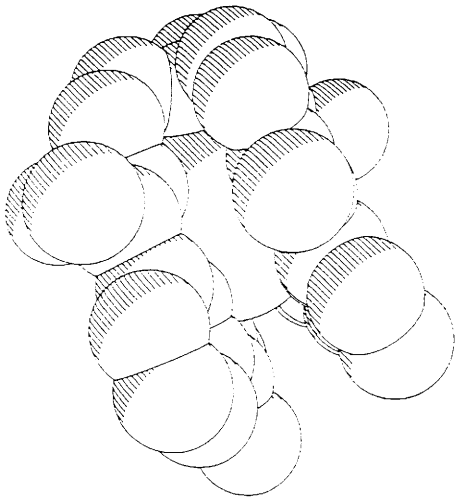
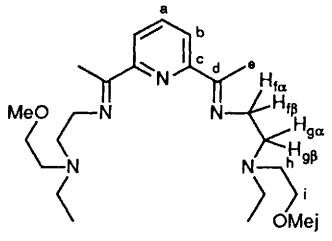
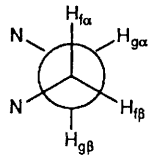


Fig. 4 Space-filling diagram of the $[BaL]^{2+}$ cation

Table 5 Proton and ^{13}C NMR assignments for the 24-membered bibracchial macrocyclic complex $[BaL][ClO_4]_2$





Atom	δ_C (63 MHz)	δ_H (250 MHz)	J/Hz
a	141.2	7.95 (t, 2 H)	$^3J(H_aH_b)$ 8
b	125.7	7.67 (d, 4 H)	
c	154.9	—	
d	169.3	—	
e	14.1	2.17 (s, 12 H)	$^3J(H_{g\alpha}H_{f\alpha})$ 1 or 4
fα	57.3	*ca.* 3.68 (br t, 4 H)	$^3J(H_{g\alpha}H_{f\beta})$ 1 or 4
fβ		*ca.* 3.52 (br dd, 4 H)	$^2J((H_{g\alpha}H_{g\beta})$ 13.5
gα	55.5	2.68 (ddd, 4 H)	$^3J(H_{g\beta}H_{f\alpha})$ 13.5
gβ		3.37 (td, 4 H)	$^3J(H_{g\beta}H_{f\beta})$ 6
h	52.7	2.87 (t, 4 H)	$^3J(H_hH_i)$ 5.5
i	70.8	3.81 (t, 4 H)	
j	60.4	3.29 (s, 6 H)	

are poorly resolved, although the expected line shape (*i.e.* a triplet and a doublet respectively) may be clearly identified. When recorded at higher field (400 instead of 250 MHz), changes in this region of the spectrum indicate that the broadened nature of the signals originates from second-order effects.

The two resonances appearing in the spectrum at δ_H 2.87 and 3.81 are assigned to the pendant-arm hydrogen atoms H_h and H_i respectively. The simple triplet nature of these signals [$^3J(H_hH_i)$ 5.5 Hz] shows that the pendant arms have a greater degree of rotational freedom as compared to the ethyl groups of the macrocyclic ring. The ^1H and ^{13}C NMR data for $[BaL][ClO_4]_2$ are summarised in Table 5.

The dinucleating capability of the 24-membered bibracchial macrocycle L was readily demonstrated by transmetallation of the mononuclear barium complex with copper(II). When a refluxing methanolic solution of the barium complex was treated with copper(II) perchlorate hexahydrate the complex $[Cu_2L][ClO_4]_4$ was obtained as a dark green powder in 72% yield (Scheme 1).

The IR spectra of the starting material and the product were very similar, indicating that the macrocycle remained intact during the transmetallation procedure. The positive-ion FAB mass spectrum was consistent with the proposed characterisation, peaks at m/z 1001, 902 and 803 corresponding to cationic species generated by the sequential loss of perchlorate ions from the parent molecule.

Crystals suitable for an X-ray structure determination were obtained by vapour diffusion of diethyl ether into a solution of $[Cu_2L][ClO_4]_4$ in acetonitrile. In the crystalline state the bibracchial macrocycle L of the dicopper(II) complex adopts an open conformation (Fig. 5), in contrast to the folded cleft-like structure found in the barium(II) complex. The two copper(II) ions are bound within the pyridine diimine head units of the macrocycle, in identical environments related by a crystallographic inversion centre. The metal ions are separated by a Cu ··· Cu distance of 5.56 Å, with the donor atoms constituting two isolated co-ordination sites. In accordance with this observation the effective magnetic moment μ_{eff} of $[Cu_2L][ClO_4]_4$ at room temperature is 1.73 per copper, indicating the absence of any spin interaction within the copper(II) pair.

The co-ordination geometry around each copper(II) ion may be described as severely distorted square-based pyramidal. The four basal donors are provided by the nitrogen atoms of the macrocyclic ring, with copper–nitrogen bond lengths ranging from 1.93 Å with the pyridine nitrogen N(1) to 2.06 Å with one of the imino nitrogens N(2). The apical site is occupied by the ethereal oxygen donor O(1) of the pendant arm with Cu–O(1) 2.38 Å. The steric restrictions placed on the donor atoms by the ligand constitution account for the significant deviations that occur from the ideal square-based pyramidal geometry. It is apparent from Fig. 5 that the tertiary-amino nitrogen atom N(3) is distorted from the basal plane in accordance with the desire of the pendant arm ethereal oxygen O(1) to attain an orthogonal, apical co-ordination mode. In addition to the interactions of each copper(II) ion with the macrocyclic ligand L, there is a long range, electrostatic interaction of 2.65 Å with an oxygen atom O(2) of a perchlorate ion. The bond lengths and bond angles describing the co-ordination geometry around the copper(II) ions are presented in Table 6.

Precisely why the macrocycle in $[Cu_2L][ClO_4]_4$ opens out destroying the molecular cleft is unclear particularly as the cleft is retained in the related disilver(I) complexes;[4] the process is however not unprecedented.[1] It is possible that the higher charge of the copper(II) ions leads to an enhanced electrostatic repulsion between the encapsulated metal cations and that this, together with the favoured co-ordination opportunity offered by the planar 'head' units, provides the stimulus for the observed conformational change. The opening of the cleft is associated with changes in the torsion angles for consecutive bonds between the imino nitrogen atoms of the 'lateral' units, from $T(trans),G^+(gauche),G^+,G^-,G^-,T$ in $[BaL][ClO_4]_2$ to G^-,T,G^-,T,G^-,T in $[Cu_2L][ClO_4]_4$ (Table 7).

The UV/VIS spectrum of $[Cu_2L][ClO_4]_4$ at wavelengths lower than 350 nm is dominated by the intense π to π* transition of the organic ligand. d–d Transitions give rise to a band with λ_{max} at 627 nm (ε = 283 dm^3 mol^{-1} cm^{-1}) containing a shoulder at 681 nm.

In view of the electrochemically stable nature of the barium(II) ions used in the template synthesis of L, the possibility of introducing copper(I) ions *via* a transmetallation reaction was investigated. Employing acetonitrile as a solvent under anaerobic and moisture-free conditions, a colourless solution of $[Cu(MeCN)_4]BF_4$ was added to a colourless solution of $[BaL][ClO_4]_2$ resulting in the immediate appearance of an intense brown-orange colouration. A similar feature has been observed with a number of copper(I) complexes of ligands containing pyridine diimine units,[36–39] indicating that transmetallation had been achieved. After cooling to 238 K, dioxygen was bubbled through the solution for 15 min without any discernible changes occurring. However, as the solution

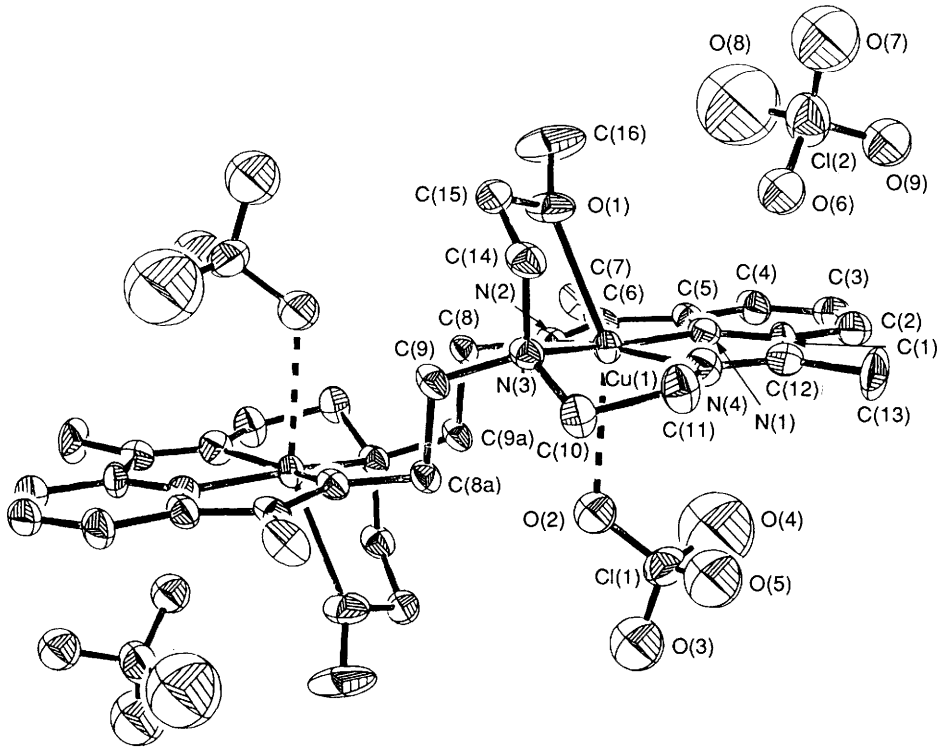


Fig. 5 The molecular structure of $[Cu_2L][ClO_4]_4$

Table 6 The co-ordination environments of the copper atoms in $[Cu_2L][ClO_4]_4$ with e.s.d.s in parentheses

Bond lengths/Å		Bond angles/° at Cu				
Cu(1)–N(1)	1.935(8)					
Cu(1)–N(2)	2.063(10)	78.9(4)				
Cu(1)–N(3)	2.055(9)	161.5(4)	119.0(3)			
Cu(1)–N(4)	1.941(11)	80.1(5)	157.0(4)	82.9(4)		
Cu(1)–O(1)	2.385(12)	101.4(4)	80.2(4)	78.7(4)	113.1(5)	
Cu(1)–O(2)	2.647	93.0	80.9	94.6	91.1	153.5
		N(1)	N(2)	N(3)	N(4)	O(1)

Table 7 Torsion angles (°) for the consecutive bonds between the imino nitrogen atoms in the 'lateral' units of $[BaL][ClO_4]_2$ and $[Cu_2L][ClO_4]_4$

	$[BaL][ClO_4]_2$			
	Molecule 1	Molecule 2	$[Cu_2L][ClO_4]_4$	
N(2)–C(8)	175	−180	N(2′)–C(8′)	−84
C(8)–C(9)	51	−56	C(8′)–C(9)	−167
C(9)–N(3)	87	−81	C(9)–N(3)	−63
N(3)–C(13)	−67	62	N(3)–C(10)	175
C(13)–C(14)	−45	50	C(10)–C(11)	−39
C(14)–N(4)	170	−173	C(11)–N(4)	−167
N(6)–C(24)	−179	−165		
C(24)–C(25)	59	−49		
C(25)–N(7)	77	−83		
N(7)–C(29)	−65	58		
C(29)–C(30)	−48	59		
C(30)–N(8)	176	−175		

was allowed to warm to room temperature a dark green colouration was observed to develop. This could not be removed either by application of a vacuum or by purging the solution with nitrogen, thus demonstrating that the copper(I) species had been irreversibly oxidised. Addition of diethyl ether resulted in the precipitation of a dark green solid which could not be characterised satisfactorily. The conformational flexibility of the macrocyclic ligand, leading to the loss of the molecular cleft on transmetallation, has been demonstrated in the above crystal structures. Given the open nature of the dicopper complex it is likely that any dicopper(II)–peroxo species formed within the macrocyclic cavity would not be prevented from undergoing intermolecular autoxidation reactions. Thus it appears that a prospective room-temperature synthetic dicopper dioxygen carrier requires the incorporation into its ligand architecture of a more rigidly defined cleft or cavity sterically to protect the binding site.

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