

Attempted Functionalisation of a Mononuclear Barium Complex of a 24-Membered Bibracchial Tetraimine Schiff-base Macrocyclic derived from Tris(2-aminoethyl)amine using Salicylaldehyde†

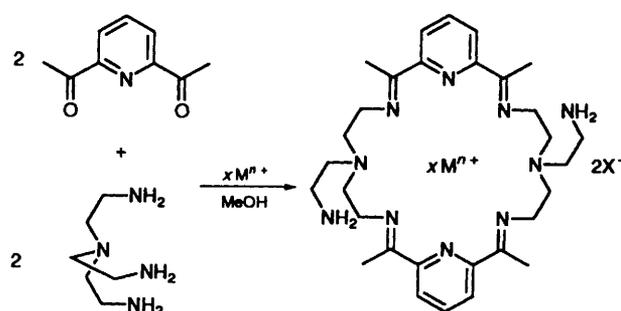
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Functionalisation of a mononuclear barium complex of a 24-membered bibracchial tetraimine Schiff-base macrocycle (L^1) derived from the barium-templated cyclocondensation of 2,6-diacetylpyridine and tris(2-aminoethyl)amine was attempted using salicylaldehyde. The reaction leads to the isolation of the tripodal ligand tris[2-(salicylideneamino)ethyl]amine (L^2) and the complex $BaL^2_2(ClO_4)_2$. The crystal structures of the parent macrocyclic complex, $[BaL^1][ClO_4]_2$ [monoclinic, space group $P2_1/c$ (no. 14), $a = 11.755(7)$, $b = 21.733(17)$, $c = 15.621(15)$ Å, $\beta = 90.50(7)^\circ$, $Z = 4$], and $BaL^2_2(ClO_4)_2$ [monoclinic, space group $P2_1/c$ (C_{2h}^2 , no. 14), $a = 12.299(15)$, $b = 9.530(15)$, $c = 25.798(32)$ Å, $\beta = 108.679(9)^\circ$, $Z = 2$] have been determined.

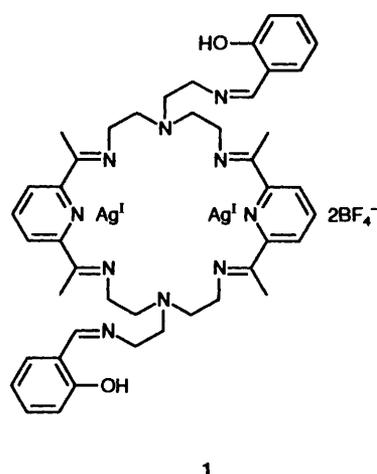
The cyclocondensation of tris(2-aminoethyl)amine, tren, and heterocyclic dialdehydes in a [2 + 3] molar ratio has given a range of Schiff-base cryptates.¹ The reaction of tren with 2,6-diacetylpyridine leads to an intractable product, but if barium(II)² or silver(I)³ templates are employed the isolated product is not a cryptate but the metal complex of a [2 + 2] macrocycle bearing two primary amine pendant arms (Scheme 1).^{2,3} Such complexes are of particular interest as the reactive nature of primary amino groups allows the possibility for further functionalisation of the pendant arms, and in the case of the dinuclear silver complexes this has been achieved *via* reaction with salicylaldehyde to give the macrocyclic complex 1. Transmetalation of 1 with copper(II) salts led to the isolation of a trinuclear copper(II) complex which was presented as a first generation model for the triangular copper(II) site in ascorbate oxidase.³ In order to facilitate the generation of low-oxidation-state metal complexes by transmetalation reactions a redox-inert metal is required and so we have investigated the interaction of $[BaL^1][ClO_4]_2$ and salicylaldehyde with a view to using the anticipated functionalised macrocyclic complex in transmetalation reactions.

Results and Discussion

The complex $[BaL^1][ClO_4]_2$ was prepared in 40% yield *via* the barium-templated [2 + 2] cyclocondensation of tren and 2,6-diacetylpyridine.² The non-macrobicyclic nature of this complex is evident from the IR spectrum in which the presence of unreacted primary amine groups is indicated by the appearance of two strong peaks at 3288 and 3333 cm^{-1} , assigned to the symmetric and unsymmetric NH_2 stretching modes. An intense absorption at 1627 cm^{-1} arises from the stretching vibration of the imino $C=N$ bonds. In addition the spectrum lacked any bands attributable to carbonyl groups. The product was further characterised by positive-ion FAB mass spectrometry and elemental analysis. The complex gave a base mass spectral peak at m/z 783, corresponding to a cation



Scheme 1 Metal-ion templated synthesis of the diprimary amine pendant-armed macrocyclic complexes $[BaL^1][ClO_4]_2$ and $[Ag_2L^1][ClO_4]_2$



generated *via* the loss of a single counter ion from the parent molecule.

Recrystallisation of $[BaL^1][ClO_4]_2$ from methanol afforded single crystals of $[BaL^1][ClO_4]_2 \cdot CH_3OH$ suitable for a crystal structure determination. The asymmetric unit consists of one molecule of the macrocyclic dication, two perchlorate anions, and a methanol solvent molecule. The methanol and one of the

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

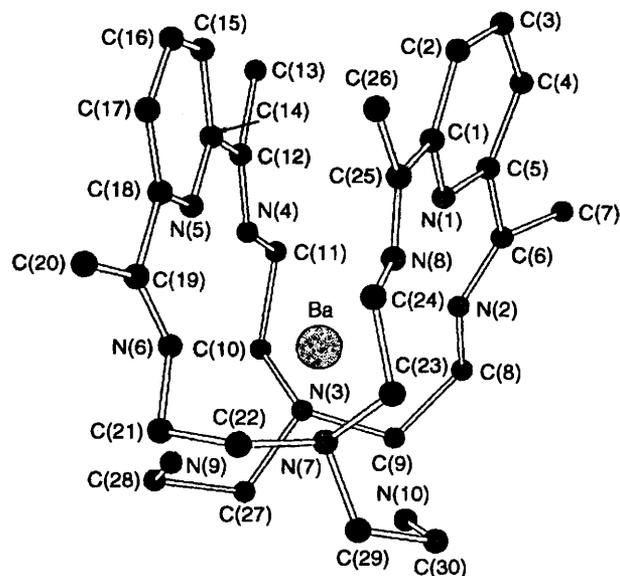
Table 1 Selected bond lengths (Å) and angles (°) for $[\text{BaL}^1][\text{ClO}_4]_2 \cdot \text{CH}_3\text{OH}$

Ba-N(1)	2.947(12)	Ba-N(2)	3.009(13)
Ba-N(3)	3.048(14)	Ba-N(4)	3.000(13)
Ba-N(5)	2.901(12)	Ba-N(6)	2.949(13)
Ba-N(8)	2.986(13)	Ba-N(9)	2.879(16)
Ba-N(10)	2.903(16)	Ba-N(7)	3.216(15)
N(1)-Ba-N(2)	54.2(3)	N(1)-Ba-N(3)	107.9(4)
N(2)-Ba-N(3)	57.6(4)	N(1)-Ba-N(4)	76.8(3)
N(2)-Ba-N(4)	67.3(3)	N(3)-Ba-N(4)	57.7(3)
N(1)-Ba-N(5)	79.8(3)	N(2)-Ba-N(5)	112.1(3)
N(3)-Ba-N(5)	107.1(3)	N(4)-Ba-N(5)	54.4(3)
N(1)-Ba-N(6)	116.6(3)	N(2)-Ba-N(6)	166.1(3)
N(3)-Ba-N(6)	124.5(4)	N(4)-Ba-N(6)	101.5(3)
N(5)-Ba-N(6)	54.2(3)	N(1)-Ba-N(8)	53.1(3)
N(2)-Ba-N(8)	102.3(4)	N(3)-Ba-N(8)	159.9(4)
N(4)-Ba-N(8)	116.4(3)	N(5)-Ba-N(8)	78.1(3)
N(6)-Ba-N(8)	74.7(4)	N(1)-Ba-N(9)	161.5(4)
N(2)-Ba-N(9)	119.1(4)	N(3)-Ba-N(9)	61.7(4)
N(4)-Ba-N(9)	84.7(4)	N(5)-Ba-N(9)	88.7(4)
N(6)-Ba-N(9)	65.9(4)	N(8)-Ba-N(9)	138.4(4)
N(1)-Ba-N(10)	115.0(4)	N(2)-Ba-N(10)	87.3(4)
N(3)-Ba-N(10)	81.2(4)	N(4)-Ba-N(10)	138.6(4)
N(5)-Ba-N(10)	160.5(4)	N(6)-Ba-N(10)	106.5(4)
N(8)-Ba-N(10)	100.2(4)	N(9)-Ba-N(10)	79.7(5)
Ba-N(1)-C(5)	123.2(9)	Ba-N(1)-C(1)	116.2(9)
Ba-N(2)-C(6)	124.1(10)	Ba-N(2)-C(8)	114.6(10)
Ba-N(3)-C(10)	117.1(10)	Ba-N(3)-C(9)	102.6(10)
Ba-N(3)-C(27)	105.4(10)	Ba-N(4)-C(11)	116.9(9)
Ba-N(4)-C(12)	110.6(10)	Ba-N(5)-C(18)	117.8(9)
Ba-N(5)-C(14)	112.1(9)	Ba-N(6)-C(21)	112.0(10)
Ba-N(6)-C(19)	123.2(10)	Ba-N(8)-C(25)	115.0(10)
Ba-N(9)-C(28)	117.9(12)	Ba-N(10)-C(30)	114.1(11)
Ba-N(8)-C(24)	118.1(9)		

perchlorate anions are disordered over two interpenetrating sites. The molecular structure of the complex cation (Fig. 1) is very similar to that of the $\text{Ba}(\text{ClO}_4)_2$ complex of the corresponding methoxyethyl pendant-armed macrocycle.⁴ The macrocycle adopts a folded, or cleft-like, conformation completely encapsulating the metal. Selected bond lengths and angles are given in Table 1 and atomic coordinates in Table 2. Similar donor atoms have similar bond lengths to the metal with the exception of the tertiary amine nitrogen atoms. Thus eight of the nitrogen atoms are co-ordinated to the metal with bond lengths in the range Ba-N, 2.879(16)–3.009(13) Å, with the remaining donors, N(3) and N(7), co-ordinated at 3.048(14) and 3.216(15) Å respectively. Bond lengths and angles within the macrocycle show no significant deviations from the values found in closely related compounds.²⁻⁴ Hydrogen bonds exist between the two approximately half-occupancy methanol hydroxyl groups and the perchlorate anions.

The complex is chiral due to the conformation of the five-membered chelate rings, Ba-N(3)-C(27)-C(28)-N(9) and Ba-N(7)-C(29)-C(30)-N(10), which can be distinguished as either δ or λ .⁵ Furthermore, the arrangement of the chelate rings around the metal may produce either one of a pair of distinct helical conformations, Λ or Δ . In the crystal structure both the $\Delta(\lambda\lambda)$ conformation and the enantiomeric $\Lambda(\delta\delta)$ conformation are found.

The pyridyl rings of the macrocycle [1: N(1), C(1), C(2), C(3), C(4) and C(5); 2: C(14), C(15), C(16), C(17), C(18) and N(5)] are planar [root-mean-square (r.m.s.) deviations 0.026 and 0.009 Å respectively] and mutually inclined at 14°. The imine bonds are twisted out of the planes of the pyridyl rings possibly as an effect of the metal interacting with the imine nitrogen lone pairs. One imine fragment, N(4), C(12), C(13), C(14), is almost coplanar with the adjoining pyridyl ring, 2, and twisted by just 5° relative to the plane of the diametrically opposed imine, N(8), C(25),

**Fig. 1** Molecular structure of the $[\text{BaL}^1]^{2+}$ cation

C(26), C(1). Since the planes of these two imine moieties lie only 3.5 Å apart it is likely that the conjugated π systems will be interacting.

A calculation of the energy levels of the two planar pyridyl diimine fragments indicates that the macrocycle conformation in $[\text{BaL}^1][\text{ClO}_4]_2$ provides a favourable overlap of the approximately parallel π systems (Fig. 2).^{*} A similar result was obtained for the $\text{Ba}(\text{ClO}_4)_2$ complex of the corresponding methoxyethyl pendant-armed macrocycle.⁹

Although the presence of the metal atoms has not been included in the calculations, which may significantly alter the energy levels, the fact that the structural motif of two overlapping, parallel, conjugated aromatic units is conserved not only in these complexes but also in related structures does suggest that an associative interaction is occurring. This proposal is further supported by the work of Gould *et al.*¹⁰ which shows not only that face-to-face stacking interactions of aromatic rings are energetically favourable for interplanar separations of 3.1–3.4 Å, but that the rings are frequently displaced from a 'plate-like' stacking arrangement. The average distances between 'overlapping' rings are defined by the perpendicular distances between the centroids of the pyridinyl-aromatic rings and the planes of the opposing pyridinyl-aromatic rings. These distances are respectively 3.49 and 3.43 Å in $[\text{BaL}^1][\text{ClO}_4]_2$ and the corresponding methoxyethyl pendant-armed macrocyclic complex.

The ¹H NMR spectrum of $[\text{BaL}^1][\text{ClO}_4]_2$ recorded at 250 MHz in CD₃CN shows a triplet (δ_{H} 8.02) and a doublet (δ_{H} 7.72) assigned to the *para* (H_a) and *meta* pyridyl (H_b) protons respectively [³ $J(\text{H}_a-\text{H}_b) = 8$ Hz] and there is only one resonance attributable to a methyl group [$\delta_{\text{H}}(\text{H}_c)$ 2.09]. The protons of the aliphatic region give rise to three multiplets at δ_{H} 3.49 (H_{ra} and H_{rb}), 3.03 (H_{ga}) and 2.61 (H_{gb}) as a result of the equivalence of all the macrocyclic ring CH₂CH₂ groups. The coupling patterns of H_{ga} and H_{gb} indicate that rotation about the C_r-C_g bond is restricted resulting in the magnetic inequivalence of the geminal hydrogen pairs. The unresolved nature of the δ_{H} 3.49 resonance stems from the close similarity of the H_{ra} and H_{rb} chemical shifts. The proposed coupling relationships have been corroborated by the ¹H-¹H two-

* All calculations were performed using the program HMO, version 1.1.⁶ Heteroatom parameters were taken from ref. 7 and the eigenvectors and eigenvalues were calculated by the Jacobi diagonalisation method.⁸

Table 2 Atomic coordinates ($\times 10^4$) for $[\text{BaL}^1][\text{ClO}_4]_2 \cdot \text{CH}_3\text{OH}$

Atom	x	y	z	Atom	x	y	z
Ba	2385(1)	1491(1)	1357(1)	C(9)	1256(19)	2759(7)	67(13)
C(S1)	5907(59)	888(39)	5444(37)	N(3)	1448(12)	2131(6)	-235(9)
O(S1)	6767	1220	5864	C(10)	475(14)	1839(9)	-670(11)
C(S2)	5996(83)	3913(49)	474(41)	C(11)	-329(14)	1486(7)	-90(10)
O(S2)	5629	4297	1135	N(4)	318(11)	1032(5)	415(8)
Cl(1)	6591(3)	2818(2)	4507(3)	C(12)	-175(13)	628(6)	838(9)
O(11)	6681(2)	3374(1)	4931(1)	C(13)	-1483(14)	526(8)	849(12)
O(12)	5483(5)	2609(4)	4548(7)	C(14)	502(13)	176(6)	1339(9)
O(13)	6890(8)	2896(4)	3661(4)	C(15)	-20(13)	-290(7)	1813(11)
O(14)	7308(1)	2394(1)	4887(1)	C(16)	667(15)	-706(7)	2231(12)
Cl(2A)	2684(11)	4418(6)	1642(9)	C(17)	1823(14)	-680(8)	2166(12)
O(21A)	2665	4586	2501	C(18)	2249(13)	-196(7)	1681(9)
O(22A)	1575	4337	1343	N(5)	1621(9)	222(5)	1288(7)
O(23A)	3285	3870	1552	C(19)	3548(14)	-122(6)	1578(9)
O(24A)	3212	4879	1170	C(20)	4288(14)	-651(8)	1877(15)
Cl(2B)	2347(8)	4231(4)	1613(7)	N(6)	3864(10)	397(6)	1330(9)
O(21B)	2838	4646	2185	C(21)	5072(14)	562(9)	1260(12)
O(22B)	1394	4496	1230	C(22)	5468(14)	859(8)	2073(11)
O(23B)	2025	3701	2051	N(7)	4819(10)	1402(5)	2306(9)
O(24B)	3133	4077	987	C(23)	4611(15)	1414(8)	3242(11)
N(1)	606(10)	1516(5)	2674(8)	C(24)	3767(13)	932(9)	3501(11)
C(1)	642(12)	1069(7)	3250(9)	N(8)	2625(11)	1104(6)	3184(8)
C(2)	-326(16)	866(9)	3685(11)	C(25)	1785(13)	827(7)	3481(9)
C(3)	-1335(19)	1175(11)	3552(15)	C(26)	1818(15)	262(9)	4082(12)
C(4)	-1366(14)	1670(9)	3022(14)	C(27)	2416(18)	2147(10)	-853(11)
C(5)	-393(12)	1813(7)	2570(9)	C(28)	2958(18)	1529(11)	-1043(13)
C(6)	-370(13)	2335(7)	1924(10)	N(9)	3529(14)	1301(8)	-243(10)
C(7)	-1441(14)	2734(8)	1854(13)	C(29)	5408(14)	1956(8)	2060(14)
N(2)	428(10)	2380(5)	1426(9)	C(30)	4748(16)	2558(8)	2052(13)
C(8)	394(18)	2842(8)	706(12)	N(10)	3884(15)	2554(7)	1347(12)

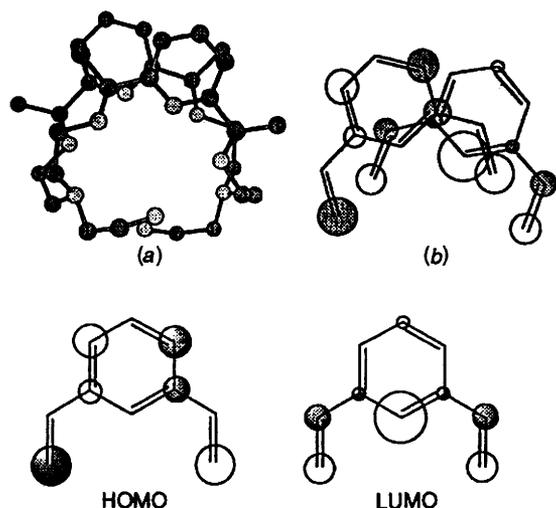
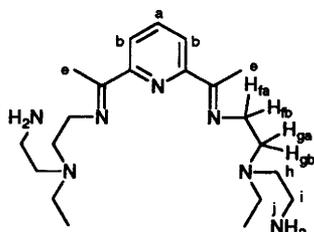


Fig. 2 (a) View perpendicular to the least-squares plane through the pyridyl rings and (b) overlap of the frontier orbitals of the pyridinyl diimine fragments in $[\text{BaL}^1][\text{ClO}_4]_2$ showing coincidence of the nodal planes of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO)



dimensional correlation (COSY) NMR spectrum of the complex.

The pendant-arm ethyl groups give rise to two signals at δ_{H}

2.68 and 2.88. The clearly resolved coupling pattern of the former multiplet constitutes one half of an AA'XX' system, and is assigned to the methylene hydrogen atoms (H_{h}) adjacent to the tertiary amino nitrogens. The latter signal (H_{i}) is broadened due to additional spin interactions with the primary amino protons at δ_{H} 1.86. This may be demonstrated by deuterium exchange of the amino hydrogen atoms with D_2O . The resolution of the H_{i} signal at δ_{H} 2.88 is significantly improved allowing clear identification of the expected line shape for the other half of the AA'XX' system. The fact that the two protons constituting each methylene hydrogen pair show the same chemical shift values and yet are magnetically inequivalent indicates that the pendant arms adopt predominantly a single rotameric conformation. It is reasonable to suggest that this arises from the co-ordination of the primary amino nitrogen atoms to the barium ion. If the temperature is raised to 333 K the ^1H NMR spectrum of $[\text{BaL}^1][\text{ClO}_4]_2$ is considerably simplified reflecting an increased molecular motion of the macrocycle. The signals arising due to the pendant arm (H_{h} and H_{i}) and H_{f} protons appear essentially as triplets, whilst those of the remaining methylene groups H_{g} are broadened to such an extent that they occur as a low broad hump between δ_{H} 3.1 and 2.6.

It has not yet proved possible to isolate a discrete product from the reaction of the barium complex with salicylaldehyde in 1:2 stoichiometric ratio. When an excess of salicylaldehyde was used a yellow solid precipitated and was collected. This was recrystallised from methanol to yield a first crop of yellow needles; the filtrate then gave on standing a second crop of yellow crystals. Both crops were further recrystallised from methanol and they provided suitable crystals for X-ray crystallography. The crystals recovered from the filtrate gave a band at 1634 cm^{-1} in the IR spectrum, but no bands corresponding to a primary amine or to the presence of a perchlorate anion were found. The parent peak in the FAB mass spectrum was at m/z 459 and this information together with the microanalysis and a comparison of the NMR (^1H and ^{13}C)

spectral data with literature values suggested that the known tripodal ligand tris[2-(salicylideneamino)ethyl]amine (L^2) had been synthesised,^{11,12} an X-ray structural analysis confirmed this, the structure being identical with that reported by Gündüz *et al.*¹³ The needle-like crystals from the first crop gave a band at 1650 cm^{-1} in the IR spectrum with no band corresponding to a primary amine but with a strong band at 1090 cm^{-1} indicating the presence of a perchlorate anion. The NMR spectra were similar to those for L^2 and the FAB mass spectrum gave a base peak at m/z 459 suggesting that the tripodal ligand was present. There was also a small intensity peak present at m/z 595 which corresponds to $[\text{BaL}^2]^+$. This together with the microanalysis indicated that the compound formed was $\text{BaL}^2_2(\text{ClO}_4)_2$, a formulation which was confirmed by solution of the crystal structure.

The asymmetric unit of the crystal structure is illustrated in Fig. 3; an extended packing diagram, which shows the full co-ordination geometry of the molecule, is in Fig. 4. Selected bond lengths and angles are given in Table 3 and atomic coordinates in Table 4. The asymmetric unit comprises a ligand (L^2) molecule, a barium cation, which lies on a crystallographic inversion centre, and a perchlorate counter anion. The ligand bridges adjacent barium cations (related by one unit-cell translation along the crystallographic b axis), using two of the three phenolic oxygen atoms so that each barium forms four such Ba–O bonds (two centrosymmetrically related pairs, Ba–O 2.65 and 2.62 Å), giving an approximately square, necessarily planar co-ordination geometry. The co-ordination polyhedron around the barium is completed by a pair of centrosymmetrically related, approximately symmetrically bidentate, perchlorate anions (Ba–O 2.95 and 2.89 Å): the angle between the square plane and the plane of the perchlorate chelate is 82.1° . The three phenyl rings are each planar (r.m.s. deviations 0.005, 0.003 and 0.005 Å), and each approximately coplanar with their adjacent substituent oxygen and imine fragments (r.m.s. deviations of whole fragments 0.010, 0.026 and 0.016 Å). The three

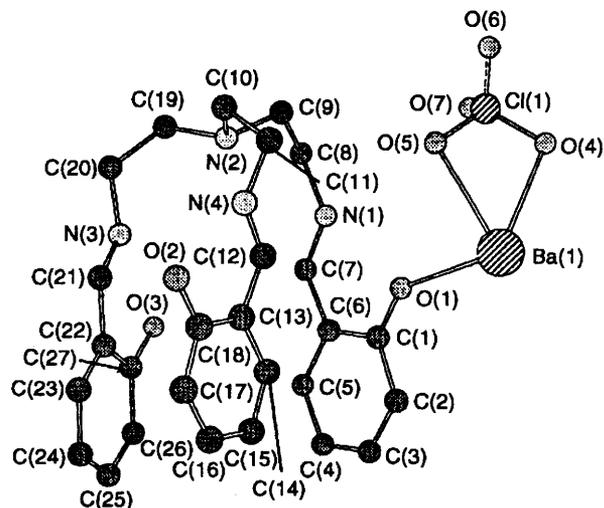


Fig. 3 The asymmetric unit of $\text{BaL}^2_2(\text{ClO}_4)_2$

N(tertiary)–C–N(imine) torsion angles are similar in the range -65 to -72° , but the three adjacent C–C–N=C torsion angles differ markedly with values of $+129$ and $+97^\circ$ for the non-bridging residue. This contrasts with the geometry found in the crystal structure of free L^2 ,¹³ in which the variation in these torsion angles is much less with a mean value of approximately $+125^\circ$. The wider range found in this barium complex can presumably be attributed to the bridging mode of two of the residues. The *cis* conformations of all three salicylideneimine residues permits the formation of internal hydrogen bonds [O...N 2.63, 2.62 and 2.60; N...H 1.76, 1.76 and 1.75 Å respectively as compared with mean values of 2.57 (O...N) and 1.63 Å (N...H) for free L^2 (ref. 13)], and leaves no opportunity for intermolecular hydrogen bonding. Thus the salicylideneimine residue based on O(3) is pendant and seems to be structurally 'innocent'. In theory, it looks as if it could be replaced by a shorter, non-donor residue (even methyl!) to leave the bridging capability unimpaired. Alternatively, perhaps some additional use could be made of the 'free', potentially donor phenolic oxygen to produce a two- or three-dimensional bridged network.

The angles between phenyl rings with their adjacent substituents are: 95° between planes (1) O(2)–C₆H₄C–N(4) and (2) O(1)–C₆H₄C–N(1); 108° between planes (3) O(3)–C₆H₄C–N(3) and (1) and 13° between (3) and (2). The relative orientation of planes (1) and (3) is displaced and rotated at about 45° and at an approximate separation distance of 4 Å.

It is possible that the tripodal products arise from *trans* imination reactions which lead to displacement of the pyridyldiimine head groups from the macrocycle or from hydrolysis of the Schiff-base macrocycle followed by formation of the tripod by reaction of salicylaldehyde with tren.

Experimental

Physical measurements were made as described in ref. 3. **CAUTION:** Although no problems were encountered during the course of this work, attention is drawn to the potentially explosive nature of perchlorates.

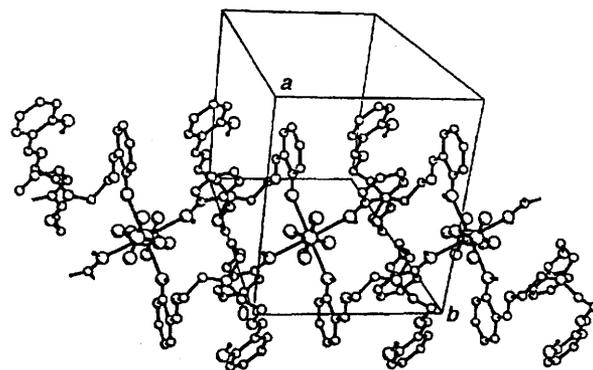


Fig. 4 The crystal packing of $\text{BaL}^2_2(\text{ClO}_4)_2$

Table 3 Selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations (e.s.d.s) for $\text{BaL}^2_2(\text{ClO}_4)_2$

Ba(1)–Cl(1)	3.546(5)	Ba(1)–O(1)	2.646(4)
Ba(1)–O(4)	2.947(6)	Ba(1)–O(5)	2.893(6)
Ba(1)–O(2A)	2.622(5)		
O(1)–Ba(1)–O(4)	98.0(1)	O(4)–Ba(1)–O(5)	46.6(1)
O(1)–Ba(1)–O(5)	68.6(1)	O(1)–Ba(1)–O(2A)	85.8(1)
O(4)–Ba(1)–O(2A)	69.2(1)	O(5)–Ba(1)–O(2A)	102.5(1)
C(18)–O(2)–Ba(1A)	146.6(3)	Ba(1)–O(1)–C(1)	141.2(3)
Ba(1)–O(5)–Cl(1)	104.9(2)	Ba(1)–O(4)–Cl(1)	102.2(2)

Table 4 Atomic coordinates ($\times 10^4$) for $\text{BaL}^2_2(\text{ClO}_4)_2$

Atom	x	y	z	Atom	x	y	z
Ba(1)	0	5 000	5 000	C(8)	-1 637(4)	7 029(5)	2 790(2)
Cl(1)	886(1)	4 407(1)	3 839(1)	C(9)	-647(4)	8 063(5)	2 954(2)
N(1)	-2 097(3)	6 736(4)	3 239(1)	C(10)	73(3)	10 241(5)	3 395(2)
N(2)	-963(3)	9 469(4)	3 076(1)	C(11)	413(3)	9 890(6)	4 004(2)
N(3)	-3 188(3)	11 110(4)	2 834(2)	C(12)	-1 226(3)	9 827(5)	4 332(2)
N(4)	-380(3)	10 511(4)	4 255(1)	C(13)	-1 977(3)	10 390(4)	4 591(2)
O(1)	-1 841(3)	6 032(4)	4 255(1)	C(14)	-2 857(4)	9 525(5)	4 663(2)
O(2)	-1 027(3)	12 561(3)	4 768(1)	C(15)	-3 547(4)	9 979(7)	4 944(3)
O(3)	-4 964(3)	9 543(4)	2 762(2)	C(16)	-3 407(4)	11 317(5)	5 160(2)
O(4)	917(4)	3 385(4)	4 258(2)	C(17)	-2 585(4)	12 192(5)	5 099(2)
O(5)	465(4)	5 689(4)	3 999(1)	C(18)	-1 835(3)	11 756(4)	4 814(2)
O(6)	1 973(4)	4 664(7)	3 804(2)	C(19)	-1 559(4)	10 244(5)	2 572(2)
O(7)	124(5)	4 000(6)	3 331(2)	C(20)	-2 200(4)	11 510(6)	2 667(2)
C(1)	-2 940(4)	6 108(4)	4 139(2)	C(21)	-3 482(4)	11 866(5)	3 169(2)
C(2)	-3 513(5)	5 863(5)	4 531(2)	C(22)	-4 494(4)	11 586(5)	3 325(2)
C(3)	-4 674(5)	5 996(6)	4 397(2)	C(23)	-4 801(5)	12 485(7)	3 675(3)
C(4)	-5 356(4)	6 363(6)	3 874(2)	C(24)	-5 760(5)	12 274(8)	3 826(3)
C(5)	-4 848(4)	6 624(6)	3 493(2)	C(25)	-6 423(5)	11 121(8)	3 630(3)
C(6)	-3 655(3)	6 508(5)	3 601(2)	C(26)	-6 162(4)	10 206(7)	3 283(2)
C(7)	-3 179(4)	6 816(5)	3 190(2)	C(27)	-5 188(4)	10 437(5)	3 123(2)

'2 + 2' Cyclisation of Tris(2-aminoethyl)amine with 2,6-Diacetylpyridine in the Presence of Barium(II) Perchlorate.—A solution of tris(2-aminoethyl)amine (1.46 g, 10 mmol) in methanol (50 cm³) was added dropwise to a refluxing solution of barium(II) perchlorate (1.68 g, 5 mmol) and 2,6-diacetylpyridine (1.63 g, 10 mmol) in methanol (80 cm³) over a period of 30 min. The resulting solution was refluxed for 1.5 h then filtered whilst hot and left to cool. The product was recovered as a pale cream solid which was recrystallised from methanol to give $[\text{BaL}^1][\text{ClO}_4]_2$ (1.76 g, 40% yield) (Found: C, 40.80; H, 5.30; Cl, 7.95; N, 15.40. $\text{C}_{30}\text{H}_{46}\text{BaCl}_2\text{N}_{10}\text{O}_8$ requires C, 40.80, H, 5.25; Cl, 8.05; N, 15.85%). IR (KBr disc): $\nu(\text{NH}_2)$ 3288 and 3333, $\nu(\text{C}=\text{N})$ 1627 cm⁻¹. Mass spectrum (positive-ion FAB): m/z 783, $[\text{BaL}^1(\text{ClO}_4)]^+$. ¹³C NMR (CD_3CN): δ 168.8, 155.5, 141.5, 125.4, 61.6, 56.9, 52.0, 39.9 and 16.9.

Reaction of $[\text{BaL}^1][\text{ClO}_4]_2$ with Salicylaldehyde.—Salicylaldehyde (5 cm³, 41 mmol) was added slowly to a suspension of the barium macrocycle complex (0.35 g, 0.4 mmol) in methanol (4 cm³) and stirred for 5 min at room temperature. On standing the product precipitated as a yellow solid which was washed with diethyl ether and dried. The product was dissolved in methanol (35 cm³) and the resulting solution filtered and left to stand. The product $\text{BaL}^2_2(\text{ClO}_4)_2$ crystallised as yellow needles (in 13% yield) which were filtered off, washed with diethyl ether and dried (Found: C, 51.80; H, 4.80; N, 8.80. $\text{C}_{54}\text{H}_{60}\text{BaCl}_2\text{N}_8\text{O}_{14}$ requires C, 51.75; H, 4.85; N, 8.95%). IR (KBr disc): $\nu(\text{C}=\text{N})$ 1650 cm⁻¹. Mass spectrum (positive-ion FAB): m/z 595, $[\text{BaL}^2]^+$. NMR: ¹H (CD_3OD), δ 2.88 (t, 2 H, CH₂), 3.58 (t, 2 H, CH₂), 6.21 (m, 1 H, aryl H), 6.55 (m, 1 H, aryl H), 6.84 (m, 1 H, aryl H), 7.27 (m, 1 H, aryl H) and 7.88 (s, 1 H, CH); ¹³C (CD_3CN), δ 167.6, 164.7, 134.0, 133.5, 119.4, 119.0, 118.6, 57.7 and 56.8.

The filtrate was left to stand and a second crystalline precipitate was recovered. This was washed with diethyl ether and dried to give tris[2-(salicylideneamino)ethyl]amine (L^2) in 13.9% yield (Found: C, 70.55; H, 6.55; N, 12.30. $\text{C}_{27}\text{H}_{30}\text{N}_4\text{O}_3$ requires C, 70.70; H, 6.60; N, 12.20%). IR (KBr disc): $\nu(\text{C}=\text{N})$ 1634 cm⁻¹. Mass spectrum (positive-ion FAB): m/z 459, $[\text{HL}^2]^+$. NMR: ¹H (CDCl_3), δ 2.85 (t, 2 H, CH₂), 3.56 (t, 2 H, CH₂), 6.05 (m, 1 H, aryl H), 6.60 (m, 1 H, aryl H), 6.93 (m, 1 H, aryl H), 7.24 (m, 1 H, aryl H), 7.80 (s, 1 H, CH) and 13.80 (s, 1 H, OH); ¹³C (CD_3CN), δ 166.1, 161.0, 131.8, 131.7, 118.5, 118.4, 116.7, 57.9 and 55.8.

Crystal Structure Determinations.—Crystal data for $[\text{BaL}^1][\text{ClO}_4]_2 \cdot \text{CH}_3\text{OH}$. $\text{C}_{31}\text{H}_{50}\text{BaCl}_2\text{N}_{10}\text{O}_9$, $M = 915.04$,

crystallises from methanol as colourless rhombic prisms, crystal dimensions 0.5 \times 0.25 \times 0.2 mm, monoclinic, space group $P2_1/c$ (C_{2h}^5 , no. 14), $a = 11.755(7)$, $b = 21.733(17)$, $c = 15.621(15)$ Å, $\beta = 90.50(7)^\circ$, $U = 3991(6)$ Å³, $Z = 4$, $D_c = 1.523$ g cm⁻³, Mo-K α radiation ($\lambda = 0.710 69$ Å), $\mu(\text{Mo-K}\alpha) = 11.88$ cm⁻¹, $F(000) = 1863.68$.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet R3 four-circle diffractometer by the ω -scan method. The 3538 independent reflections (of 5815 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.353 and 0.397). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. An ordered perchlorate anion was refined with constrained T_d symmetry and a common isotropic thermal parameter for the four oxygen atoms. The second perchlorate was disordered in two interpenetrating sites (0.42:0.58), and each component was refined with constrained T_d symmetry and with a single isotropic thermal parameter for chlorines and oxygens. The two components of a disordered methanol (0.57:0.43) were refined with a constrained C–O (1.40 Å). Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement, based on $|F|$, converged at a final $R = 0.1004$ ($R' = 0.0998$, 428 parameters, mean and maximum δ/σ 0.054, 0.299), with allowance for the thermal anisotropy of all non-hydrogen atoms. The minimum and maximum final electron densities were -1.17 and $+1.83$ e Å⁻³ adjacent to the barium atom. A weighting scheme $w^{-1} = \sigma^2(F) + 0.0017(F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from ref. 14 and from the program package SHELXTL¹⁵ as implemented on a Data General DG30 computer.

Crystal data for $\text{BaL}^2_2(\text{ClO}_4)_2$. $\text{C}_{54}\text{H}_{60}\text{BaCl}_2\text{N}_8\text{O}_{14}$, $M = 1253.30$, crystallises from methanol as yellow blocks, crystal dimensions 0.54 \times 0.74 \times 0.26 mm, monoclinic, space group $P2_1/c$ (C_{2h}^5 , no. 14), $a = 12.299(15)$, $b = 9.530(15)$, $c = 25.798(32)$ Å, $\beta = 108.679(9)^\circ$, $U = 2865(7)$ Å³, $Z = 2$, $D_c = 1.458$ g cm⁻³, Mo-K α radiation ($\lambda = 0.710 69$ Å), $\mu(\text{Mo-K}\alpha) = 8.71$ cm⁻¹, $F(000) = 1283.79$.

Three-dimensional, room-temperature X-ray data were collected in the range $6.5 < 2\theta < 50.0^\circ$ on a Stoe Stadi 2 diffractometer by the ω -scan method. The 3722 independent reflections (of 5618 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, and for

absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.604 and 0.803). Since systematic weakness was observed in reflections $k + l = 2n + 1$ (A-centred tendency), the barium atom was fixed at position $0, \frac{1}{2}, \frac{1}{2}$. The structure was solved by Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions and along intermolecular hydrogen bonds and refined in riding mode. Refinement, based on $|F|$, converged at $R = 0.0356$ (358 parameters, final mean and maximum δ/σ 0.009, 0.035), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of -0.681 and 0.550 e \AA^{-3} close to the barium atom. Complex scattering factors as above.

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

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