Trihapto–Hexahapto Fluxional Behaviour of a Macrocyclic Ligand: Template Synthesis, Proton Nuclear Magnetic Resonance Spectra, and the Crystal and Molecular Structure of an Eleven-co-ordinate Barium(II) Complex †

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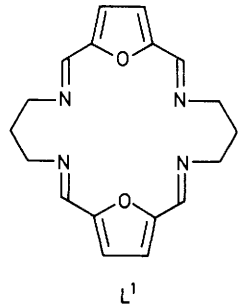
The alkaline-earth-metal ions Ca^{2+}, Sr^{2+}, and Ba^{2+}, but not Mg^{2+}, are templates for the high-yield synthesis of 1 : 1 complexes of the 20-membered macrocycle L^1 derived from the cyclic condensation of 2 mol of 2,5-diformylfuran with 2 mol of 1,3-diaminopropane. Lead(II) is also effective as a template for the macrocycle synthesis. In the case of Ba^{II} only, complexes having a 2 : 1 ligand : metal stoicheiometry could also be prepared by anion exchange. Crystals of $[BaL^1_2(H_2O)_2][Co(NCS)_4]$ are monoclinic with a = 11.57(1), b = 19.99(1), c = 23.18(1) Å, β = 107.5(1)°, Z = 4, and space group $P2_1/c$. 4 329 Reflections above background were measured by diffractometer and refined by least-squares methods to R 0.062. The barium atom in the cation is bonded to all six heteroatoms of one macrocycle but only to three of the second macrocycle, this being severely folded so that one furan di-imine moiety is unco-ordinated. Two water molecules are also bonded to the barium atom giving an overall co-ordination number of 11. This structure is discussed in relation to those of other eleven-co-ordinate compounds. The hexahapto–trihapto co-ordination observed in the solid state is retained in solution as determined from the temperature-dependent ^{1}H n.m.r. spectrum of the analogous complex $[BaL^1_2(MeCN)_2][BPh_4]_2$ in CD_3CN. Below *ca.* 20 °C the resonances due to the imino-protons (HC=N) and the methylene protons (C=N–CH_2) adjacent to the imine group each appear as pairs of well separated lines having a 3 : 1 intensity ratio. These are attributed to slowly exchanging co-ordinated and unco-ordinated furan di-imine moieties, respectively. Increase in temperature causes coalescence of the components of each doublet into a single line. The two sets of temperature-dependent spectra are described by the same free energy of activation ($\Delta G^\ddagger$ = *ca.* 62.5 kJ mol^{-1}) indicating that they are associated with the same dynamic process, *viz.* interconversion of four equivalent configurations of the complex cation. The results are discussed in relation to the sizes of the metal cations and the flexibility and cavity dimensions of this and related macrocycles.

Growing interest in the chemistry of ' binuclear metal sites ' has stimulated the development of new binucleating ligands capable of holding two transition-metal ions in close proximity.[1] Among these are the macrocyclic tetraimine ligands derived from the cyclic (2 + 2) condensation of 2,6-diformylpyridine (or derivative) or 2,5-diformylfuran with a range of diprimary amines.[2] Commonly these macrocycles are synthesised by template methods using Group 1A, 2A, or Main Group metal ions followed by replacement of the template ion from the macrocycle by the transition-metal ions of interest.[2] We have previously reported [3,4] briefly on some di-copper complexes of the 20-membered macrocycle L^1. The precursor alkaline-earth-metal ion complexes of this macrocycle are also of interest in their own right and we here describe the synthesis and properties of a series of complexes of Ca^{II}, Sr^{II}, Ba^{II}, and also Pb^{II}. The structure of an eleven-co-ordinate barium(II) complex containing two macrocycle molecules is described together with the results of a variable-temperature ^{1}H n.m.r. study which reveals unusual fluxional behaviour involving the two non-equivalent macrocyclic ligands.



L^1

Results and Discussion

Synthesis and Characterisation of the Complexes.—Reaction of 2,5-diformylfuran with 1,3-diaminopropane in MeOH or EtOH using varying molar ratios led only to oils or gums having properties consistent with an oligomeric or polymeric constitution. However, if the reaction is carried out in the presence of a salt (perchlorate or thiocyanate) of the metal ions Ca^{2+}, Sr^{2+}, Ba^{2+}, or Pb^{2+} crystalline complexes of the macrocycle L^1 are obtained in good yield (60—95%). The synthesis is a remarkably facile one requiring only warming or gentle reflux for short periods and represents a dramatic demonstration of the template action of the metal ion. Magnesium(II) salts were ineffective as templates, the reaction products in these cases being, once again, gums or amorphous powders of indefinite composition.

The crystalline complexes prepared by the template method all have a 1 : 1 ligand : metal stoicheiometry (see Table 1). Two additional complexes of Ba^{II} having a 2 : 1 ligand : metal ratio could also be prepared by a metathetical method involving addition of $Na(BPh_4)$ or $Co(NCS)_2$ to solutions of [BaL^1-

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† *Supplementary data available* (No. SUP 23608, 30 pp.): thermal parameters, anion and macrocycle dimensions, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: B.M. ≈ 9.27 × 10^{-24} A m^2.

Table 1. Analytical, i.r., and electrical conductance data for the complexes

Complex	Analysis (%)[a]			P^+ m/e	I.r. bands (cm^{-1})		λ[b]/S cm^2 mol^{-1}
	C	H	N		ν(C=N)	ν(ClO$_4$)	
[BaL^1(ClO$_4$)$_2$]·MeOH	32.9 (32.9)	3.5 (3.5)	7.8 (7.8)		1 626	1 130, 1 105, 1 046, 630, 620	242
[BaL^1(ClO$_4$)$_2$]·EtOH	33.7 (34.0)	3.7 (3.7)	7.8 (7.9)		1 628	1 130, 1 110, 1 050, 628, 622, 615	238
[BaL^1(NCS)$_2$]·H$_2$O	40.0 (40.3)	3.7 (3.8)	14.1 (14.1)	324	1 634, 1 625		228
[BaL$^1_2$(MeCN)$_2$][BPh$_4$]$_2$	69.7 (70.1)	5.7 (5.8)	9.3 (9.3)	324	1 670, 1 630		206
[BaL$^1_2$(H$_2$O)$_2$][Co(NCS)$_4$]					1 670, 1 630		
[SrL^1(ClO$_4$)$_2$]	35.6 (35.4)	3.3 (3.3)	9.3 (9.2)		1 626, 1 614	1 136, 1 106, 1 042, 1 006, 630, 622, 612	262
[SrL^1(H$_2$O)$_2$][BPh$_4$]$_2$	71.8 (72.9)	6.1 (5.9)	5.1 (5.1)	324	1 626, 1 614		
[CaL^1(ClO$_4$)$_2$]	38.6 (38.4)	3.5 (3.6)	10.1 (10.0)		1 624	1 140, 1 114, 1 042, 1 014, 636, 622, 614	258
[CaL^1(H$_2$O)$_2$][BPh$_4$]$_2$	75.7 (76.2)	6.2 (6.3)	5.4 (5.5)	324	1 624		
PbL^1(ClO$_4$)$_2$	29.4 (29.6)	2.8 (2.8)	7.5 (7.7)		1 618	1 130, 1 090, 1 040, 1 010, 625, 612	

[a] Calculated values are in parentheses. [b] For 10^{-3} mol dm^{-3} MeCN solutions at 20 °C.

(ClO$_4$)$_2$]·EtOH in a MeCN–EtOH solvent mixture. No complexes of this stoicheiometry could be prepared in the case of the smaller cations Ca^{2+}, Sr^{2+}, or Pb^{2+}.

The macrocyclic nature of the ligand in all the complexes was demonstrated by the collective evidence of their properties, *viz.* their crystalline nature, elemental analysis, i.r., mass, and ^{1}H n.m.r. spectra, and the crystal structure determination of one member of the series.

Mass spectra of the thiocyanate and tetraphenylborates gave P^+ at m/e 324 corresponding to the free macrocycle as the highest mass peak. I.r. spectra all showed a medium-intensity band, sometimes split, at 1 610—1 630 cm^{-1} attributable to the co-ordinated ν(C=N) vibration. The two barium(II) complexes containing two molecules of macrocycle per metal atom showed, in addition, a band of reduced intensity at 1 670 cm^{-1} which can be assigned (see later) to unco-ordinated ν(C=N). In none of the spectra was there any absorption at 3 200—3 400 or at *ca.* 1 700 cm^{-1} which could be attributed to the presence of unreacted amine or carbonyl.

Low solubility in suitable solvents precluded the determination of ^{1}H n.m.r. spectra except for the two 1 : 1 perchlorate complexes of Ba^{II} and the 2 : 1 complex [BaL$^1_2$(MeCN)$_2$][BPh$_4$]$_2$. The perchlorate complexes gave simple spectra in CD$_3$CN consisting of a singlet at δ 8.17 (4 H, imine HC=N protons), a singlet at δ 6.97 (4 H, furan ring protons), a triplet at δ 3.90 (8 H, CH$_2$ protons adjacent to the imine groups), and a quintet at δ 2.01 (4 H, central CH$_2$ protons of the propane chains). The ^{1}H n.m.r. spectrum of [BaL$^1_2$(MeCN)$_2$][BPh$_4$]$_2$ containing two ligand molecules per metal ion was essentially the same except for the resonances due to the imino-protons and the methylene groups adjacent to the imino-nitrogens. The profiles of each of these resonances were temperature dependent, separating into two signals of unequal intensity at low temperature. Discussion of these spectra is deferred until after the description of the structure of the complex [BaL$^1_2$(H$_2$O)$_2$][Co(NCS)$_4$].

The occurrence of two ν(C=N) vibrations in the i.r. spectra of the bis(macrocycle)barium(II) complexes and the apparent non-equivalence of some of the protons in the ^{1}H n.m.r. spectra suggested that the two molecules of macrocycle are co-ordinated in different ways. Crystals of the complex [BaL$^1_2$(H$_2$O)$_2$][Co(NCS)$_4$] suitable for *X*-ray analysis were grown. The magnetic moment ($\mu_{eff.}$ = 4.53 B.M. at 293 K) and electronic spectrum ($\nu_{max.}$ at 16 600 cm^{-1}, ε = 1 760 dm^3 mol^{-1} cm^{-1} in MeCN) are as expected for the tetrahedral [Co(NCS)$_4$]$^{2-}$ anion.[5]

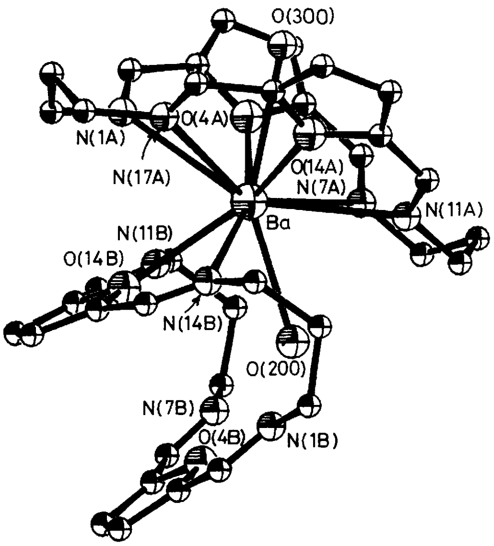


Figure 1. The structure of the [BaL$^1_2$(H$_2$O)$_2$]$^{2+}$ cation

The Structure of [BaL$^1_2$(H$_2$O)$_2$][Co(NCS)$_4$].—The structure of this complex consists of discrete [BaL$^1_2$(H$_2$O)$_2$]$^{2+}$ cations and [Co(NCS)$_4$]$^{2-}$ anions. The cation is shown in Figures 1 and 2 together with the atomic numbering scheme. The barium atom is eleven-co-ordinate being bonded to all six donor atoms of one macrocycle (macrocycle A), and to three donor atoms (one oxygen and two nitrogens) of the second macrocycle (macrocycle B) and to two water molecules. As shown in the Figures the conformations of the two macrocycles are quite different (see least-squares planes in Table 2).

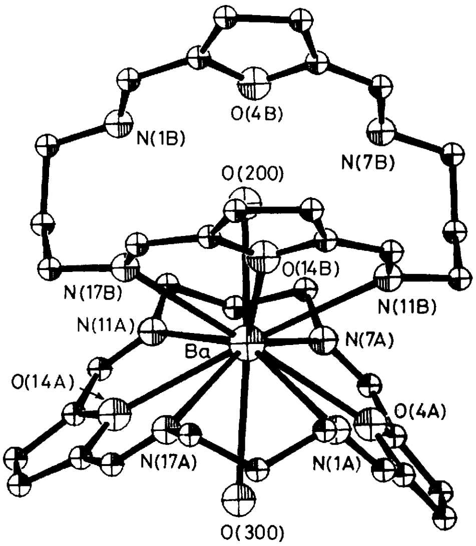


Figure 2. The structure of the $[BaL^{1}_{2}(H_2O)_2]^{2+}$ cation

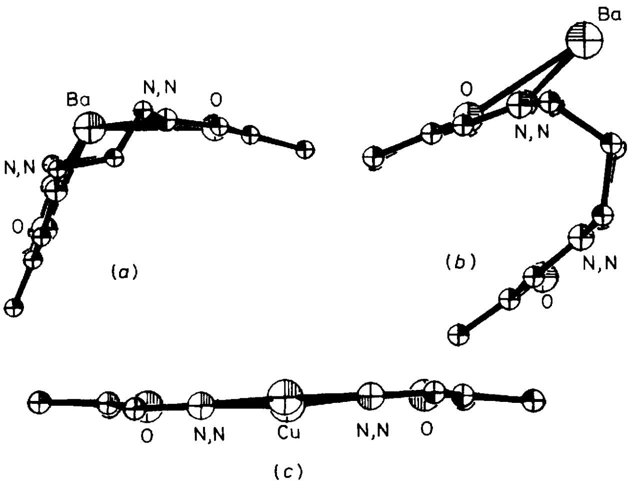


Figure 3. The conformation of macrocycles A (*a*) and B (*b*) in $[BaL^{1}_{2}(H_2O)_2]^{2+}$ and of the same macrocycle in $[Cu_2L^{1}(SCN)_2]$ (*c*)

In macrocycle A the four nitrogen atoms are coplanar but the barium atom is 0.79 Å to one side of the plane while the two furan oxygen atoms sit 0.78 and 0.70 Å to the other side [Figure 3(*a*)].

The four Ba–N distances [3.016(7)—3.109(9) Å] are nearly equivalent and slightly longer than the Ba–O distances [2.859(6) and 2.861(8) Å]. The two furan rings intersect the ' N_4 ' plane at angles of 48.1 and 35.3°. In macrocycle B only one ' N,O,N ' moiety is bonded to the metal ion. Despite this, the four nitrogen atoms remain planar. However, the Ba^{2+} ion is now 1.69 Å to one side of the plane and the two furan oxygen atoms are 1.05 and 1.12 Å on the other side. The angles of intersection of the furan rings with the ' N_4 ' plane are now 80.4 and 87.8° and reflect a very severe folding of the macrocycle [Figure 3(*b*)].

There is little difference in conformation between the co-ordinated and unco-ordinated halves of macrocycle B. The Ba–N [3.084(12) and 3.097(8) Å] and Ba–O distances [2.861(7) Å] of the co-ordinated half of macrocycle B are not significantly different from those of macrocycle A. There is, however, a difference in the siting of the metal atom with respect to the chelating N,O,N moieties in the two macrocycles. For macrocycle A, the metal atom is displaced by 0.53 and 0.44 Å from the least-squares plane of the N,O,N groups, but with macrocycle B the metal atom is displaced 0.97 Å (on the opposite side) from the least-squares plane of the co-ordinated N,O,N group (Figure 3).

Table 2. Least-squares planes and atom deviations (Å) for $[BaL^{1}_{2}(H_2O)_2][Co(NCS)_4]$; atoms marked with an asterisk do not contribute to the planes

Plane 1: N(1B) 0.03, N(7B) −0.03, N(11B) 0.03, N(17B) −0.03, Ba* 1.69, O(4B)* −1.05, O(14B)* −1.12

Plane 2: N(1A) −0.03, N(7A) 0.03, N(11A) −0.03, N(17A) 0.03 Ba* −0.79, O(4A)* 0.78, O(14A)* 0.70

It is interesting to compare the macrocycle conformations occurring in the present structure with that found in the dicopper(I) complex $[Cu_2L^{1}(SCN)_2]$ of the same macrocycle. In this structure, the copper(I) ions are tetrahedrally co-ordinated, each being bonded to two macrocycle imine nitrogens and to two bridging sulphur atoms of the thiocyanate groups. The structure is centrosymmetric and the metal atoms are coplanar (maximum deviation, 0.07 Å) with the six hetero-atoms of the macrocycle [Figure 3(*c*)]. In contrast to the present structure the metal–furan oxygen distances are very much longer (at 2.93 and 2.95 Å) than the metal–nitrogen distances (2.04 and 2.05 Å) and, indeed, are probably best considered as non-co-ordinated.

The positions of the two co-ordinated water molecules are interesting in relation to the conformations of the macrocycle molecules in the cation $[BaL^{1}_{2}(H_2O)_2]^{2+}$. Particularly noteworthy is the position of O(300) on the same side of the metal as macrocycle A. The six angles subtended at the metal by O(300) with the six donor atoms of macrocycle A range from 57.8(3) to 83.2(3)°. It can therefore be regarded as capping the hexagonal macrocycle (see Table 2, Plane 2). This water molecule is clearly in a much more crowded position than the second water molecule [O(200)] which lies on the other (more open) side of the metal atom, *i.e.* on the same side as macrocycle B. It is therefore not surprising that the Ba–O(300) bond length is significantly different from that of Ba–O(200) [*cf.*, 2.997(14) and 2.767(6) Å]. The O(200)–Ba–O(300) angle is 150.7(3)°.

The structure in relation to other eleven-co-ordinate compounds. There are only a few structures of eleven-co-ordinate metal complexes, and there has been little analysis of the ideal geometries. We have studied the geometry of seven such compounds including the present molecule using our method [6] of fitting co-ordinate geometries to ideal polyhedra.

Because of the irregularity of eleven-co-ordination, there are no polyhedra of high symmetry. Several low-symmetry polyhedra have been considered. One polyhedra is based on the twelve-co-ordinate icosahedron but with one site missing. The icosahedron can be described as having a 1 : 5 : 5 : 1 geometry (looking down one of its $\overline{10}$ axes; there are six such axes and all sites are equivalent). It is simplest to consider an axial site being removed to give a 1 : 5 : 5 monocapped pentagonal antiprism of C_{5v} symmetry.[7] Some authors (*e.g.* ref. 8) have created a polyhedron of type 1 : 5 : 4 : 1 by removing an equatorial site, but because all sites are equivalent there are only very minor differences between the two descriptions.

Other possible geometries are of the types 1 : 4 : 6 and 1 : 6 : 4 both constrained to C_{2v} symmetry. However, we found none to conform to the former, presumably because the capping atom prefers to cap as large a number of atoms in a face as possible. The 1 : 6 : 4 polyhedron proved to be

Table 3. R.m.s. values of eleven-co-ordinate structures for the two ideal polyhedra

Complex	Ref.	1 : 5 : 5	1 : 6 : 4
$[Ce(NO_3)_4(H_2O)_2(NC_5H_4{-}C_5H_4N)]^-$	8	0.17	0.26
$Sm(NO_3)_5(H_2O)^{2-}$	*a*	0.14	0.16
$La(NO_3)_3(H_2O)_5{\cdot}H_2O$	*b*	0.26	0.17
$[Eu(NO_3)_3(C_{10}H_{20}O_5)]$ [c]	7	0.11	0.20
$Th(NO_3)_3(H_2O)_3$	*d*	0.23	0.14
$Th_2(NO_3)_6(H_2O)_6(OH)_2$	*e*	0.29	0.12
$[BaL^1{}_2(H_2O)_2][Co(NCS)_4]$		0.16	0.20

[a] J. H. Burns, *Inorg. Chem.*, 1979, **18**, 3044. [b] B. Eriksson, L. O. Larsson, L. Niinsto, and J. Valkonen, *Inorg. Chem.*, 1980, **19**, 1207. [c] $C_{10}H_{20}O_5$ = 1,4,7,10-13-pentaoxacyclopentadecane. [d] U. Ueki, D. H. Templeton, and A. Zalkin, *Acta Crystallogr.*, 1966, **20**, 836. [e] G. Johansson, *Acta Chem. Scand.*, 1968, **22**, 389.

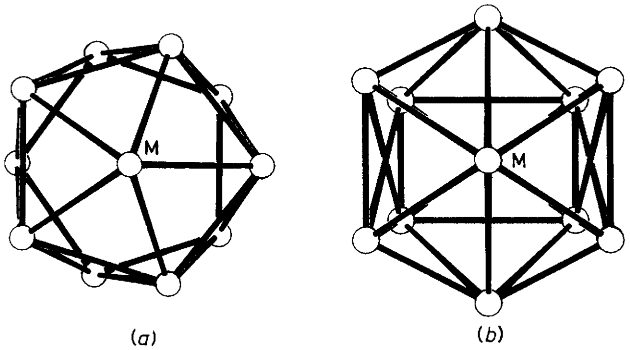


Figure 4. Eleven-co-ordinate polyhedra: (*a*) The 1 : 5 : 5 polyhedron looking down the C_5 axis; (*b*) The 1 : 6 : 4 polyhedron looking down the C_2 axis

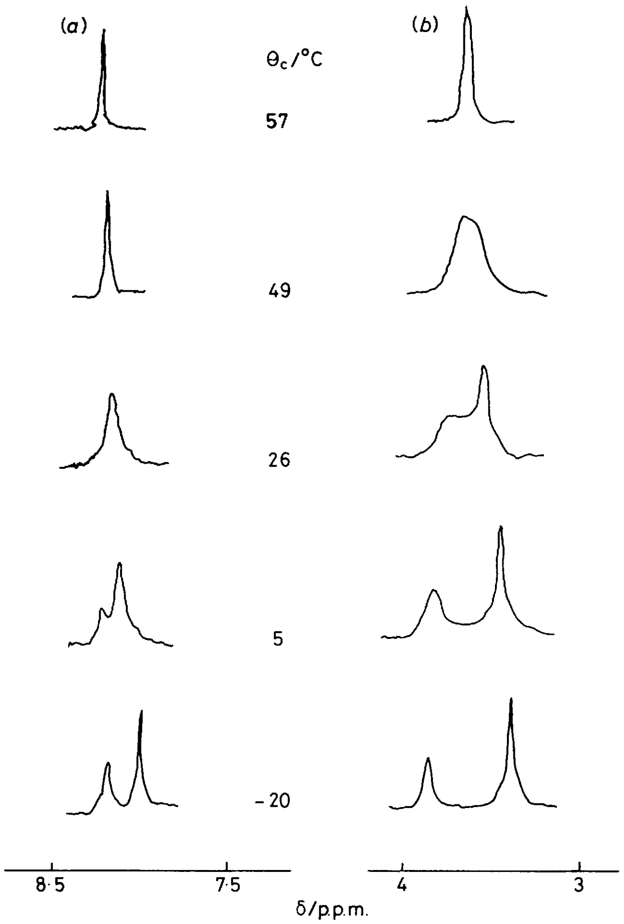


Figure 5. The 250-MHz ^1H n.m.r. spectra of the HC=N proton (*a*) and $C{=}N{-}CH_2$ protons (*b*) of $[BaL^1{}_2(MeCN)_2][BPh_4]_2$ in CD_3CN at selected temperatures

common. We then tried to fit a number of eleven-co-ordinate structures to the two ideal 1 : 5 : 5 and 1 : 6 : 4 polyhedra. The co-ordinates were abstracted from the Cambridge Data Centre, and the results are given in Table 3. The present structure fits best a 1 : 5 : 5 geometry with O(14B) in the unique position [root-mean-square (r.m.s.) deviation 0.16 Å]. As stated above, atom O(300) does cap a face of the macrocycle A (with six donor atoms) but the geometry of the remaining four atoms in no way approximates to a rectangle as three of them (donor atoms N,O,N from macrocycle B) are planar and bonded to the metal. The r.m.s. deviation from that geometry is 0.20 Å.

All the other structures fit reasonably well one of the polyhedra, bearing in mind the constraints of the chelate ligands. We found that for both polyhedra the r.m.s. deviations were increased considerably by variations in the *z* co-ordinate (*z* being defined as the highest symmetry axis). This was also noted by Bunzli *et al.*[7] who found that in their 1 : 5 : 5 polyhedron the pentagonal base was distorted into a triangle and a quadrilateral with a common edge and a dihedral angle of 142°. The same phenomenon is noted in the hexagonal plane of the 1 : 6 : 4 geometry where it is often better described as 1 : 4 : 2 : 4. However, in view of the limited number of eleven-co-ordinate structures and the fact that all those known contain restrictive ligands, we do not describe here the distortions from the ideal geometry.

In the Figure 4 we show the two ideal forms projected down the highest symmetry axis. The best fits to the 1 : 6 : 4 geometry are the two thorium structures.

The Temperature-dependent ^1H *N.M.R. Spectra of* $[BaL^1{}_2(MeCN)_2][BPh_4]_2$.—It was mentioned above that the ^1H n.m.r. spectrum of $[BaL^1{}_2(MeCN)_2][BPh_4]_2$ is temperature dependent. This complex shows two well separated ν(C=N) vibrations in the i.r. spectrum. It is therefore a reasonable assumption that this complex also contains one sexidentate macrocycle and one tridentate macrocycle as found crystallographically for $[BaL^1{}_2(H_2O)_2][Co(NCS)_4]$.

It was found that the profiles of the resonances due to the imine protons and methylene protons adjacent to the imine group are temperature dependent. These are the protons closest to the imine nitrogen donors and therefore the most susceptible to shifts arising from co-ordination. Little alteration with temperature was observed for either the furan-ring protons or the central methylene protons of the propane arms of the macrocycle.

Figure 5 shows the 250-MHz spectra of the HC=N and $C{=}N{-}CH_2$ protons as a function of temperature in CD_3CN. Considering the $C{=}N{-}CH_2$ protons first it can be seen that these resonate as an unresolved singlet at temperatures above about 50 °C. As the temperature is lowered the resonance broadens, separates into two broad singlets, and finally at below about 0 °C appears as two fairly sharp and well defined signals separated by 139 Hz and having a 1 : 3 relative intensity ratio. Similar behaviour is observed for the imine HC=N proton. This is a sharp singlet above about 30 °C whereas at −20 °C it occurs as separate singlets 51 Hz apart, the two components occurring once again in the intensity ratio of 1 : 3.

This type of behaviour is typical of a dynamic equilibrium of protons between non-equivalent sites. In the light of the

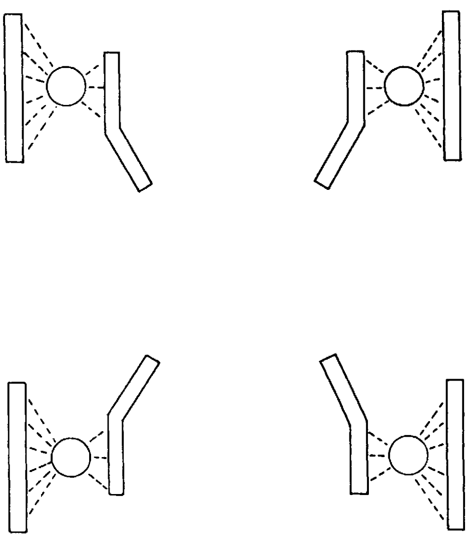
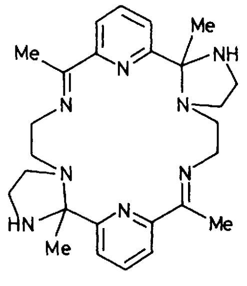


Figure 6. Representation of the four equivalent configurations of the BaL^1_2 unit in the complex cation $[BaL^1_2(MeCN)_2]^{2+}$

structure determination of $[BaL^1_2(H_2O)_2][Co(NCS)_4]$, the inequivalence can be associated with whether the imine nitrogen is co-ordinated or not. The occurrence in a 1 : 3 ratio of the components of the resonance in the low-temperature spectra is in keeping with the crystal-structure determination which shows that three furan di-imine groups are co-ordinated and one unco-ordinated. The occurrence of the more intense component at higher field in each case reflects the expected shielding effect on co-ordination.

The coalescence temperatures (T_c) for the pairs of resonances were estimated as 49 °C for the $C{=}N{-}CH_2$ protons and 26 °C for the $HC{=}N$ protons at 250 MHz. From these values and the separation ($\Delta\nu$) between the components of each resonance in the low-temperature spectra, the free energy of activation for dynamic processes was calculated [9] to be 63.5 ± 1 and 61.5 ± 2 kJ mol^{-1} for the $C{=}N{-}CH_2$ and $HC{=}N$ protons, respectively. These values are the same within experimental uncertainty and confirm that there is only one dynamic process involved, namely a thermally controlled fluxional interconversion between four equivalent configurations, as represented diagrammatically in Figure 6.

The Structures of the 1 : 1 *Complexes*.—The analytical, i.r., mass, and ^1H n.m.r. spectral data given earlier are sufficient to establish that the 1 : 1 complexes all contain the same macrocyclic ligand L^1. Assuming that all six heteroatoms of the macrocycle are co-ordinated to form a relatively planar girdle it remains to consider whether the anions and the solvate molecules, where present, are also co-ordinated. All the perchlorate complexes showed distinct splitting (Table 1) of both the asymmetric stretching and asymmetric bending modes of the perchlorate ion at 1 000—2 000 and 610—640 cm^{-1} respectively, indicating co-ordination of at least one of these anions. The presence of a band at 1 090 cm^{-1} in the spectrum of $PbL^1(ClO_4)_2$ suggests that one ClO_4^- is unco-ordinated, while the absence of this band in the spectra of the other complexes is an indication that both ClO_4^- anions are co-ordinated in these cases. Thus assuming a unidentate mode, we have a seven-co-ordinate structure (presumably hexagonal pyramidal) for Pb^{II} in $PbL^1(ClO_4)_2$ and an eight-co-ordinate structure (presumably hexagonal bipyramidal) for Ca^{II} and Sr^{II} in $[CaL^1(ClO_4)_2]$ and $[SrL^1(ClO_4)_2]$ respectively, as found previously [10,11] for complexes of these ions with related macrocyclic ligands. Significantly, the tetraphenylborate salts of the calcium(II) and strontium(II) complexes separated as dihydrates which showed $\nu(OH)$ as a moderately sharp absorption at 3 440—3 550 cm^{-1} suggestive of co-ordination and therefore of eight-co-ordinate structures. The same applies to $\nu(OH)$ of $[BaL^1(NCS)_2]{\cdot}H_2O$ and the two alcoholates of Ba^{II}. In all three compounds, the barium ion is probably nine-co-ordinate; in the first, it is bonded to the macrocycle, two thiocyanates, and water; in the alcoholates, to the macrocycle, two alcoholates, and water.



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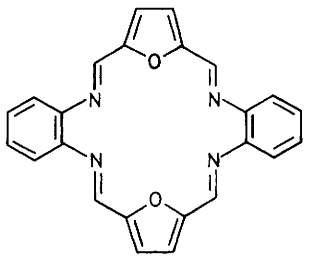

L^3

Where solubility permitted, the electrical conductances of the complexes in acetonitrile (Table 1) correspond to uni-bivalent electrolyte behaviour indicating that the co-ordinated anions are displaced by solvent.

General Discussion.—The results described extend earlier observations [2–4,12–14] relating to the usefulness of the larger alkaline-earth-metal ions as templates for the high-yield synthesis of large ring polyimines. The special effectiveness of these metal ions as templates is clearly associated with the thermodynamic stability of the complexes they form with the product macrocycles. This stability is, in turn, related to the match in sizes of the metal ions with respect to the cavity dimensions of the macrocycle, as well as to the absence of strong stereochemical preferences on the part of these ' hard ' metal ions. The importance of the size of the template ion is dramatically shown by the failure of the Mg^{2+} ion to act as template for the synthesis. It is also of interest in this regard that while Ca^{2+} and Sr^{2+} form only 1 : 1 complexes, Ba^{2+} forms both 1 : 1 and 2 : 1 complexes. However, this is unlikely to be simply a size effect since we have previously shown [15] that in a barium(II) complex of the 18-membered inner-ring macrocycle L^2 the metal atom is bonded in a relatively planar manner to all six nitrogen atoms (maximum deviation from the ' BaN_6 ' plane 0.07 Å), as well as to two axially sited bidentate perchlorate ions. The reason for the formation of 2 : 1 complexes by Ba^{2+} but not Ca^{2+} or Sr^{2+} may owe more to the tendency of the Ba^{2+} ion towards higher co-ordination numbers so that in the absence of potentially co-ordinating anions such as thiocyanate or perchlorate this is best achieved by binding a second ligand molecule. While the resulting 2 : 1 ligand : metal stoicheiometry might suggest a twelve-co-ordinate sandwich structure such as is found [16] for a barium(II) complex of the smaller planar (less flexible) macrocycle L^3, this has been shown not to be the case. Instead the two macrocycle molecules provide only nine of the total of eleven donor atoms in the complex. The reason for this unusual structure is probably that a twelve-co-ordinate sandwich structure would introduce unacceptably close contacts between atoms of the two non-planar macrocycles. It seems that the need to achieve a strain-free high-co-ordination-number configuration is best met by sexidentate chelation on the part of one macrocycle and tridentate chelation on the part of the other, together with the binding of two water molecules.

The stability of the complexes of these ' hard ' metal ions with an uncharged ligand consisting mainly of relatively ' soft ' unsaturated nitrogen donors is somewhat unexpected, and clearly owes much to the high ligand denticity. There is no evidence for ligand dissociation in acetonitrile solution, even in the case of the 2 : 1 barium(II) complex in which one macrocycle is bound only by one furan di-imine moiety as conclusively proven by the ^{1}H n.m.r. measurements. Moreover, the relatively high activation barrier (*ca.* 62.5 kJ mol^{-1}) for equilibration between equivalent configurations of the complex cation is again unexpected in view of prevalent notions regarding the low thermodynamic stability and high kinetic lability of complexes of the heavier alkaline-earth-metal ions in polar solvents.

Despite the relatively high stability of these complexes, the co-ordinated alkaline-earth-metal ions may readily be replaced by other metal ions including $\mathrm{Pb^{II}}$, $\mathrm{Ag^{I}}$, $\mathrm{Co^{II}}$, $\mathrm{Cu^{I}}$, $\mathrm{Cu^{II}}$, and $\mathrm{Zn^{II}}$. As mentioned earlier, $\mathrm{Pb^{II}}$ is also a template for the macrocycle synthesis but the others are not. In the case of $\mathrm{Pb^{II}}$ and $\mathrm{Ag^{I}}$, the products of the transmetallation are mononuclear, while for the (smaller) transition-metal ions the resulting complexes are binuclear and differ from the alkaline-earth-metal complexes in that the furan oxygen atoms are not co-ordinated.

Some dicopper complexes have already been reported briefly;[3,4] a description of the other derivatives is beyond the scope of this paper and will be published separately. However, we draw attention at this stage to the usefulness of the heavier alkaline-earth-metal ions in the synthesis of binuclear transition-metal complexes not readily accessible by other routes.

Experimental

Preparation of the Complexes.—2,5-Diformylfuran was prepared as described in the literature[17] while 1,3-diaminopropane was used as supplied commercially without further purification.

$[\mathrm{BaL^1(ClO_4)_2}]\cdot\mathrm{ROH}$ (R = Me *or* Et). 2,5-Diformylfuran (0.024 mol), 1,3-diaminopropane (0.024 mol), and $\mathrm{Ba(ClO_4)_2}$ were dissolved in ROH (R = Me or Et) (300 cm^3) and heated to reflux for 1 h. For R = Et the product started to separate after about 10 min, while for R = Me the product separated on standing overnight at room temperature. Yield 60—65%.

$[\mathrm{BaL^1(NCS)_2}]\cdot\mathrm{H_2O}$. 2,5-Diformylfuran (0.004 mol), 1,3-diaminopropane (0.004 mol), and $\mathrm{Ba(NCS)_2}$ (0.002 mol) were refluxed in MeOH (100 cm^3) for 30 min. White crystals of product separated in 10 min. Yield 75%.

$[\mathrm{BaL^1_2(MeCN)_2}][\mathrm{BPh_4}]_2$. Sodium tetraphenylborate (0.06 mol) was added to a stirred solution of $[\mathrm{BaL^1(ClO_4)_2}]\cdot\mathrm{EtOH}$ (0.007 mol) in warm MeCN–EtOH (2 : 1, 75 cm^3). On standing overnight, white crystals of the product separated. A further batch of crystals was obtained on concentration of the filtrate. Yield 60%.

$[\mathrm{BaL^1_2(H_2O)_2}][\mathrm{Co(NCS)_4}]_2$. Cobalt(II) thiocyanate (0.0024 mol) dissolved in the minimum quantity of EtOH was filtered into a hot stirred solution of $[\mathrm{BaL^1(ClO_4)_2}]\cdot\mathrm{EtOH}$ (0.0024 mol) in EtOH–MeCN (2 : 1, 90 cm^3). Red-brown crystals of $\mathrm{Co_2L^1(OEt)(NCS)_3}$[18] separated after several hours. On leaving the filtrate overnight, dark blue crystals of the product separated in 45% yield.

$[\mathrm{SrL^1(ClO_4)_2}]$, $[\mathrm{CuL^1(ClO_4)_2}]$, *and* $\mathrm{PbL^1(ClO_4)_2}$. These were prepared as described for $[\mathrm{BaL^1(ClO_4)_2}]\cdot\mathrm{EtOH}$ in EtOH. Yields were 62, 95, and 90% respectively.

$[\mathrm{SrL^1(H_2O)_2}][\mathrm{BPh_4}]_2$ *and* $[\mathrm{CaL^1(H_2O)_2}][\mathrm{BPh_4}]_2$. These were

Table 4. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ba(1)	4 496(0)	2 692(0)	−465(0)
Co	−1 602(1)	4 149(1)	2 424(1)
S(1)	−1 539(3)	1 863(2)	2 952(2)
S(2)	−1 039(3)	5 905(2)	3 809(1)
S(3)	1 383(3)	4 852(2)	1 559(2)
S(4)	−5 455(4)	4 421(3)	1 064(3)
N(1)	−1 526(9)	3 209(6)	2 652(4)
N(2)	−1 405(10)	4 778(6)	3 099(4)
N(3)	−314(10)	4 372(6)	2 066(4)
N(4)	−3 183(9)	4 278(5)	1 833(4)
C(1)	−1 541(10)	2 647(7)	2 776(5)
C(2)	−1 239(10)	5 251(7)	3 386(5)
C(3)	386(11)	4 570(6)	1 853(5)
C(4)	−4 116(13)	4 334(6)	1 502(7)
N(1A)	5 355(8)	3 540(4)	−1 358(3)
C(2A)	6 238(10)	3 941(6)	−1 169(5)
C(3A)	6 915(9)	3 973(6)	−529(5)
O(4A)	6 644(5)	3 491(3)	−161(3)
C(5A)	7 374(9)	3 610(5)	413(4)
C(6A)	7 277(9)	3 124(6)	861(4)
N(7A)	6 451(7)	2 688(4)	738(3)
C(8A)	6 489(10)	2 182(6)	1 228(4)
C(9A)	5 521(11)	2 364(7)	1 540(5)
C(10A)	4 224(10)	2 101(6)	1 198(5)
N(11A)	3 650(9)	2 559(5)	682(4)
C(12A)	2 785(12)	2 900(7)	726(6)
C(13A)	2 083(11)	3 318(6)	233(5)
O(14A)	2 408(6)	3 324(4)	−289(3)
C(15A)	1 588(11)	3 728(6)	−698(6)
C(16A)	1 749(13)	3 799(6)	−1 308(6)
N(17A)	2 559(9)	3 489(5)	−1 445(4)
C(18A)	2 526(14)	3 535(8)	−2 107(5)
C(19A)	3 556(12)	3 896(7)	−2 200(5)
C(20A)	4 785(12)	3 533(6)	−2 023(5)
C(21A)	8 094(9)	4 146(6)	419(5)
C(22A)	7 771(10)	4 394(6)	−194(5)
C(23A)	1 061(12)	3 715(8)	162(8)
C(24A)	768(12)	3 971(8)	−433(8)
N(1B)	2 448(8)	585(4)	−590(4)
C(2B)	2 364(11)	176(6)	−1 026(5)
C(3B)	3 407(11)	−20(5)	−1 195(5)
O(4B)	4 512(6)	245(3)	−848(3)
C(5B)	5 377(11)	56(6)	−1 110(6)
C(6B)	6 565(13)	309(7)	−816(7)
N(7B)	6 817(8)	729(5)	−394(5)
C(8B)	8 094(10)	961(6)	−151(6)
C(9B)	8 172(10)	1 698(6)	−28(6)
C(10B)	7 872(11)	2 137(7)	−589(7)
N(11B)	6 548(9)	2 111(5)	−908(5)
C(12B)	6 307(13)	1 876(6)	−1 414(7)
C(13B)	5 041(16)	1 741(6)	−1 789(6)
O(14B)	4 173(7)	1 886(3)	−1 522(3)
C(15B)	3 051(15)	1 684(6)	−1 904(5)
C(16B)	2 039(12)	1 727(6)	−1 669(6)
N(17B)	2 137(8)	1 948(5)	−1 153(4)
C(18B)	1 058(10)	1 937(6)	−937(6)
C(19B)	1 298(9)	1 516(6)	−376(5)
C(20B)	1 365(10)	781(6)	−450(5)
C(21B)	3 607(17)	−387(7)	−1 646(6)
C(22B)	4 866(16)	−334(7)	−1 584(7)
C(23B)	3 226(21)	1 437(8)	−2 413(7)
C(24B)	4 454(20)	1 456(7)	−2 355(6)
O(200)	4 746(6)	1 376(3)	−78(3)
O(300)	4 432(11)	4 159(7)	−208(7)

Table 5. Molecular dimensions (distances in Å, angles in °) in the barium co-ordination sphere

Ba(1)–N(11B)	3.084(12)	Ba(1)–N(1A)	3.065(9)	Ba(1)–N(11A)	3.107(10)	Ba(1)–O(200)	2.767(6)
Ba(1)–O(14B)	2.861(7)	Ba(1)–O(4A)	2.859(6)	Ba(1)–O(14A)	2.861(8)	Ba(1)–O(300)	2.997(14)
Ba(1)–N(17B)	3.097(8)	Ba(1)–N(7A)	3.016(7)	Ba(1)–N(17A)	3.109(9)		

N(11B)–Ba(1)–O(14B)	54.40(24)	O(4A)–Ba(1)–N(11A)	108.15(21)	O(14B)–Ba(1)–O(200)	73.52(19)
N(11B)–Ba(1)–N(17B)	107.13(25)	N(7A)–Ba(1)–N(11A)	63.33(23)	N(17B)–Ba(1)–O(200)	72.55(20)
O(14B)–Ba(1)–N(17B)	54.56(25)	N(11B)–Ba(1)–O(14A)	168.86(24)	N(1A)–Ba(1)–O(200)	136.18(23)
N(11B)–Ba(1)–N(1A)	62.91(26)	O(14B)–Ba(1)–O(14A)	118.15(20)	O(4A)–Ba(1)–O(200)	116.95(18)
O(14B)–Ba(1)–N(1A)	73.60(21)	N(17B)–Ba(1)–O(14A)	68.58(23)	N(7A)–Ba(1)–O(200)	73.82(20)
N(17B)–Ba(1)–N(1A)	109.39(23)	N(1A)–Ba(1)–O(14A)	108.12(23)	N(11A)–Ba(1)–O(200)	70.77(23)
N(11B)–Ba(1)–O(4A)	66.00(22)	O(4A)–Ba(1)–O(14A)	115.26(20)	O(14A)–Ba(1)–O(200)	112.61(22)
O(14B)–Ba(1)–O(4A)	113.92(22)	N(7A)–Ba(1)–O(14A)	107.50(22)	N(17A)–Ba(1)–O(200)	134.94(22)
N(17B)–Ba(1)–O(4A)	164.07(22)	N(11A)–Ba(1)–O(14A)	54.53(22)	N(11B)–Ba(1)–O(300)	120.2(3)
N(1A)–Ba(1)–O(4A)	54.74(19)	N(11B)–Ba(1)–N(17A)	114.06(29)	O(14B)–Ba(1)–O(300)	135.7(3)
N(11B)–Ba(1)–N(7A)	82.42(25)	O(14B)–Ba(1)–N(17A)	77.43(23)	N(17B)–Ba(1)–O(300)	120.13(29)
O(14B)–Ba(1)–N(7A)	131.17(22)	N(17B)–Ba(1)–N(17A)	62.57(25)	N(1A)–Ba(1)–O(300)	68.0(3)
N(17B)–Ba(1)–N(7A)	140.79(24)	N(1A)–Ba(1)–N(17A)	62.06(26)	O(4A)–Ba(1)–O(300)	58.40(29)
N(1A)–Ba(1)–N(7A)	108.71(22)	O(4A)–Ba(1)–N(17A)	106.03(23)	N(7A)–Ba(1)–O(300)	82.86(29)
O(4A)–Ba(1)–N(7A)	54.48(21)	N(7A)–Ba(1)–N(17A)	148.54(24)	N(11A)–Ba(1)–O(300)	83.2(3)
N(11B)–Ba(1)–N(11A)	136.45(26)	N(11A)–Ba(1)–N(17A)	109.01(27)	O(14A)–Ba(1)–O(300)	57.8(3)
O(14B)–Ba(1)–N(11A)	133.67(23)	O(14A)–Ba(1)–N(17A)	54.81(25)	N(17A)–Ba(1)–O(300)	65.7(3)
N(17B)–Ba(1)–N(11A)	86.80(25)	N(11B)–Ba(1)–O(200)	74.54(25)	O(200)–Ba(1)–O(300)	150.7(3)
N(1A)–Ba(1)–N(11A)	151.07(23)				

prepared in *ca.* 70% yield by metathesis from solutions of the corresponding barium compound.

Crystallography.—Crystal data. $[BaL^1_2(H_2O)_2][Co(NCS)_4]$, $C_{40}H_{44}BaCoN_{12}O_6S_4$, $M = 1\,172.38$, Monoclinic, $a = 11.57(1)$, $b = 19.99(1)$, $c = 23.18(1)$ Å, $\beta = 107.5(1)°$, $U = 5\,113.0$ Å^3, $D_m = 1.51$, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $F(000) = 2\,360$, Mo-K_α radiation $\lambda = 0.7107$ Å, $\mu = 16.63$ cm^{-1}, space group $P2_1/c$, absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$.

Structure determination. The crystal was mounted on a Stoe STADI2 diffractometer and data were collected *via* a variable width ω scan. Background counts were 20 s and a scan rate of 0.0330° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 6 784 Independent reflections with $2\theta < 45°$ were measured of which 4 329 having $I > 3\sigma(I)$ were used in subsequent refinement. The structure was solved by the Patterson method. The positions of the remaining non-hydrogen atoms were obtained from Fourier synthesis. The hydrogen atoms were positioned in trigonal or tetrahedral positions and those in the same part of the macrocycles were given a common thermal parameter which was refined.

The structure was then refined using full-matrix least squares with SHELX 76.[19] The weighting scheme used was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $(\sin \theta/\lambda)$. This was $w = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics. The non-hydrogen atoms were refined anisotropically. Scattering factors were taken from ref. 20. Calculations were made using SHELX 76 on the CDC 7600 computer at the University of Manchester Computer Centre. The final R was 0.062 (R' 0.065).

Atomic co-ordinates are listed in Table 4, details of the most important interatomic distances in Table 5.

Physical Measurements.—I.r. spectra were recorded in the range 4 000—200 cm^{-1} as KBr discs and as Nujol mulls using Perkin-Elmer 577 and 598 grating spectrometers. Proton n.m.r. spectra were determined in CD_3CN solution using a Bruker WM 250 Fourier-transform instrument with tetramethylsilane as internal standard. A conductivity cell of constant 0.0352, constructed from bright platinum electrodes, was employed in conjunction with a conventional resistance/capacitance bridge. Mass spectra were recorded using either A.E.I. MS 30 or MS 902 spectrometers, at an ionising voltage of 70 eV (*ca.* 1.12×10^{-17} J).

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