Complexation of Alkali- and Alkaline-earth-metal Cations by a Conjugated Tetraimine Macrocyclic Ligand: Synthesis, Sodium-23 Nuclear Magnetic Resonance Spectra, and the *X*-Ray Structure of a Twelve-co-ordinate Barium(II) 'Sandwich' Complex *

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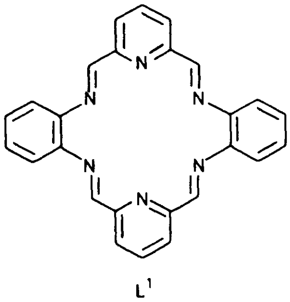
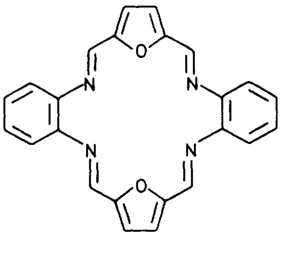
Reaction of 2,5-diformylfuran with *o*-phenylenediamine in methanol in the presence of a salt of K^+, Ca^{2+}, Ba^{2+}, or Pb^{2+} yields complexes of the 18-membered conjugated macrocyclic tetraimine L^2 derived from the cyclic (2 + 2) condensation of 2 mol of dialdehyde with 2 mol of diamine. The complexes all have a 1 : 1 ligand : metal stoicheiometry except those of Ba^{2+} which contain two macrocyclic ligands per metal atom. Crystals of $[BaL^2{}_2][BPh_4]_2$ are monoclinic with $a = 23.25(1)$, $b = 14.92(1)$, $c = 23.69(1)$ Å, $\beta = 101.0(1)°$, $Z = 4$, and space group $A2/a$ (no. 15). 1 468 Reflections above background were measured by diffractometer and refined to R 0.10. In the $[BaL^2{}_2]^{2+}$ cation the metal atom is sandwiched between two almost parallel 'N_4' planes 2.6 Å apart, the furan rings being tilted by 24.2 and 26.3° with respect to these planes. The barium atom is twelve-co-ordinate being bonded to the four nitrogen and two oxygen atoms of each ring [Ba–N 2.96(3)—3.08(3), Ba–O 2.91(2)—3.02(3) Å]. The smaller ions Li^+, Na^+, and Mg^{2+} are ineffective as templates for the macrocycle synthesis but complexes of Na^+ (and of $[NH_4]^+$) could be prepared by neutralisation of the diacid salt $[H_2L^2][ClO_4]_2$ with aqueous NaOH (or aqueous NH_3). The free macrocycle could not be isolated although 'recrystallisation' of the complexes of Na^+ or $[NH_4]^+$ from hot alcohol afforded the metal-free alcohol addition products $L^2 \cdot 2MeOH$ and $L^2 \cdot EtOH$. The complexes have been characterised by i.r., u.v.–visible, mass, and ^1H n.m.r. spectra. Sodium-23 n.m.r. spectra of equimolar solutions of $NaL^2(ClO_4)$ and $NaClO_4 \cdot H_2O$ in [$^2H_6$]dimethyl sulphoxide showed separate resonances at temperatures below about 30 °C indicating slow exchange of Na^+ between macrocycle and solvent. The free energy of activation for exchange was estimated to be 59 kJ mol^{-1}. The stoicheiometries and relative stabilities of the complexes are interpreted in terms of the sizes of the metal ions in relation to the fixed hole size of the macrocycle.

The co-ordination chemistry of the heavier alkali-metal and alkaline-earth-metal ions is almost entirely restricted to their complexes with chelating ligands having 'hard' oxygen or oxygen + saturated nitrogen donor atoms; the best known and most important of these are the crown ethers [1] and cryptands.[2] Stable complexes with ligands containing 'soft' donor atoms are by comparison extremely rare. We have recently reported [3] some complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+} with the planar, conjugated, sexidentate 'N_6' macrocycle L^1. The stability of the complexes of these metal ions with a ligand containing only unsaturated (sp^2 hybridised) nitrogen atoms and involving a high degree of electron delocalisation was unexpected.

In this paper we describe the results of an extension of the study to complexes of the related conjugated 'N_4O_2' macrocycle L^2 having furan instead of pyridyl groups. It is shown that this macrocycle forms stable complexes not only with the larger alkaline-earth-metal ions but also with several of the alkali-metal ions, and with the ammonium and lead(II) ions. The relationships between the sizes (and charges) of the metal ions and the macrocycle 'hole' are examined and the *X*-ray structure of a sandwich complex of Ba^{2+} is described.



L^1



L^2

Results and Discussion

Synthesis of the Complexes.—The macrocycle L^2 was synthesised *via* a (2 + 2) condensation of 2,5-diformylfuran with *o*-phenylenediamine using a metal ion as template, the macrocycle being isolated as the metal complex (Table 1). The most effective templates were salts (perchlorate, halide, or thiocyanate) of K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} (see Experimental section for details); $Pb(ClO_4)_2 \cdot 3H_2O$ was also an effective template. For these metal complexes the synthesis was remarkably facile involving, simply, reaction of equimolar quantities of dialdehyde and diamine in refluxing methanol in the presence of the appropriate metal salt for periods ranging from *ca.* 5 min to *ca.* 2 h depending on the metal ion. The crystalline orange or red products separated in 50—90% yield.

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* *Supplementary data available* (No. SUP 23650, 18 pp.): thermal parameters, H-atom co-ordinates, macrocycle and anion dimensions, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical, mass spectral, and electrical conductance data for the complexes

	Analysis (%)								
	Found			Calc.					
	C	H	N	C	H	N	$\tilde{\nu}_{max.}$ ^{a}/cm^{-1}	m/e of P^+	Λ ^{b}/S cm^2 mol^{-1}
$[BaL^2_2][ClO_4]_2$	51.2	3.0	10.0	51.4	2.9	10.0	30 200 (7.3)		268
$[BaL^2_2][BPh_4]_2$								392	
$[BaL^2_2][NCS]_2$	57.6	3.3	13.2	57.8	3.1	13.5	30 200 (6.9)	392	286
$SrL^2(ClO_4)_2{\cdot}H_2O$	41.4	2.6	8.0	41.4	2.6	8.0	30 100 (3.5)		285
$CaL^2(ClO_4)_2{\cdot}H_2O$	44.2	2.9	8.5	44.4	2.8	8.6	29 600 (3.8)		279
$CaL^2(NCS)_2$	56.0	3.0	14.9	56.9	2.8	15.3	29 600 (3.7)	392	*c*
$KL^2(ClO_4)$	54.5	3.0	10.6	54.3	3.0	10.6	30 100 (3.7)		144
$KL^2(NCS)$	61.2	3.4	13.9	61.3	3.3	14.3	30 100 (3.7)	392	164
KL^2I	51.8	3.1	10.2	51.6	2.9	10.0	29 600 (4.0)	392	130
$NaL^2(ClO_4)$	55.8	3.2	10.7	56.0	3.1	10.9	29 400 (4.2)		153
$NaL^2(NCS)$	63.4	3.4	14.7	63.4	3.7	14.8	29 400 (3.7)	392	*c*
$[(NH_4)L^2][ClO_4]$	57.1	4.0	13.5	56.5	4.0	13.7			140
$PbL^2(ClO_4)_2{\cdot}H_2O$	35.3	2.4	6.7	35.3	2.2	6.9	29 300 (4.5)		*c*
$PbL^2(NCS)_2$	43.6	2.3	11.5	43.6	2.3	11.7	29 700 (4.4)	392	*c*
$[H_2L^2][ClO_4]_2$	48.6	3.1	9.4	48.6	3.1	9.4			*c*
$L^2{\cdot}2MeOH$	68.1	5.7	12.2	68.0	5.6	12.1		392, 394	
$L^2{\cdot}EtOH$	71.2	5.1	12.8	71.1	5.0	12.9		392, 294	

[a] In acetonitrile solution. Values of $10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1} are given in parentheses. [b] For 10^3 mol dm^{-3} MeCN solutions at 20 °C. [c] Insoluble.

Derivatives containing anions other than that used in the template synthesis were readily obtained by metathesis. Salts of Rb^+ and Cs^+ also appeared to act as templates for the macrocycle synthesis giving orange microcrystalline products having i.r. spectra (see below) virtually identical to those of the complexes mentioned above. However, analytical data indicated variable metal : macrocycle ratios in different preparations and because of this uncertain stoicheiometry these complexes are not considered further in this report.

The necessity for the presence of the template metal ion was dramatically shown by the observation that in its absence the reaction products were oils of indefinite composition. Salts of Li^+, Na^+, and Mg^{2+} were ineffective as templates, the products of these reactions being oils or gums or dark coloured amorphous powders, again of indefinite composition, and showing i.r. absorptions at *ca.* 1 700 cm^{-1} indicative of unreacted carbonyl groups. However, complexes of Na^+ and $[NH_4]^+$, but not of Li^+ or Mg^{2+}, could be prepared by a different route as described later.

Characterisation of the Complexes.—The complexes prepared are listed in Table 1 along with analytical and selected physical data. They are of two types. Those of Ba^{2+} have a 2 : 1 macrocycle : metal stoicheiometry while the remainder have a 1 : 1 ligand : metal ratio. The crystalline complexes have low to moderate solubility in polar organic solvents such as dimethyl sulphoxide or acetonitrile in which they are uni-univalent or uni-bivalent electrolytes according to the valence of the cation (Table 1).

Mass spectra of several of the thiocyanate and tetraphenylborate complexes were measured. Parent-ion peaks were not observed. Instead the spectra showed strong peaks at *m/e* 392 corresponding to the free macrocycle. No peaks of significant intensity at higher *m/e* values were observed.

The complexes all showed strong similarities in their physical properties, i.r., u.v.–visible, and ^{1}H n.m.r. spectra. Apart from variations due to the different anions, and the presence of water in some cases, the i.r. spectra are nearly identical. In particular, they showed the strong band at 1 600—1 610 cm^{-1} characteristic of the co-ordinated C=N group adjacent to a phenyl ring. None of the spectra exhibited any absorption at 3 250—3 400 or at *ca.* 1 700 cm^{-1} which could be attributed to unreacted amine or carbonyl functions.

The i.r. spectra of the perchlorate complexes fall into two distinct classes according to whether the ClO_4 ν_3 and ν_4 asymmetric stretching and bending modes occurring at *ca.* 1 090 and at *ca.* 620 cm^{-1} are split. The bis(macrocycle) complex $[BaL^2_2][ClO_4]_2$ showed only unsplit ν_3 and ν_4 bands as did also the lead(II) and ammonium complexes. All of the remaining perchlorate complexes showed distinct splitting of both these bands, clearly indicating perchlorate co-ordination. We are unable to distinguish, with confidence, between uni- and bi-dentate co-ordination modes, however. For those complexes containing water the ν(OH) stretch was observed as a fairly sharp band at 3 450—3 500 cm^{-1} rather than as the broad structureless band usually associated with lattice water; we therefore suggest that in these complexes the water molecule is co-ordinated to the metal ion. For the thiocyanates, ν_{asym}(NCS) occurred at 2 055 cm^{-1} in $[BaL^2_2][NCS]_2$ and $(NH_4)L^2(NCS)$ but at somewhat higher frequencies in the other complexes, and is therefore probably co-ordinated, *via* the nitrogen atom, in the latter cases.

As found for the i.r. spectra there was little dependence of the electronic spectra of the complexes on the nature of the cation. All the spectra consisted of a strong band between 29 000 and 30 500 cm^{-1} ($\varepsilon = 3 \times 10^4$—$5 \times 10^4$ dm^3 mol^{-1} cm^{-1} in CH_3CN solution) and a shoulder of variable intensity on the low-energy side of the main band. The position and intensity of the principal absorption band are consistent with assignment to a $\pi \longrightarrow \pi^*$ transition of the complexed macrocycle. The insensitivity of the energy of the transition to change in the nature of the Group 1A or 2A cation is in keeping with a predominantly coulombic (ion–dipole) metal–macrocycle interaction.

Proton n.m.r. data for a selection of the complexes [$(CD_3)_2SO$ solution] are in Table 2. The chemical shifts and integrated relative intensities are fully consistent with the proposed macrocycle structure. The simplicity of the spectra may be taken as evidence against any significant dissociation of the complexes into free metal ion and free macrocycle in solution (see also below).

The collective evidence of the analytical and spectroscopic results described above is sufficient to prove that the compounds under consideration are complexes of the 18-membered

Table 2. Proton n.m.r. data for the complexes in $(CD_3)_2SO$ solution; s = singlet, m = multiplet

	δ/p.p.m.		
Complex	Imine protons	Furan-ring protons	Phenyl-ring protons
$[BaL^2_2][ClO_4]_2$	8.24(s)	6.80(s)	7.20(m)
$SrL^2(ClO_4)_2\cdot H_2O$	8.60(s)	7.30(s)	7.40(m)
$CaL^2(ClO_4)_2\cdot H_2O$	8.25(s)	6.90(s)	7.05(m)
$KL^2(ClO_4)$	8.07(s)	6.72(s)	7.05(m)
$NaL^2(ClO_4)$	8.50(s)	7.12(s)	7.35(m)
$PbL^2(ClO_4)_2\cdot H_2O$	8.80(s)	7.23(s)	7.40(m)

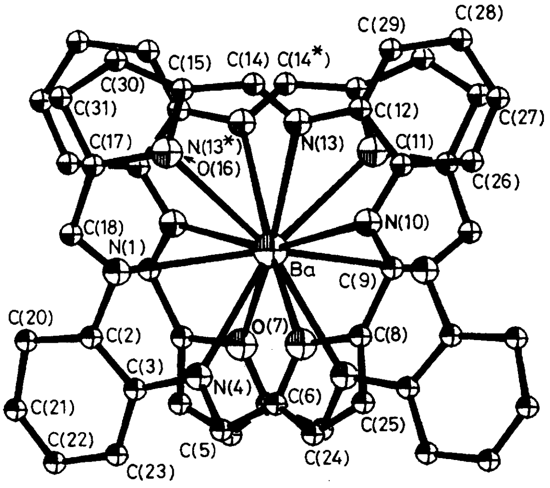

Figure 1. The structure of $[BaL^2_2]^{2+}$

macrocycle L^2 derived from the cyclic (2 + 2) condensation of 2,5-diformylfuran with *o*-phenylenediamine. This conclusion is confirmed by the results of the *X*-ray diffraction study of the 'sandwich' complex $[BaL^2_2][BPh_4]_2$ given in the following section. While the detailed structures of the 1 : 1 complexes of the smaller metal ions are unknown, there can be little doubt that in most of these cases the metal ion sits within the macrocycle cavity being bonded to all six donor atoms with one or two additional ligands (H_2O, ClO_4^-, I^-, or NCS^-) occupying axial sites with respect to the hexagonal 'MN_4O_2' plane.

The Structure of $[BaL^2_2][BPh_4]_2$.—The unit cell consists of four $[BaL^2_2]^{2+}$ cations and eight $[BPh_4]^-$ anions. The cation has imposed C_2 symmetry with the barium atom on the two-fold axis. Two views of the cation are given in Figures 1 and 2 together with the atomic numbering scheme. The barium atom is twelve-co-ordinate, each macrocycle using all six donor atoms. The Ba–N bond distances range from 2.96(3) to 3.08(3) Å and the Ba–O distances from 2.91(2) to 3.02(3) Å. Despite its conjugated nature there are notable deviations from planarity in the co-ordinated macrocycles (see least-squares planes in Table 3). The four nitrogen atoms of each macrocycle form a plane but the two furan rings are tilted by 24.2 and 26.3° with respect to the 'N_4' plane, the two oxygen atoms lying on the opposite side of the plane from the barium atom (see Figure 2). The two 'N_4' planes on either side of the two-fold axis are parallel (angle of intersection 1.1°) and are only *ca.* 2.6 Å apart. This leads to some surprisingly close contacts between the two macrocycles in the $[BaL^2_2]^{2+}$ cation.

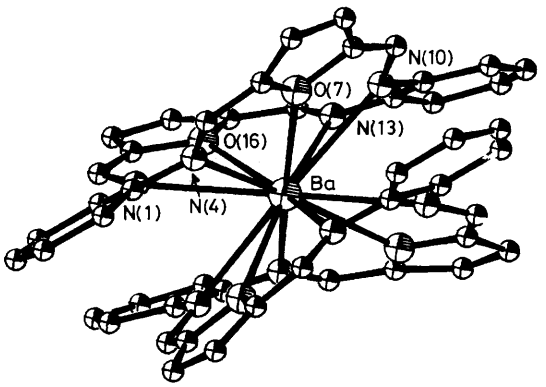

Figure 2. The structure of $[BaL^2_2]^{2+}$

Table 3. Least-squares-planes calculations. Distances of atoms from the planes are given in Å. Atoms not contributing to the plane are italicised

Plane 1: N(1) 0.03, N(4) −0.03, N(10) 0.03, N(13) −0.03, *O*(7) 0.49, *O*(17) 0.43, *Ba* −1.31

Plane 2: C(15) 0.03, O(16) −0.04, C(17) 0.03, C(30) −0.05, C(31) −0.00

Plane 3: C(6) −0.00, O(7) 0.03, C(8) −0.04, C(24) −0.03, C(25) 0.04

Plane 4: Ba, O(7), O(16) 0.00

Angles (°) between planes: 1—2, 24.6; 1—3, 26.3; 2—3, 50.8; 1—4, 89.3; 1—1*, 1.1; 4—4*, 75.0

* Represents the symmetry-related plane.

Those less than 3.2 Å are N(10) ··· N(1) 2.87 Å, O(7) ··· N(4) 3.15 Å, O(16) ··· N(13) 3.17 Å, and O(16) ··· C(12) 3.17 Å. It is, of course, possible that there is some disorder associated with the cation, as with the anions, but this was not discernible.

The geometry of the co-ordination sphere of the barium atom is illustrated in Figure 3. The two macrocycles above and below the metal atom are in a staggered configuration with an angle of 75° from an eclipsed configuration. An angle of 90° would produce a form with D_{2d} symmetry (2:4:4:2) with the S_4 axis coincident with the axis of rotation, *i.e.* perpendicular to the plane of Figure 3. In Figure 4, we show the relationship between this geometry and the eight-co-ordinate dodecahedron[4,*] which also has D_{2d} symmetry. The four oxygen atoms occupy positions equivalent to the A sites of the dodecahedron. Each B site is then occupied by two nitrogen atoms in pairs, N(1), N(4) and N(10), N(13) [Figure 4(*a*)]. Thus, the midpoints of these nitrogen pairs (called N/N) are coincident with the B sites in the dodecahedron [Figure 4(*b*)]. Of course, in the dodecahedron the angles made by A and B sites with the S_4 axis are, on average, 36.9 (A) and 69.5° (B) whereas, for the present structure, the angles are 53.2° for O and 61.6° for N/N. As discussed previously,[4] the reaction pathway for the conversion of the dodecahedron into the cube involves these two angles becoming equivalent at 54.7°. It might appear, therefore, that the present structure is closer to the cube limit of the pathway but this is not the case as the root mean square (r.m.s.) deviations are, respectively, 0.09 (D_{2d}) and 0.19 Å (O_h). The structure fits poorly (r.m.s. 0.26 Å)

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* For the original discussion of the dodecahedron see J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1962, **1**, 235.

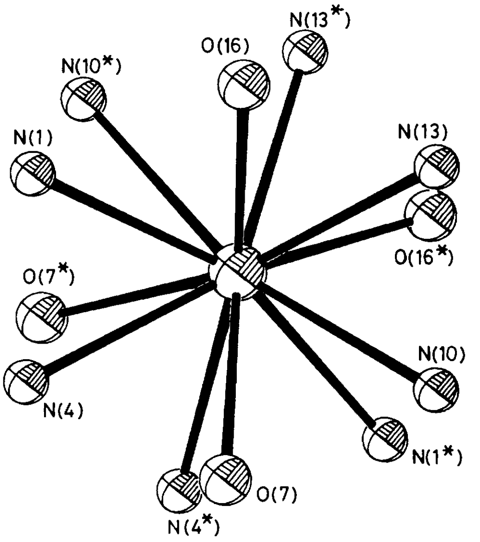


Figure 3. The co-ordination sphere of the Ba^{2+} ion in $[BaL^2{}_2]^{2+}$

to the most usual twelve-co-ordinate polyhedron, *viz.* the icosahedron.

Metal-free Derivatives of the Macrocycle and the Preparation of Sodium and Ammonium Complexes.—It has already been noted that in the metal template reactions the macrocycle could be isolated only in the complexed state. In the course of attempts to liberate the free macrocycle by treatment of its complexes with acid, followed by neutralisation with base, a number of metal-free derivatives were obtained. Treatment of solutions of the complexes with $HClO_4$ caused immediate precipitation of a purple solid. (The same material was obtained on attempted replacement of the alkali- or alkaline-earth-metal ions by Fe^{III} or Cu^{II}.) The purple solid analysed as the diperchlorate salt $[H_2L^2][ClO_4]_2$ of the doubly protonated macrocycle. (**CAUTION**: This material detonated on one occasion on contact with a hot spatula.) Because of its virtual insolubility in all common solvents, physical measurements on this compound were restricted to its i.r. spectrum. The occurrence of a strong broad ν(NH) absorption at 3 190 cm^{-1} and of two ν(C=N) bands at 1 645 and 1 615 cm^{-1} are consistent with protonation of two of the four imine nitrogen atoms.

When a suspension of the $[H_2L^2][ClO_4]_2$ in MeOH was treated with a 2—3-fold excess of aqueous NaOH or aqueous NH_3 the purple solid dissolved on warming and stirring. On subsequent cooling orange crystals of $NaL^2(ClO_4)$ or $(NH_4)L^2(ClO_4)$ separated. If, however, the reaction mixture was heated to reflux, different (yellow) crystals containing no sodium (or ammonium) or perchlorate ions were obtained. It will be shown below that this product is a dimethanol addition product of the macrocycle, $L^2\cdot2MeOH$. The same material was obtained on attempted recrystallisation of $NaL^2(ClO_4)$ or $(NH_4)L^2(ClO_4)$ from hot methanol. Use of ethanol as 'recrystallisation' solvent afforded the mono-ethanol adduct $L^2\cdot EtOH$.

When the neutralisation of the acid salt $[H_2L^2][ClO_4]_2$ was carried out in methanol using LiOH the product was again $L^2\cdot2MeOH$. No pure products could be isolated from reactions employing $Mg(OH)_2$. It thus appears that while complexes of L^2 with Li^+, Mg^{2+}, Na^+, and $[NH_4]^+$ cannot be prepared by template methods, complexes of Na^+ and $[NH_4]^+$, but not the smaller Li^+ or Mg^{2+}, may be prepared from the macrocycle (as its diacid salt) once it has been formed by use of another metal ion as template. The above observations further suggest that the complex of Na^+ (and of $[NH_4]^+$) is less stable than those of K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} since the latter could be recovered unchanged from refluxing alcohol. As discussed below this is probably due both to the low charge and relatively small size of the Na^+ ion.

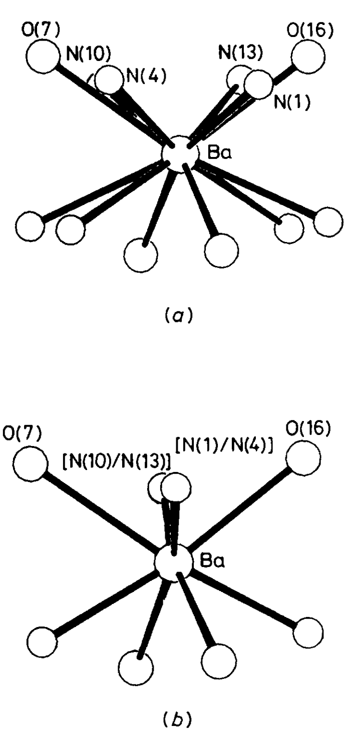
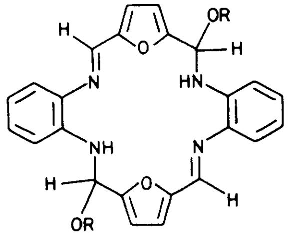


Figure 4. The barium co-ordination sphere showing the S_4 axis (*a*) and viewed as a dodecahedron with the positions of pairs of nitrogen atoms averaged (*b*)

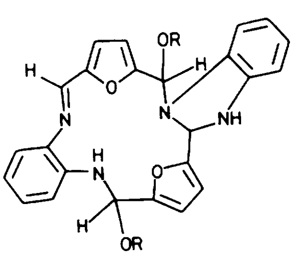
The natures of $L^2\cdot2MeOH$ and $L^2\cdot EtOH$ were inferred from chemical analysis and from i.r. and mass spectra. Mass spectra of both compounds gave strong peaks at *m/e* 392 and 394 corresponding to the free macrocycle L^2 and H_2L^2, respectively. No peaks were observed at higher *m/e* values. The strongest peaks in the spectra occurred, in the case of the methanol adduct, at *m/e* 31 and 32, corresponding to CH_2OH and CH_3OH, and in the case of the ethanol adduct at *m/e* 31, 45, and 46 corresponding to CH_2OH, CH_2CH_2OH, and CH_3CH_2OH.

Distinctive features in the i.r. spectra of both compounds were a fairly sharp ν(NH) vibration of 3 370 cm^{-1} and increased absorption in the ν(CH) region between 2 800 and 3 000 cm^{-1}. In the case of the methanol adduct the symmetric ν(CH) stretch of OCH_3 appeared as a well separated band at 2 800 cm^{-1}. When CD_3OD was used as preparative medium ν(NH) shifted to 2 504 cm^{-1} [ν(NH)/ν(ND) = 1.34] while ν_{sym}(CH) shifted to 2 070 cm^{-1} [ν(CH)/ν(CD) = 1.35]. Both compounds also exhibited a strong band at *ca.* 1 060 cm^{-1} which may be assigned to the ν(C–O) stretch.

While the above observations leave no doubt regarding the covalent addition of ROH (R = Me or Et) to the macrocycle L^2 it is more difficult to decide whether the addition has been accompanied by ligand rearrangement. Earlier work on related Schiff-base macrocycles has demonstrated the ease with which secondary amine groups can undergo intramolecular nucleophilic addition across adjacent C=N bonds.[5–7] Thus, for $L^2\cdot2MeOH$, structures of type (2) are possible alternatives to those of type (1). Because of low



(1)



(2)

solubility in suitable solvents it was not possible to make a distinction between structures of types (1) and (2) by means of ^1H n.m.r. spectroscopy. Such spectra as were obtained were too weak to allow satisfactory interpretation. Their apparent complexity would favour a structure such as (2), however.

Sodium-23 *N.M.R. Spectra.*—The relatively high intrinsic n.m.r. sensitivity of the ^{23}Na nucleus, together with its 100% natural abundance, makes sodium-23 n.m.r. a convenient tool for the study of the interaction of Na^+ with solvent and ligand molecules.[8,9] The low thermodynamic stability and high kinetic lability of most complexes of Na^+ leads to rapid cation exchange between complexed and free (solvated) forms in solution. In a few cases, however, slow exchange of alkali-metal cations (Na^+, K^+, or Cs^+) has been observed by means of n.m.r. spectroscopy of the metal ion [10–13] as well as of ^1H [14] and ^{13}C.[13] This is so for alkali-metal-ion complexes of certain cryptand macrobicycles. For example, two separate ^{23}Na resonances, corresponding to the complexed and free metal ions, have been observed for solutions of sodium halide in ethylenediamine [10] or methanol–D_2O [11] containing a one-half stoicheiometric amount of cryptand C222* at temperatures below about 50 °C. From measurements of the coalescence temperature the free energy of activation ($\Delta G^{\ddagger}$) for the exchange was estimated to be *ca.* 62 kJ mol^{-1} (NaBr in ethylenediamine) [10] and *ca.* 64 kJ mol^{-1} [NaCl in methanol–D_2O (95 : 5)].[11] It was therefore of interest to examine the ^{23}Na n.m.r. spectra of $NaL^2(ClO_4)$ in the presence and absence of free Na^+ in solution.

The 250-MHz ^{23}Na resonance in $NaL^2(ClO_4)$ occurs 330 Hz to higher field in $[^2H_6]$dimethyl sulphoxide–$[^2H_6]$-acetone (95 : 5) than that of $NaClO_4{\cdot}H_2O$ in the same solvent. The linewidth of the complexed Na^+ ion (125 Hz) at 25 °C is considerably greater than that of the free (solvated) ion (75 Hz) and presumably reflects the greater asymmetry of the ^{23}Na ion ($I = \frac{3}{2}$) in the complex. When $NaL^2(ClO_4)$ and $NaClO_4{\cdot}H_2O$ were present together in stoicheiometric amounts (0.015 mol dm^{-3}) separate signals were seen at temperatures below about 30 °C (Figure 5). On raising the temperature the separate resonances began to merge, finally coalescing at *ca.* 37 °C (250 MHz) and allowing an estimate of the free energy of activation for the exchange, 59 kJ mol^{-1}.

When either $Sr(ClO_4)_2$ or $Pb(ClO_4)_2{\cdot}3H_2O$ was added in excess to the mixture at the lower temperatures the separate resonances collapsed to a single resonance of increased intensity at a chemical shift identical to that of $NaClO_4{\cdot}H_2O$ alone. This clearly demonstrates that the Na^+ ion is displaced from the macrocycle by the added cation and confirms earlier conclusions that the sodium complex is thermodynamically less stable than those of the other metal ions.

Sodium-23 n.m.r. measurements were also made in CD_3CN solution. In this solvent the chemical shift separation between the resonances of free and complexed ^{23}Na was much smaller so that resolution into separate peaks was not observed for solutions containing both free and complexed cation. However, at temperatures below about 10 °C a marked asymmetry on the high-field side of the resonance was apparent indicating slow exchange in this solvent also.

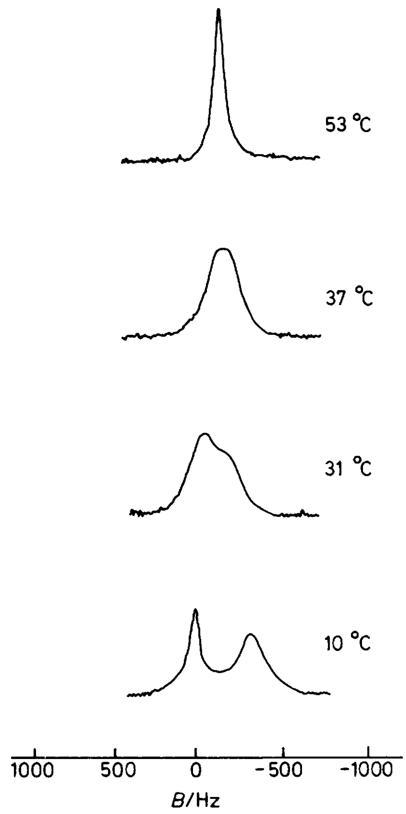


Figure 5. The 250-MHz ^{23}Na n.m.r. spectra of 0.015 mol dm^{-3} $NaL^2(ClO_4)$ containing a stoicheiometric amount of $NaClO_4{\cdot}H_2O$ in $[^2H_6]$dimethyl sulphoxide–$[^2H_6]$acetone (95 : 5) at selected temperatures. The resonance frequency of $NaClO_4{\cdot}H_2O$ in the same solvent at 10 °C is arbitrarily taken as zero

General Discussion and Conclusions.—The results demonstrate the usefulness of several Group 1A and 2A metal ions as templates for the high-yield synthesis of the 18-membered conjugated macrocycle L^2. It was not possible to prepare the macrocycle in the absence of template ion nor was it possible to isolate it by liberation from its complexes except in the form of the diacid salt or alcohol addition products. The instability of metal-free macrocyclic Schiff bases of this type has been noted previously.[15]

The results also demonstrate a selectivity in the complexation of the Group 1A and 2A metal ions. The ions K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} (also Pb^{2+}) all act as templates for the cyclic (2 + 2) condensation of the precursor dialdehyde and diprimary amine to give stable complexes. The Na^+ and $[NH_4]^+$ ions do not, at least under the same experimental conditions, although complexes of these ions are readily obtained (from the diprotonated form of the macrocycle) once the ring has been synthesised by the use of another metal ion as template. Complexes of Li^+ and Mg^{2+} could not be prepared by any method.

The results may be accounted for in terms of (*i*) the match (or mismatch) in the sizes of the metal ions in relation to the hole size of the macrocycle, and (*ii*) the charge on the metal ion. The barium complexes have a 2 : 1 ligand : metal stoicheiometry while those of all the other metal cations have a 1 : 1 stoicheiometry. While the *X*-ray analysis of the barium

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* 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

complex reveals some distortion from planarity in the co-ordinated macrocycle it can properly be described as a ' sandwich ' complex. The diagonal distance between opposite pairs of furan oxygen or imine nitrogen atoms is *ca.* 5.4 Å so we may define the hole radius as *ca.* 2.7 Å. Taking the eight-co-ordinate diameters [16] of the metal ions as a basis of comparison of their effective sizes in these complexes we see that Ba^{2+} (eight-co-ordinate diameter 2.84 Å) is a little too large for the hole and 2 : 1 ' sandwich ' compounds result. The bivalent metal ions Ca^{2+}, Sr^{2+}, and Pb^{2+} (eight-co-ordinate diameters 2.24, 2.50, and 2.62 Å, respectively) are all of an appropriate size to sit comfortably within the macrocycle cavity, and 1 : 1 complexes are obtained. The Mg^{2+} ion, on the other hand, is clearly too small (eight-co-ordinate diameter 1.80 Å) to be effectively bonded to all six donor atoms of the macrocycle and no complexes could be isolated. However, considerations of metal-ion size alone are insufficient to explain the stoicheiometries of the alkali-metal-ion complexes. The K^+ ion (eight-co-ordinate diameter 3.02 Å) is at least as large as Ba^{2+} and therefore might have been expected to form analogous sandwich complexes. The fact that it does not must be attributed to the smaller ionic charge. The Na^+ ion (eight-co-ordinate diameter 2.32 Å) is comparable in size to Ca^{2+}. Both ions would appear to be somewhat small in relation to the size of the macrocycle hole. This is reflected, in the case of Na^+, in the failure to act as a template for the macrocycle synthesis, and in the susceptibility of the imino-groups to nucleophilic addition by ROH. Previous studies [7] on complexes of the related macrocycle L^1 have shown that replacement of an alkaline-earth-metal ion by a too-small transition-metal ion in MeOH solution leads to an inner-ring contraction, the first step of which is MeOH addition across a C=N bond.

Despite the relative instability of the sodium complex cation in MeOH or EtOH it is surprisingly stable kinetically in $(CH_3)_2SO$ and MeCN. In fact, the free energy of activation for exchange of Na^+ between complex and solvent is only marginally smaller than that found [10,11] for the sodium complex of cryptand C222. This is somewhat unexpected since in the cryptate the cation is encapsulated within a three-dimensional array of donor atoms while in the complex of the two-dimensional macrocycle L^2 having exposed axial faces easy exit and entry of cation might be envisaged. The stability is perhaps the more unexpected when it is remembered that the macrocycle is conjugated and delocalised, comprising mainly ' soft ' donor groups of a type not normally associated with complexation of ' hard ' cations.

Experimental

Preparation of the Complexes.—2,5-Diformylfuran was prepared by the method of Haworth and Jones.[17] *o*-Phenylenediamine was recrystallised from water before use. The metal salts were used as supplied commercially without further purification.

$[BaL^2_2][ClO_4]_2$. 2,5-Diformylfuran (0.008 mol), *o*-phenylenediamine (0.008 mol), and $Ba(ClO_4)_2$ (0.002 mol) were dissolved in refluxing methanol (200 cm^3). Orange crystals started to separate after a few min. The reflux was continued for 1 h. The crystals were filtered off, washed with methanol, and oven dried at *ca.* 50 °C. Yield 65%. The salt $[BaL^2_2][NCS]_2$ was prepared similarly using $Ba(NCS)_2$ instead of $Ba(ClO_4)_2$. The orange product separated after 45 min. Yield 55%. The salt $[BaL^2_2][BPh_4]_2$ was prepared by metathesis by reaction of $[BaL^2_2][ClO_4]_2$ in MeCN–MeOH (1 : 1 v/v) solvent with $NaBPh_4$. Yield 75%. The complexes $CaL^2(ClO_4)_2{\cdot}H_2O$ and $SrL^2(ClO_4)_2{\cdot}H_2O$ were prepared as orange crystals in 70 and 65% yield as described for $[BaL^2_2][ClO_4]_2$; $CaL^2(NCS)_2$ was obtained from $CaL^2(ClO_4)_2{\cdot}H_2O$ by treatment with NaNCS in methanol solution. Yield 70%.

KL^2I. 2,5-Diformylfuran (0.002 mol), *o*-phenylenediamine (0.002 mol), and KI (0.001 mol) were refluxed together in methanol (80 cm^3) for 2 h. Orange crystals of the product separated in 63% yield on concentration.

$KL^2(ClO_4)$. The complex KL^2I (0.0036 mol) was dissolved in the minimum quantity of hot methanol and filtered into a solution of $NaClO_4{\cdot}H_2O$ (0.005 mol) also in methanol. On stirring for 20 min the orange product began to crystallise out. Yield 68%. The complex $KL^2(NCS)$ was prepared similarly using NaNCS instead of $NaClO_4{\cdot}H_2O$. Yield 77%. The complex $PbL^2(ClO_4)_2{\cdot}H_2O$ was prepared as for $[BaL^2_2][ClO_4]_2$. The red product separated within minutes in 75% yield.

$[H_2L^2][ClO_4]_2$. To a warm solution of $[BaL^2_2][ClO_4]_2$ (0.0004 mol) in MeOH–MeCN (1 : 1, 100 cm^3) was added $HClO_4$ (0.0014 mol) dissolved in a little methanol. The purple product separated almost immediately in near quantitative yield.

$NaL^2(ClO_4)$. To a suspension of purple $[H_2L^2][ClO_4]_2$ (0.0017 mol) in hot methanol (800 cm^3) was added NaOH (0.008 mol) dissolved in methanol, with stirring. The purple solid gradually dissolved and the orange product separated on cooling and concentrating. Yield 72%. The complex $NaL^2(NCS)$ was prepared by metathesis from $NaL^2(ClO_4)$ in 95% yield.

$(NH_4)L^2(ClO_4)$. To a suspension of $[H_2L^2][ClO_4]_2$ (0.0017 mol) in ethanol (200 cm^3) was added aqueous NH_3 (0.0067 mol). During the stirring the purple solid was gradually replaced by the orange product. Yield 92%.

$L^2{\cdot}2MeOH$. This was obtained on attempting to recrystallise $NaL^2(ClO_4)$ from refluxing methanol. Yield 53%. The adduct $L^2{\cdot}EtOH$ was obtained when ethanol was used as solvent.

Crystal Data.—$[BaL^2_2][BPh_4]_2$, $C_{96}H_{72}B_2BaN_8O_4$, M = 1 560.6, Monoclinic, a = 23.25(1), b = 14.92(1), c = 23.69(1) Å, β = 101.0(1)°, U = 8 074.4 $Å^3$, D_m = 1.30, Z = 4, D_c = 1.29 g cm^{-3}, $\mu(Mo\text{-}K_{\bar{\alpha}})$ = 5.68 cm^{-1}, $\lambda(Mo\text{-}K_{\bar{\alpha}})$ = 0.7107 Å, $F(000)$ = 3 208, space group $A2/a$ (no. 15).

Structure Determination.—A crystal of approximate size 0.3 × 0.4 × 0.5 mm was mounted on a Stoe Stadi-2 diffractometer and data collected *via* variable width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). Absorption and extinction corrections were not applied. 3 941 Independent reflections with $2\theta < 40°$ were measured and 1 468 with $I > 2\sigma(I)$ were used in subsequent refinement. The positions of the barium atoms (on the two-fold axes) were obtained by the Patterson method and the positions of non-hydrogen atoms in the macrocycle were found from the Fourier syntheses. However, the anion was disordered. We approximated the disorder by refining two superimposed anions (A and B) which had two phenyl rings in common [consisting of atoms C(41)—C(46) and C(51)—C(56)] but with different boron positions (denoted B–A and B–B) and with two further rings each consisting of atoms C(61)—C(66) and C(71)—C(76) (A or B). All phenyl rings were successfully refined as rigid groups but each carbon atom was given an independent thermal parameter which was refined. The two anions were given population parameters of x and $(1 - x)$ but, in the event, x refined to 0.50(1). A further complication was that anion B had ring C(7n) close to the two-fold axis. The positions of the hydrogen atoms in the macrocycle were included in trigonal positions and refined using a common thermal parameter. In view of the disorder, no attempt was made to include the hydrogen atoms of the anion. The refinement was carried out

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ba(1)	2 500(0)	5 610(2)	5 000(0)	C(45)	4 193(11)	3 257(14)	3 839(15)
N(1)	1 168(12)	5 300(24)	4 843(12)	C(46)	3 999(11)	2 371(14)	3 807(15)
C(2)	971(21)	4 477(43)	4 616(16)	C(51)	4 071(10)	167(19)	3 166(10)
C(3)	1 324(32)	3 749(47)	4 846(24)	C(52)	4 031(10)	−742(19)	3 288(10)
N(4)	1 872(18)	3 905(25)	5 214(15)	C(53)	4 415(10)	−1 352(19)	3 110(10)
C(5)	2 058(25)	3 249(31)	5 564(20)	C(54)	4 839(10)	−1 052(19)	2 810(10)
C(6)	2 569(25)	3 582(33)	5 953(17)	C(55)	4 879(10)	−142(19)	2 688(10)
O(7)	2 767(11)	4 376(21)	5 967(9)	C(56)	4 496(10)	467(19)	2 866(10)
C(8)	3 283(17)	4 479(47)	6 431(14)	B–A	3 873(39)	753(70)	3 609(37)
C(9)	3 506(21)	5 376(35)	6 455(22)	C(61a)	3 128(12)	390(28)	3 433(17)
N(10)	3 327(17)	5 976(33)	6 089(12)	C(62a)	2 929(12)	−257(28)	3 017(17)
C(11)	3 621(19)	6 749(45)	6 181(13)	C(63a)	2 331(12)	−425(28)	2 852(17)
C(12)	3 273(22)	7 563(36)	5 961(17)	C(64a)	1 930(12)	56(28)	3 103(17)
N(13)	2 705(19)	7 303(21)	5 715(12)	C(65a)	2 129(12)	703(28)	3 519(17)
C(14)	2 300(32)	7 868(29)	5 731(15)	C(66a)	2 727(12)	871(28)	3 684(17)
C(15)	1 699(27)	7 673(55)	5 512(18)	C(72a)	3 892(12)	535(30)	4 770(18)
O(16)	1 595(14)	6 904(25)	5 282(11)	C(73a)	4 215(12)	450(30)	5 327(18)
C(17)	979(22)	6 715(43)	5 079(14)	C(74a)	4 811(12)	252(30)	5 415(18)
C(18)	788(20)	5 816(24)	4 885(17)	C(75a)	5 086(12)	138(30)	4 945(18)
C(20)	462(24)	4 341(38)	4 237(19)	C(76a)	4 763(12)	224(30)	4 387(18)
C(21)	341(23)	3 365(59)	4 031(18)	C(71a)	4 167(12)	422(30)	4 300(18)
C(22)	755(36)	2 707(45)	4 271(29)	B–B	3 448(40)	1 054(66)	3 194(38)
C(23)	1 198(26)	2 894(40)	4 614(16)	C(61b)	2 832(14)	1 129(36)	2 605(15)
C(24)	2 904(27)	3 116(30)	6 409(23)	C(62b)	2 519(14)	1 901(36)	2 407(15)
C(25)	3 272(28)	3 569(39)	6 711(17)	C(63b)	2 023(14)	1 841(36)	1 973(15)
C(26)	4 230(18)	6 915(38)	6 426(14)	C(64b)	1 840(14)	1 010(36)	1 735(15)
C(27)	4 462(33)	7 785(53)	6 452(21)	C(65b)	2 153(14)	239(36)	1 933(15)
C(28)	4 087(34)	8 498(41)	6 221(24)	C(66b)	2 649(14)	298(36)	2 367(15)
C(29)	3 542(24)	8 319(35)	6 001(18)	C(71b)	3 073(23)	813(37)	3 783(15)
C(30)	1 200(36)	8 159(38)	5 441(17)	C(72b)	2 477(23)	686(37)	3 777(15)
C(31)	735(21)	7 608(48)	5 196(21)	C(73b)	2 287(23)	476(37)	4 285(15)
C(41)	3 766(11)	1 991(14)	3 275(15)	C(74b)	2 691(23)	392(37)	4 798(15)
C(42)	3 727(11)	2 497(14)	2 774(15)	C(75b)	3 287(23)	519(37)	4 804(15)
C(43)	3 922(11)	3 382(14)	2 805(15)	C(76b)	3 478(23)	730(37)	4 297(15)
C(44)	4 155(11)	3 763(14)	3 338(15)				

Table 5. Bond lengths (Å) and angles (°) in the barium co-ordination sphere

Ba(1)–N(1)	3.083(28)	Ba(1)–O(7)	2.914(25)	Ba(1)–N(13)	3.03(3)
Ba(1)–N(4)	3.03(4)	Ba(1)–N(10)	2.959(29)	Ba(1)–O(16)	3.02(3)

N(1)–Ba(1)–N(4)	52.3(10)	N(4)–Ba(1)–N(10)	105.3(11)	O(7)–Ba(1)–N(13*)	162.7(8)
N(1)–Ba(1)–O(7)	93.4(7)	N(4)–Ba(1)–N(13)	129.6(10)	O(7)–Ba(1)–O(16*)	121.6(7)
N(1)–Ba(1)–N(10)	127.1(9)	N(4)–Ba(1)–O(16)	97.0(10)	O(7)–Ba(1)–O(7*)	101.5(10)
N(1)–Ba(1)–N(13)	103.9(10)	N(4)–Ba(1)–O(7*)	65.1(9)	N(10)–Ba(1)–N(13)	49.6(11)
N(1)–Ba(1)–O(16)	52.9(9)	N(4)–Ba(1)–N(10*)	92.7(11)	N(10)–Ba(1)–O(16)	93.1(9)
N(1)–Ba(1)–N(4*)	111.1(11)	N(4)–Ba(1)–N(13*)	140.0(10)	N(10)–Ba(1)–N(13*)	109.9(11)
N(1)–Ba(1)–O(7*)	75.6(9)	N(4)–Ba(1)–O(16*)	162.4(10)	N(10)–Ba(1)–O(16*)	73.2(9)
N(1)–Ba(1)–N(10*)	56.8(9)	N(4)–Ba(1)–N(4*)	65.4(8)	N(10)–Ba(1)–N(10*)	158.7(11)
N(1)–Ba(1)–N(13*)	90.6(10)	O(7)–Ba(1)–N(10)	54.9(10)	N(13)–Ba(1)–O(16)	52.1(9)
N(1)–Ba(1)–O(16*)	142.6(9)	O(7)–Ba(1)–N(13)	95.8(7)	N(13)–Ba(1)–O(16*)	63.2(9)
N(1)–Ba(1)–N(1*)	162.7(10)	O(7)–Ba(1)–O(16)	106.4(7)	N(13)–Ba(1)–N(13*)	66.9(9)
N(4)–Ba(1)–O(7)	51.2(8)	O(7)–Ba(1)–N(10*)	143.9(10)	O(16)–Ba(1)–O(16*)	100.6(10)

using full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.10 ($R' = 0.10$).

Calculations were made using SHELX 76 [18] at the University of Manchester Computing Centre. Atomic co-ordinates are given in Table 4 and the molecular dimensions in the barium co-ordination sphere in Table 5.

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Received 29th November 1982; *Paper* 2/1999