Calcium, Strontium, and Barium Complexes of Pyridyl-containing Macrocyclic Schiff Bases

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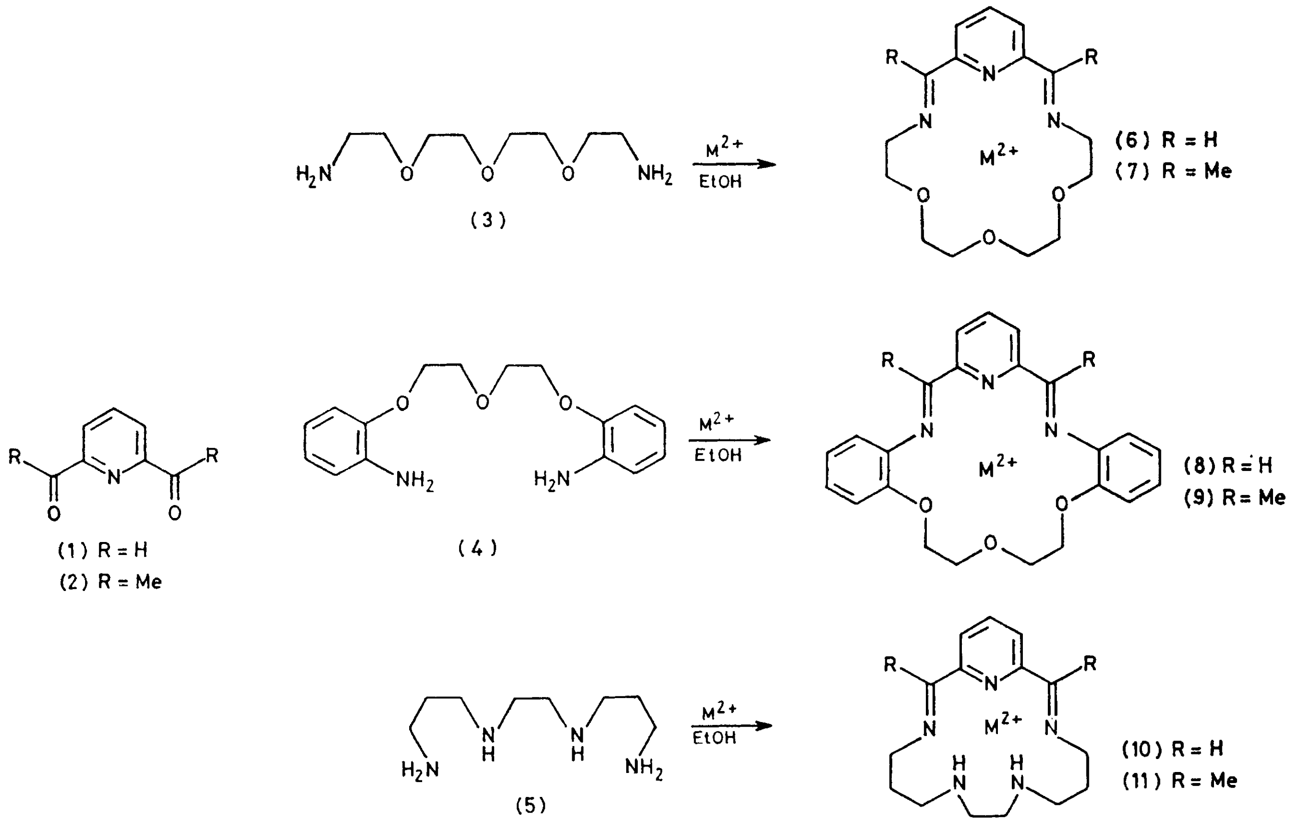
Reaction of 2,6-diacetylpyridine, or pyridine-2,6-dicarbaldehyde, with 3,6,9-trioxaundecane-1,11-diamine, 1,5-bis(2-aminophenoxy)-3-oxapentane, or 4,7-diazadecane-1,10-diamine in ethanol in the presence of $M[NCS]_2$ or $M[ClO_4]_2$ (M = Ca, Sr, or Ba) gives complexes of the type $[M(NCS)_2L]$ or $[M(ClO_4)_2L]$ where L is the corresponding macrocyclic Schiff base. In the absence of the metal salt the macrocycles are formed in very small yield or not at all. Alkali-metal salts are ineffective in promoting the synthesis of the macrocycles, and magnesium only promotes the formation of a macrocycle derived from the tetra-amine.

THE publication in 1967 of Pedersen's paper[1] describing the synthesis of cyclic polyethers and their alkali-metal and alkaline-earth metal complexes led to a renaissance of interest in this area of chemistry. There has since been a proliferation of synthetic ligands involving nitrogen, oxygen, and sulphur donor atoms and incorporating a variety of two- and three-dimensional ring- and cage-like structures.[2] The interest in the coordination chemistry of the alkaline-earth metals has been dominated by the biological importance of calcium and magnesium[3-6] and has led to a search for synthetic systems capable of acting as models for the more complex biological ligands which bind to these metals.

The utilisation of magnesium as a template for the synthesis of macrocyclic Schiff-base ligands has been reported.[7,8] We report here the metal-promoted synthesis of macrocyclic Schiff-base complexes of calcium, strontium, and barium. Prior to this work, macrocyclic complexes of these metals were restricted to complexes of cyclic polyethers, cryptates, and antibiotics. Preliminary communication of our work has been made.[9]



(3)

(6) R = H
(7) R = Me

(4)

(8) R = H
(9) R = Me

(5)

(10) R = H
(11) R = Me

RESULTS AND DISCUSSION

A relationship between the stability of an alkaline-earth metal macrocyclic complex and the closeness of fit between the cation and available macrocyclic cavity has been established,[10,11] the preferred cation generally being that which most closely fits the cavity. This requirement, when allied with the number and nature of ligand donor atoms, provides a basis for selectivity in complex formation amongst the alkaline-earth metals.

Magnesium was found to promote the synthesis of a series of quinquedentate macrocyclic Schiff-base ligands derived from pyridine-2,6-dicarbaldehyde (1), or 2,6-diacetylpyridine (2), and functionally substituted α,ωdiamines, whereas calcium did not induce macrocycle formation but led to the production of intractable tars.[8]

TABLE 1

Analytical data (%)

Complex	Found			Calc.		
	C	H	N	C	H	N
$[6;\ M^{2+} = Ca(NCS)_2]$	45.3	4.6	15.6	45.6	4.7	15.7
$[6;\ M^{2+} = Sr(NCS)_2 \cdot H_2O]$	39.3	4.6	13.6	39.7	4.5	13.6
$[6;\ M^{2+} = Ba(NCS)_2 \cdot H_2O]$	36.4	4.2	12.5	36.3	4.1	12.5
$[6;\ M^{2+} = Ca(ClO_4)_2]$	33.8	3.7	7.5	33.9	3.9	7.9
$[6;\ M^{2+} = Sr(ClO_4)_2 \cdot H_2O]$	30.6	3.7	7.0	30.2	3.8	7.1
$[6;\ M^{2+} = Ba(ClO_4)_2 \cdot H_2O]$	27.8	3.7	6.6	27.9	3.6	6.5
$[7;\ M^{2+} = Ca(NCS)_2]$	47.9	5.6	14.5	48.0	5.3	14.7
$[7;\ M^{2+} = Sr(NCS)_2]$	43.9	4.7	13.3	43.6	4.8	13.4
$[7;\ M^{2+} = Ba(NCS)_2]$	40.4	4.5	11.6	39.8	4.4	12.2
$[7;\ M^{2+} = Ca(ClO_4)_2]$	36.3	4.6	7.2	36.5	4.1	7.5
$[7;\ M^{2+} = Sr(ClO_4)_2]$	34.5	4.3	6.6	33.7	4.1	6.9
$[7;\ M^{2+} = Ba(ClO_4)_2 \cdot H_2O]$	30.2	3.7	5.9	30.3	4.0	6.2
$[8;\ M^{2+} = Ca(NCS)_2]$	54.7	3.9	12.8	55.2	3.9	12.9
$[8;\ M^{2+} = Sr(NCS)_2]$	50.9	3.7	11.8	50.8	3.6	11.8
$[8;\ M^{2+} = Ba(NCS)_2 \cdot H_2O]$	45.3	3.9	10.5	45.6	3.5	10.6
$[8;\ M^{2+} = Ca(ClO_4)_2]$	44.0	2.9	6.6	44.1	3.3	6.7
$[8;\ M^{2+} = Sr(ClO_4)_2]$	40.8	3.1	6.2	40.9	3.1	6.2
$[8;\ M^{2+} = Ba(ClO_4)_2]$	38.3	2.9	5.7	38.2	2.9	5.8
$[9;\ M^{2+} = Sr(NCS)_2]$	51.9	4.5	10.5	50.9	4.2	10.9
$[10;\ M^{2+} = 0.5Ca(NCS)_2]$	53.6	5.2	23.0	54.7	6.5	23.9
$[11;\ M^{2+} = Mg(NCS)_2]$	51.6	6.5	22.5	51.7	6.1	22.3
$[11;\ M^{2+} = Ca(NCS)_2]$	49.4	5.6	21.3	49.9	5.9	21.4
$[11;\ M^{2+} = Sr(NCS)_2 \cdot H_2O]$	43.6	5.4	18.6	43.6	5.5	18.7
$[11;\ M^{2+} = Ba(NCS)_2 \cdot H_2O]$	40.4	4.6	17.3	39.8	5.1	17.1
$[11;\ M^{2+} = Sr(ClO_4)_2]$	34.5	4.3	11.7	34.7	4.6	11·9
$[11;\ M^{2+} = Ba(ClO_4)_2]$	33.2	4.6	10.2	32.0	4.2	11.0

Extension of the functionally substituted α,ω-diamine chain length, or donor capacity, leads to the provision of a larger macrocyclic cavity and to a requirement for the larger calcium, strontium, and barium cations as template agents.

The reaction of (1), or (2), with 3,6,9-trioxaundecane-1,11-diamine (3), 1,5-bis(2-aminophenoxy)-3-oxapentane (4), or 4,7-diazadecane-1,10-diamine (5) in 1 : 1 ratio in ethanol in the presence of an equimolar amount of calcium, strontium, or barium thiocyanate or perchlorate leads to the isolation of the corresponding macrocyclic complex (Tables 1 and 2). The absence of carbonyl bands in the i.r. spectra of the products, together with the appearance of an imine band, indicates that condensation and cyclisation has occurred. The presence of a peak in the mass spectrum of the appropriate macrocycle further supports this conclusion as does the ^1H n.m.r. data for the isothiocyanate complexes derived from (6) and (7). In the absence of metal ions, open-chain polymeric residues are formed illustrating that the metal ion is essential to the synthesis.

The presence of (6) as a macrocyclic ligand has been confirmed by *X*-ray crystallographic studies.[9] The structures of $[6;\ M^{2+} = Ca(NCS)_2]$ and $[6;\ M^{2+} = Sr(NCS)_2 \cdot H_2O]$ have been solved and are depicted schematically on p. 268. It can be seen that the smaller calcium cation (Pauling radius, 0.99 Å) is located more inside the macrocyclic cavity than is the strontium cation (Pauling radius, 1.13 Å). The disposition of the ligands relative to the macrocyclic plane is '*trans*' in the former and '*cis*' in the latter. The co-ordination number of calcium is eight and that of strontium nine in accord with previously reported trends for Group 2A

TABLE 2

Infrared (cm^{-1}), electrical conductance, and mass-spectral data

(*a*) Thiocyanate complexes

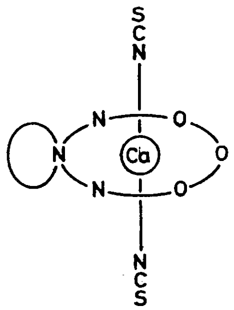
Complex	ν(C–N)	Λ/S cm^2 mol^{-1}		P^+
		In H_2O	MeCN	
$[6;\ M^{2+} = Ca(NCS)_2]$	2 065	210	71	$[6;\ M^{2+} = Ca(NCS)]^+$
$[6;\ M^{2+} = Sr(NCS)_2 \cdot H_2O]$	2 081, 2 073	194	131	$[(6) - M^{2+}]^+$
$[6;\ M^{2+} = Ba(NCS)_2 \cdot H_2O]$	2 070br	208	241	$[(6) - M^{2+}]^+$
$[7;\ M^{2+} = Ca(NCS)_2]$	2 050	253	85	$[7;\ M^{2+} = Ca(NCS)]^+$
$[7;\ M^{2+} = Sr(NCS)_2]$	2 042	259	116	$[7;\ M^{2+} = Sr(NCS)]^+$
$[7;\ M^{2+} = Ba(NCS)_2]$	2 070, 2 059	280	203	$[(7) - M^{2+}]^+$
$[8;\ M^{2+} = Ca(NCS)_2]$	2 065—2 055br	*	*	$[(8) - M^{2+}]^+$
$[8;\ M^{2+} = Sr(NCS)_2]$	2 065—2 055br	*	*	$[(8) - M^{2+}]^+$
$[8;\ M^{2+} = Ba(NCS)_2]$	2 070—2 060br	*	182	$[(8) - M^{2+}]^+$
$[9;\ M^{2+} = Sr(NCS)_2]$	2 070	*	265	$[(9) - M^{2+}]^+$
$[10;\ M^{2+} = 0.5Ca(NCS)_2]$	2 065, 2 055	*	*	
$[11;\ M^{2+} = Mg(NCS)_2]$	2 080, 2 060	*	84	$[11;\ M^{2+} = Mg(NCS)]^+$
$[11;\ M^{2+} = Ca(NCS)_2]$	2 065, 2 055	284	68	$[11;\ M^{2+} = Ca(NCS)]^+$
$[11;\ M^{2+} = Sr(NCS)_2 \cdot H_2O]$	2 050, 2 040	251	9	$[(11) - M^{2+}]^+$
$[11;\ M^{2+} = Ba(NCS)_2 \cdot H_2O]$	2 059, 2 035	292	*	$[(11) - M^{2+}]^+$

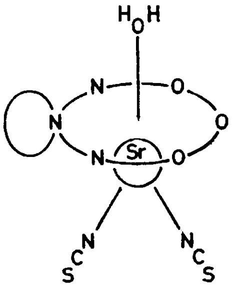
(*b*) Perchlorate complexes

Complex	ν_3	ν_4	Λ/S cm^2 mol^{-1}		P^+
$[6;\ M^{2+} = Ca(ClO_4)_2]$	1 100br	635, 620	192	290	$[6;\ M^{2+} = Ca(ClO_4)_2]^+$
$[6;\ M^{2+} = Sr(ClO_4)_2 \cdot H_2O]$	1 060	628, 620	204	277	$[(6) - M^{2+}]^+$
$[6;\ M^{2+} = Ba(ClO_4)_2 \cdot H_2O]$	1 095br	630br	185	268	$[(6) - M^{2+}]^+$
$[7;\ M^{2+} = Ca(ClO_4)_2]$	1 145, 1 110, 1 085	648, 638, 626	280	242	$[7;\ M^{2+} = Ca(ClO_4)]^+$
$[7;\ M^{2+} = Sr(ClO_4)_2]$	1 150, 1 100, 1 050	650, 636, 627, 620	286	281	$[7;\ M^{2+} = Sr(ClO_4)]^+$
$[7;\ M^{2+} = Ba(ClO_4)_2 \cdot H_2O]$	1 100br	645, 638, 625	275	295	$[(7) - M^{2+}]^+$
$[8;\ M^{2+} = Ca(ClO_4)_2]$	1 122, 1 047	652, 638, 620	*	298	$[(8) - M^{2+}]^+$
$[8;\ M^{2+} = Sr(ClO_4)_2]$	1 123, 1 045	652, 639, 625	*	296	$[(8) - M^{2+}]^+$
$[8;\ M^{2+} = Ba(ClO_4)_2]$	1 165, 1 100br, 1 038	652, 632, 624	*	292	$[(8) - M^{2+}]^+$
$[11;\ M^{2+} = Sr(ClO_4)_2]$	1 140, 1 120, 1 090	639, 632, 629	*	280	$[11;\ M^{2+} = Sr(ClO_4)]^+$
$[11;\ M^{2+} = Ba(ClO_4)_2]$	1 145, 1 120, 1 090	638, 629	*	*	$[(11) - M^{2+}]^+$

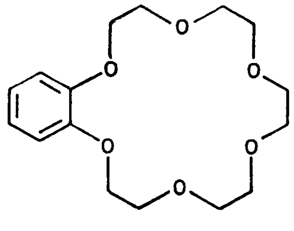
* Insoluble.

metals.[12] The complexes therefore provide access to the study of unusual co-ordination geometries in species of high co-ordination number since the six ligand donor atoms are essentially confined in one plane.[13] The complex [6; M^{2+} = $Ba(NCS)_2{\cdot}H_2O$] has been shown to be isostructural with [6; M^{2+} = $Sr(NCS)_2{\cdot}H_2O$].[14]





The change in anion position from '*trans*' to '*cis*' on moving to a cation of higher radius has been observed in related cyclic polyether complexes. It is viewed as a manifestation of the 'close-fit' requirement and the need for the metal to rest at a centre of optimum electron density. In the 1 : 1 magnesium and calcium thiocyanate complexes of benzo-15-crown-5 * the smaller magnesium cation (Pauling radius, 0.65 Å) is located within the macrocyclic cavity with the two anions '*trans*' *N*-bonded.[15] The larger calcium cation, however, remains bonded to the five ring-oxygen donors, but is displaced from the macrocyclic plane. The anions are '*cis*' *N*-bonded, and a co-ordination number of eight is achieved by co-ordination of a solvent molecule on the same side of the macrocycle as are the anions.[16]



benzo - 18 - crown - 6

Similar observations may be made on moving to larger cavity sizes. The polyethers based on an 18-crown-6 framework possess the same overall ring heteroatom constitution as complexes (6)—(9). The structure of the 1 : 1 complex of calcium thiocyanate with 18-crown-6 can be related directly to that of [6; M^{2+} = $Ca(NCS)_2$] since the calcium cation sits in the macrocyclic cavity with the two anions '*trans*' *N*-bonded.[17] Although no *X*-ray crystallographic studies on barium complexes of 18-crown-6 have yet been reported, the related complex of dicyclohexyl-18-crown-6 (A isomer: *cis-syn-cis*) with $Ba(NCS)_2{\cdot}H_2O$ has,[18] and is comparable to the proposed structure of [6; M^{2+} = $Ba(NCS)_2{\cdot}H_2O$]. The barium cation lies close to the macrocyclic plane and the anions are '*cis*' *N*-bonded beneath the ring plane, while a co-ordinated water molecule is suggested to be located above this plane and so '*trans*' to the anions.

Thiocyanate and perchlorate anions may co-ordinate in several ways. Thiocyanate can exhibit linkage isomerism, perchlorate may be uni- or bi-dentate; both may act as bridging anions or as purely ionic species. The mode of interaction may be deduced from the vibrational frequencies of the anion in any of the above situations. Ionic thiocyanates are reported to have C–N stretching frequencies at *ca.* 2 100 cm^{-1}, while *S*- and *N*-bonded thiocyanates have frequencies in the ranges 2 080—2 120 and 2 040—2 080 cm^{-1} respectively.[19] In some cases the use of the C–S stretching frequency (*N*-bonded, 780—860 cm^{-1}; *S*-bonded, 690—720 cm^{-1}) and the C–N–S bending mode (*N*-bonded, 465—480 cm^{-1}; *S*-bonded, 410—470 cm^{-1}) may aid further assignment. For the complexes reported here these two sets are obscured by ligand bands. In addition, the ranges reported in the literature [19] are derived from transition-metal complexes; the bonding of the higher alkaline-earth metal cations to the thiocyanate anion would be more ionic in character and thus give rise to higher values for ν(C–N) in both *N*- and *S*-bonding. This is illustrated in the complexes of benzo-15-crown-5 with $Ca(NCS)_2{\cdot}L$ (L = H_2O or MeOH), where the ν(C–N) bands are detected at 2 100 and 2 075 and 2 100 and 2 080 cm^{-1} respectively for the *N*-bonded anions.[16] The Ca–N–CS angle is different for the two isothiocyanate groups: each molecular structure has one Ca–N–CS angle of 153° but the other is 172° (for L = MeOH) and 160° (for L = H_2O). The non-equivalence of the isothiocyanate groups explains the splitting of the C–N stretching frequencies.[16] The perchlorate assignments are made according to literature values.[20]

If the anions present in alkaline-earth metal complexes are disposed in different environments, or utilise different bonding modes, then a complex i.r. spectrum results in the areas discussed above. In the absence of *X*-ray crystallographic studies, absolute assignment of anion disposition must remain tentative since it is difficult to present an unambiguous assignment on i.r. arguments alone.

Complexes (6) *and* (7).—The i.r. spectra of [6; M^{2+} = $M(NCS)_2$] may be related to the structures of these complexes. The complex '*trans*'-[6; M^{2+} = $Ca(NCS)_2$] shows a single C–N stretch at 2 065 cm^{-1} consistent with *N*-bonding, whereas '*cis*'-[6; M^{2+} = $Sr(NCS)_2{\cdot}H_2O$] shows a split band at 2 081 and 2 073 cm^{-1}. This complex must be compared with '*trans*'-[6; M^{2+} = Pb(NCS)(SCN)] in which a split band is present at 2 085 and 2 065 cm^{-1}.[21] This is consistent with the structural information for this complex where linkage isomerism is observed. That both '*cis*'-$(NCS)_2$ and '*trans*'-Pb-(NCS)(SCN) should give such similar i.r. bands serves to

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* The simplified nomenclature for Pedersen's cyclic polyethers is based on citing, in order, (*i*) the number and nature of peripheral groups, (*ii*) the total number of atoms in the polyether ring, (*iii*) the class name, 'crown,' and (*iv*) the number of oxygen atoms in the polyether ring.

emphasise the problem of assigning the anion disposition. The complex ' *cis* '-[6; M^{2+} = $Ba(NCS)_2{\cdot}H_2O$] shows a broad band at 2 070 cm^{-1}. Complexes [7; M^{2+} = $Ca(NCS)_2$] and [7; M^{2+} = $Sr(NCS)_2$] have single ν(C–N) bands at 2 050 and 2 042 cm^{-1} respectively; it is therefore probable that these have ' *trans* ' *N*-bonded structures. The barium complex has a split band, 2 070 and 2 059 cm^{-1}, and may therefore be ' *cis* ' *N*-bonded.

The perchlorate complexes of (6) and (7) show i.r. features corresponding to bonded rather than ionic perchlorates. The degeneracies of ν_3 and ν_4 are lifted to give several bands. A similar pattern has been observed for the complex of benzo-18-crown-6 with $Ba(ClO_4)_2{\cdot}2H_2O$ for which preliminary *X*-ray results have been reported.[22] The barium cation is co-ordinated by both perchlorate anions as unidentate groups, one above and one below the plane of the macrocyclic ring (' *trans* '), and the two water molecules are co-ordinated on the same side of the ring. It is postulated that, by analogy of ring size and donor capacity, complexes (6) and (7) have a similar ' *trans* ' configuration.

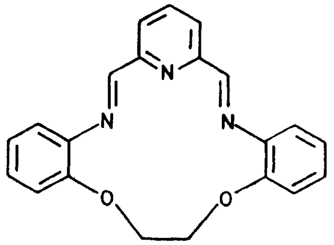
The mass spectra of complexes (6) and (7) suggest a decrease in bonding strength from calcium to barium. Whereas [6; M^{2+} = $Ca(NCS)_2$] exhibits a peak corresponding to [6; M^{2+} = $Ca(NCS)]^+$ as the highest molecular-weight peak, the strontium and barium complexes show $[(6) - M^{2+}]^+$ as the highest peak. The calcium derivatives of (7) again show $[(7;\ M^{2+} = CaX)]^+$ as the highest molecular-weight peak but in contrast to (6) the strontium complexes also show weak peaks due to $[(7;\ M^{2+} = SrX)]^+$. This is seen as a manifestation of the inductive effect of the methyl groups increasing the ligand donor potential.

Similar trends are observed for the isothiocyanate complexes in acetonitrile solutions. There is a steady gradation in property on moving from calcium (zero to 1 : 1 electrolyte) to strontium (1 : 1 to 2 : 1 electrolyte) to barium (2 : 1 electrolyte). The complexes are all 2 : 1 electrolytes in water, as are the perchlorate complexes of (6) and (7) in water and (6) in acetonitrile. The latter is a reflection of the weaker co-ordination ability of the perchlorate anion.

The tendency of calcium, and to a lesser extent strontium, to form singly charged cationic species can be related to the observations of Steinrauf concerning the interaction of alkaline-earth metals with the cyclic depsipeptide beauveracin. Calcium appears to be transported across biological membranes by beauveracin as a singly charged species,[23] and the crystal structure of the beauveracin-picrate complex shows barium to be involved as a singly charged cation.[24] Our observations supply further evidence for the availability of the singly charged cationic species that may be involved in biological activity.

Complexes (8) *and* (9).—Despite the overall similarity imposed by the same overt ring size and ligand-donor arrangement there are differences between complexes (6) and (8). The related complexes (8) are bright orange-yellow and tend to precipitate as insoluble microcrystalline materials. The colours are attributed to the extensive delocalisation in the ligand. The presence of the aromatic rings leads to a more rigid macrocyclic framework and accompanying steric constraint.

The crystal structure of the manganese perchlorate complex of the related macrocycle (12) has been reported.[25] In this complex the unidentate perchlorate groups are ' *trans* ' and ν_3 occurs at 1 106 and 1 040 cm^{-1}. Complexes [8 ; M^{2+} = $Ca(ClO_4)_2$] and [8; M^{2+} = $Sr(ClO_4)_2$] exhibit similar marked splittings of ν_3 and so eight-co-ordinated structures are proposed in which the anions are ' *trans* ' unidentate. For the remaining complexes it is not possible to make a firm structural proposition from the i.r. data.

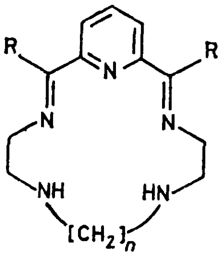


(12)

The mass spectra show as parent peaks $[(8) - M^{2+}]^+$ indicating weaker complexing than in (6) or (7). The complexes are insoluble in water and the three perchlorate complexes are 2 : 1 electrolytes in acetonitrile. Only [8; M^{2+} = $Ba(NCS)_2$] was sufficiently soluble in acetonitrile to yield a conductivity and this gave a value intermediate between those of 1 : 1 and 2 : 1 electrolytes.

Using the template procedures reported here it was only possible to prepare [9; M^{2+} = $Sr(NCS)_2$]. This complex is a 2 : 1 electrolyte in acetonitrile, has a parent peak at $[(9) - M^{2+}]^+$ in the mass spectrum, and a single peak at 2 070 cm^{-1} in the i.r. This is suggestive of a ' *trans* ' *N*-bonded structure. There is no obvious reason why only strontium should form a complex with this macrocycle.

Complexes (10) *and* (11).—The macrocycles (13) and (14) have been shown to form complexes only with magnesium.[8] The macrocycle in (11) has, through the propane–ethane–propane bridges, an extended chain length and potentially increased cavity size. Of the



(13) *n* = 2

(14) *n* = 3

macrocycles discussed here it is the only one with an N_5 donor set, and it forms complexes with magnesium, calcium, strontium, and barium thiocyanates. Only strontium and barium perchlorate complexes were isolated, evidencing an anion effect.

The crystal structure of [11; $M^{2+} = Mn(NCS)_2$] has been reported [26] and in this molecule the macrocycle is distorted from planarity such that four nitrogen donors are coplanar with the metal ion and the pyridine nitrogen drops below this plane in the direction of the axial position. The two isothiocyanates are '*trans*' but inequivalent; that on the side of the pyridine nitrogen is at 2.29 Å and that opposite to it at 2.17 Å from the metal. The metal–isothiocyanate bond angles are also different, 135 and 150.9°. Two ν(C–N) bands are observed in the i.r. spectrum, at 2 058 and 2 038 cm^{-1}, arising from the inequivalence and furnishing further evidence for caution in assignment. Complexes (11) with the larger cadmium (Pauling radius, 0.97 Å), silver (Pauling radius, 1.26 Å), and mercury (Pauling radius, 1.10 Å) have been synthesised and the structure of [11; $M^{2+} = CdBr_2 \cdot H_2O$] again shows the folded macrocycle with one sterically crowded axial site. In [11; $M^{2+} = Ag(ClO_4)$] the ligand forms a distorted pentagonal plane with little deviation.[27]

It is suggested that the structures of [11; $M^{2+} = Mg(NCS)_2$] and [11; $M^{2+} = Ca(NCS)_2$], in which ν(C–N) values at 2 080 and 2 060, and 2 065 and 2 055 cm^{-1}, are observed are '*trans*' *N*-bonded. Both the strontium and barium complexes exhibit split isothiocyanate bands and could have '*trans*' configurations. However, it is possible that the larger cations are encapsulated by a distorted pentagonal plane, as is silver, and then the '*cis*' *N*-bonded structure of [6; $M^{2+} = Sr(NCS)_2 \cdot H_2O$] could be adopted.

Conductivity measurements in acetonitrile show the magnesium and calcium complexes to be intermediate between zero and 1 : 1 electrolytes. The mass spectra show a trend similar to complexes (6) and (7). The magnesium and calcium complexes show peaks for [11; $M^{2+} = M(NCS)]^+$ and the strontium and barium complexes have $[(11) - M^{2+}]^+$ as the highest molecular-weight peak. These observations reflect the ease with which isothiocyanate may be lost from the potentially sterically crowded axial site. In [11; $M^{2+} = Mn(NCS)_2$] one isothiocyanate is readily displaced by perchlorate to form [11; $M^{2+} = Mn(NCS)(ClO_4)$].[26]

Complexes [11; $M^{2+} = Sr(ClO_4)_2$] and [11; $M^{2+} = Ba(ClO_4)_2$] show identical splittings for ν_3 and ν_4 but these do not lead to unambiguous assignments since the values do not correspond to uni- or bi-dentate perchlorate. The barium complex is insoluble but the strontium complex is a 2 : 1 electrolyte in acetonitrile. In the mass spectra the strontium complex has [11; $M^{2+} = Sr(ClO_4)]^+$ as the highest molecular-weight peak but the barium complex shows $[(11) - M^{2+}]^+$ as the highest peak. The formation of these complexes may be sterically controlled. If the smaller cations cause the ligand to fold and lead to steric constraint at an axial position only the smaller thiocyanate anion could approach at this point. Using the larger cations leads to a more planar ligand and thus a more accessible axial co-ordination site.

Attempts to synthesise alkaline-earth metal complexes by 1 : 1 : 1 reaction of (1), (5) and alkaline-earth metal salts were unsuccessful. However, if a 2 : 2 : 1 reaction was carried out in the presence of calcium thiocyanate a white microcrystalline solid analysing as [10; $M^{2+} = 0.5Ca(NCS)_2$] and having a distinctive i.r. spectrum was obtained. There are three NH bands, ν(C–N) at 2 065 and 2 055 cm^{-1}, and a strong absorption at 1 596 cm^{-1}. It was not possible to obtain a mass spectrum, and the complex is insoluble. Despite the paucity of physical data it is possible to postulate that the complex may be either a 'sandwich', (A), in which the calcium is held between the two macrocycles as occurs in the KI complex of benzo-15-crown-5, (B),[28] or that a 2 : 2 condensation has occurred leading to a wrap-around ligand, (C), and a complex resembling the KI complex of dibenzo-30-crown-10, (D).[29] It has not been possible to grow crystals suitable for *X*-ray crystal-structure analysis.

General Conclusions.—The ready formation of macrocyclic Schiff-base complexes of alkaline-earth metals by template techniques has been demonstrated. The problem of assignment of the anion disposition from i.r. spectral data in the absence of *X*-ray crystal-structural data has been emphasised. Attempts to form alkali-metal complexes under the same conditions were unsuccessful. There is a similarity of ionic radii between cations from these two groups of elements but a considerably higher 'ionic potential' * exists for the alkaline-earth metals. The successful synthesis of complexes of the latter indicate that this higher charge : radius ratio is of consequence when using effectively spherically charged cations having no apparent co-ordinative discrimination as template agents.

EXPERIMENTAL

Infrared spectra were recorded, as KBr discs, in the 250—4 000 cm^{-1} region using a Perkin-Elmer 457 grating instrument. Hydrogen-1 n.m.r. spectra were obtained at 100 MHz using a Varian HA 100 spectrometer. Conductivity measurements were carried out with a Philips PR 9510 cell (cell constant, 1.43) and using a Philips direct-reading conductivity measuring bridge (PR 9501) at 25 °C. Microanalyses were by Miss M. A. McKinnon of these laboratories.

2,6-Diacetylpyridine was used as supplied (Aldrich). Pyridine-2,6-dicarbaldehyde was prepared by the method of Papadoupoulous *et al.*,[30] 3,6,9-trioxaundecane-1,11-diamine by the method of Dietrich *et al.*,[31] 4,7-diazadecane-1,10-diamine by the method of Barefield *et al.*,[32] and 1,5-bis(2-aminophenoxy)-3-oxapentane by the methods of Tasker and Fleischer [33] and Canon *et al.*[34]

Preparation of the Complexes.—{2,16-*Dimethyl*-6,9,12-*trioxa*-3,15,21-*triazabicyclo*[15.3.1]*heneicosa*-1(21),2,15,17,19-

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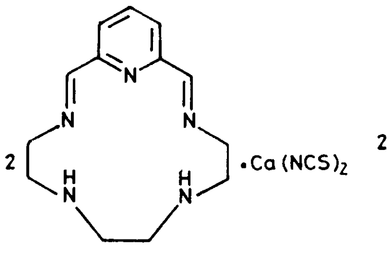
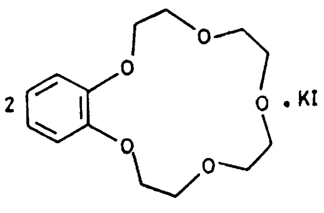
* The ionic potential of the cation is $\phi = Z^+/r$ (see J. A. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity,' S.I. Units edn., Harper and Row, New York, Evanston, San Francisco, and London, 1975).

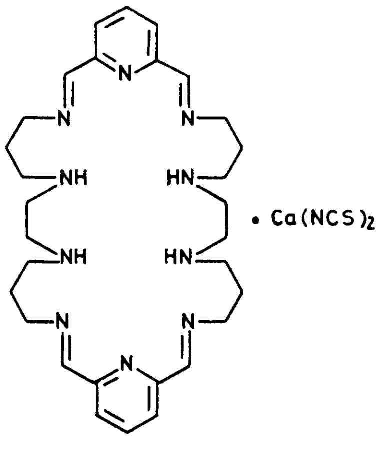
pentaene}di-isothiocyanatocalcium(II), [7; $M^{2+} = Ca(NCS)_2$]. Warm ethanolic solutions of $Ca[NCS]_2$ (0.20 g of a 78% solution in water, 0.001 mol), 2,6-diacetylpyridine (0.163 g, 0.001 mol), and 3,6,9-trioxaundecane-1,11-diamine (0.192 g, 0.001 mol) were mixed and warmed on a steam-bath for *ca.* 0.25 h during which time a white crystalline precipitate appeared. The product was filtered off, recrystallised from ethanol to which a minimum volume of water had been added, and dried over silica gel *in vacuo*.



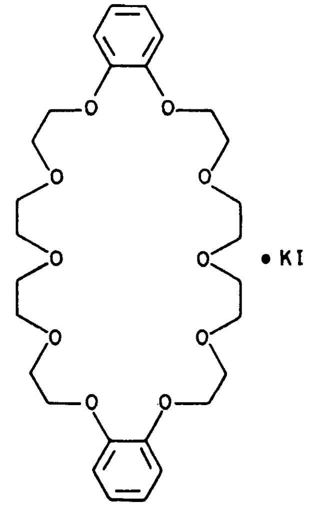
(A)



(B)



(C)



(D)

All complexes (7) were prepared by a similar template procedure; yields 50—55%. The ^1H n.m.r. spectra of the isothiocyanate complexes were recorded in $S(CD_3)_2O$: $M^{2+} = Ca(NCS)_2$, 8.38 (m, aromatic), 4.10—3.80 (m, CH_2), and 2.60 (s, CH_3) p.p.m. relative to $SiMe_4$; $M^{2+} = Sr(NCS)_2$, 8.35 (m, aromatic), 3.89 (m, CH_2), and 2.60 (s, CH_3) p.p.m.; $M^{2+} = Ba(NCS)_2$, 8.40 and 8.12 (m, aromatic), 3.86 (m, CH_2), and 2.51 (s, CH_3), p.p.m.

Di-isothiocyanato{6,9,12-*trioxa*-3,15,21-*triazabicyclo*-[15.3.1]*heneicosa*-1(21),2,15,17,19-*pentaene*}*calcium*(II), [6; $M^{2+} = Ca(NCS)_2$]. Warm ethanolic solutions of pyridine-2,6-dicarbaldehyde (0.135 g, 0.001 mol), $Ca[NCS]_2$ (0.20 g of a 78% solution in water, 0.001 mol), and 3,6,9-trioxaundecane-1,11-diamine (0.192 g, 0.001 mol) were mixed and warmed on a steam-bath for *ca.* 0.25 h, during which time a white precipitate appeared. The complex was recrystallised from ethanol to which a minimum volume of water had been added and dried over silica gel *in vacuo*.

All complexes (6) were prepared by similar template syntheses; yields 50—55%. The ^1H n.m.r. spectra of the isothiocyanate complexes were recorded in $S(CD_3)_2O$: $M^{2+} = Ca(NCS)_2$, 8.80 (s, CH=N), 8.53—8.35 and 8.00—8.20 (m, aromatic), and 4.10—3.80 (m, CH_2) p.p.m.; $M^{2+} = Sr(NCS)_2 \cdot H_2O$, 8.85 (s, CH=N), 8.54—8.36 and 8.28—8.06 (m, aromatic), 4.02 and 3.86 (d, s, CH_2), and 3.47 (s, H_2O) p.p.m.; $M^{2+} = Ba(NCS)_2 \cdot H_2O$, 8.75 (s, CH=N), 8.50—8.30 and 8.12—8.00 (m, aromatic), 4.00 and 3.80 (d, s, CH_2), and 3.42 (s, H_2O) p.p.m.

Di-isothiocyanato{10,13,16-trioxa-3,23,29-*triazatetracyclo*-[23,3,1,$0^{4,9}0^{17,22}$]*nonacosa*-1(29),2,4,6,8,17,19,21,23,25,27-*undecene*}*calcium*(II), [8; $M^{2+} = Ca(NCS)_2$]. Warm ethanolic solutions of pyridine-2,6-dicarbaldehyde (0.135 g, 0.001 mol), 1,5-bis(2-aminophenoxy)-3-oxapentane (0.288 g, 0.001 mol), and calcium thiocyanate (0.20 g of a 78% solution in water, 0.001 mol) were warmed on a steam-bath for *ca.* 0.25 h. On cooling the complex precipitated from solution as a bright yellow powder which was recrystallised from ethanol and dried over silica gel *in vacuo*.

The remaining complexes (8) and (9) were prepared similarly; if the complex was too insoluble for recrystallisation, impurities were removed by warming the complex in ethanol for *ca.* 0.5 h and filtering the resulting mixture. The yields were 40—50%.

{2,15-*Dimethyl*-3,7,10,14,20-*penta-azabicyclo*[14.3.1]*eicosa*-1(20),2,14,16,18-*pentaene*}*di-isothiocyanatocalcium*(II) [11; $M^{2+} = Ca(NCS)_2$]. Warm ethanolic solutions of 2,6-diacetylpyridine (0.163 g, 0.001 mol), calcium thiocyanate (0.20 g of a 78% solution in water, 0.001 mol), and 4,7-diazadecane-1,10-diamine (0.174 g, 0.001 mol) were mixed and warmed on a steam-bath for *ca.* 1 h. On cooling a white crystalline precipitate appeared. The crude complex was recrystallised from ethanol with a minimum volume of water added and dried over silica gel *in vacuo*.

All complexes (**11**) were prepared by a similar procedure; the yields averaged 40—50%. The 2 : 1 complex [**10**; $M^{2+} = 0.5Ca(NCS)_2$] was prepared similarly and impurities were removed from the product by warming in ethanol for *ca.* 1 h.

We thank the S.R.C. for an award (to D. H. C.).

[8/744 *Received, 20th April*, 1978]

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