Alkaline Earth Metal Complexes of Furanyl-containing Schiff Base Macrocycles; *X*-Ray Crystal and Molecular Structure of the Strontium Complex

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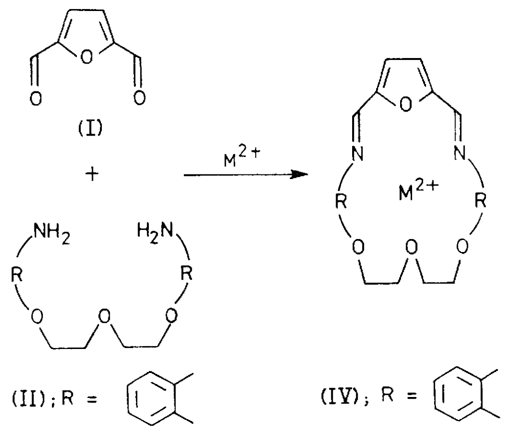
Summary Novel alkaline earth metal thiocyanate complexes are formed by the template condensation of furan-2,5-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane and 1,5-bis(2-aminophenoxy)-3-oxapentane; the *X*-ray structure of aqua-(3,15-diaza-6,9,12,20-tetraoxabicyclo[15,2,1]eicosa-2,15,17,19-tetraene)-di-isothiocyanatostrontium(II) has been determined.

The observation that many of the neutral and monocarboxylic acid antibiotics capable of complexing the alkali and alkaline earth metal cations and effecting their transfer across natural or synthetic membranes contain the 2,5-dimethyltetrahydrofuranyl group has stimulated interest in the synthesis of macrocyclic ligands containing furanyl groups.[1] Macrocyclic polyethers of this type have been reported recently, together with brief comment on their metal complexing ability.[2,3]

We have investigated the synthesis of macrocycles derived from furan-2,5-dicarbaldehyde (I) and α,ω-amino-ethers in the presence of alkaline earth metal cations. The reactions of (I) with 1,8-diamino-3,6-dioxaoctane, 1,2-bis-(2-aminophenoxy)ethane, 1,3-bis(2-aminophenoxy)propane, 1,5-bis(2-aminophenoxy)-3-oxapentane (II), and 1,11-diamino-3,6,9-trioxaundecane (III) in alcoholic media, in the absence of metal ions, gave no recognisable macrocyclic products. When Ca, Sr, and Ba thiocyanates were used as templating cations in these reactions, macrocyclic complexes were isolated with the diamines (II) and (III) only. The use of Mg^{2+} as the potential templating cation gave no recognisable macrocyclic products, and this is a further illustration of the cation size control factor previously noted in the synthesis of the comparable pyridine-containing macrocycles.[4] Only the higher alkaline earth metals form products with the macrocycles derived from the three oxygen-containing amino-ethers. The complexes (IV) and (V) were characterised by chemical analysis and i.r. and mass spectrometry, and represent the first example of such macrocyclic Schiff bases derived from furanyl-containing precursors.



Reaction conditions: (II), EtOH or BuOH; (III), BuOH, N_2, triethyl orthoformate. M = Ca, Sr, or Ba.

The i.r. spectra show no carbonyl stretching frequencies [1675 cm^{-1} in (I)] and the presence of bands in the 1610—1620 cm^{-1} region is indicative of ν(C=N). All but one of the complexes (IV; M = Ca) show a splitting of the thiocyanate CN stretching frequency,[5] though the CS stretch and NCS bending modes are obscured by ligand bands. It is not possible to deduce the mode of thiocyanate bonding, or to advance a reason for the nonequivalence as evidenced by the splitting of ν(C=N) solely from the spectral information.

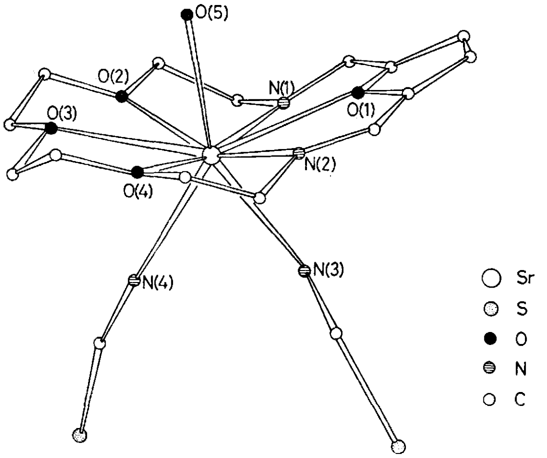


Figure. Molecular structure of Sr(L)(NCS)$_2$.H$_2$O (V).

The complex Sr(L)(NCS)$_2$.H$_2$O (L = ligand) (V), M = 502·1, forms triclinic crystals from aqueous ethanol; a = 13·556(4), b = 9·130(2), c = 9·895(2) Å, α = 107·81(4), β = 109·10(4), γ = 84·01(3)°, space group $P\bar{1}$, Z = 2. Intensity data were collected using Mo-K_α radiation on a Stöe-Stadi 2 diffractometer. For 3221 independent reflections having $I/\sigma(I) \geqslant 4$, R is currently 0·060.†

The nitrogen and oxygen atoms of the macrocycle lie at distances 2·69—2·80 Å from the strontium ion. Interaction of these six atoms with strontium together with the bonding of a water molecule from one side of the ring and two N-bonded thiocyanate groups from the other side give an effective nine-co-ordination of the strontium. The cation lies below the mean plane of the macrocycle donor atoms and towards the thiocyanate anions such that the O(5)–Sr–N,O(macrocycle) angles lie in the range 68·7—84·3°.

The Sr–O(5) distance of 2·582(8) Å shows the water molecule to be strongly co-ordinated to strontium and the two Sr–N(thiocyanate) distances (mean, 2·633 Å) are, as expected, significantly shorter than the Sr–N(macrocycle) values of 2·799(10) and 2·785(8) Å. The plane through O(5),N(3),N(4) is inclined at 85° to that associated with the furanyl ring, with the strontium effectively co-planar with both planes. The O(5),N(3),N(4) plane is orientated such that one thiocyanate anion is beneath the furanyl species and the other beneath the ethylene-oxy chain. The unsymmetrical disposition of these groups with respect to the macrocycle, along with a small difference in the Sr–N–CS bond angles (164 and 168°) would account for the splitting of ν(C≡N) observed for the complex [2085 and 2070 (shoulder) cm^{-1}]. Furthermore, the water molecule is hydrogen-bonded to one thiocyanate anion from an adjacent molecule.

The bonding and spatial arrangement of the anions in the analogous calcium and barium complexes is not necessarily similar to that in the strontium complex as relationships between ion size and ligand cavity diameter must be considered, as with the complexes of the alkali and alkaline earth metals with cyclic polyethers.[6]

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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