Alkaline Earth Metal Complexes of Pyridinyl Containing Schiff Base Macrocycles: *X*-Ray Crystal and Molecular Structures of the Calcium and Strontium Complexes

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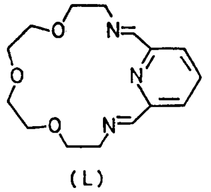
Summary Novel alkaline earth metal thiocyanate complexes are formed by the template condensation of 1,11-diamino-3,6,9-trioxaundecane with pyridine-2,6-dicarbaldehyde; the X-ray structures of (3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene)di-isothiocyanatocalcium(II) and aqua-(3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene)di-isothiocyanatostrontium(II) have been determined and the ready exchange of alkaline earth cations for lead(II) in these complexes is reported.

CALCIUM, strontium, and barium complexes of the macrocyclic Schiff base, 3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]-heneicosa-1(21),2,15,17,19-pentaene, (L), may be prepared by application of the metal ion template effect. The condensation of pyridine-2,6-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane in 1 : 1 molar ratio in butan-1-ol in the presence of the alkaline earth metal thiocyanate yields Ca(L)(NCS)$_2$, (I), Sr(L)(NCS)$_2$.H$_2$O, (II), or Ba(L)(NCS)$_2$.H$_2$O, (III), as crystalline products.



(L)

Crystal data. (I): $M = 447{\cdot}6$, monoclinic with $a = 9{\cdot}624(2)$, $b = 26{\cdot}103(7)$, $c = 8{\cdot}636(2)$ Å, $\beta = 90{\cdot}25(3)°$, space group $P2_1/c$, $Z = 4$. $R = 0{\cdot}040$ for 2084 independent reflections. (II): $M = 513{\cdot}2$, triclinic with $a = 13{\cdot}660(4)$, $b = 9{\cdot}124(2)$, $c = 10{\cdot}070(2)$ Å, $\alpha = 108{\cdot}50(4)$, $\beta = 108{\cdot}42(4)$ $\gamma = 83{\cdot}11(3)°$, space group $P\bar{1}$, $Z = 2$. R = 0·047 for 1999 independent reflections.† (III): Preliminary *X*-ray photographic work indicates this barium complex to be isostructural with the strontium complex (II).

While the metal ions in both (I) and (II) are found to be co-ordinated to the macrocyclic ligand, the smaller calcium is located much more within the cavity of the macrocycle compared to strontium. Thus the calcium ion lies in the mean plane of the macrocycle oxygen and nitrogen atoms whereas the strontium ion is displaced by 0·53 Å from this plane. The relative location of the metals with respect to the macrocycle is also reflected by the value of the N(1)–M–O(2) bond angle, which is 146·0 and 175·6° for the strontium and calcium complexes, respectively. Both metals appear to be equally disposed towards the nitrogen and oxygen atoms of the macrocycle and the mean metal–N(macrocycle) and metal–O(macrocycle) distances do not differ significantly for either strontium (2·78 Å) or calcium (2·64 Å). The difference between these mean metal–donor distances, 0·14 Å, reflects the different cation radii (Sr^{2+} 1·25, Ca^{2+} 1·12 Å), and it would seem that it is to attain suitable Ca–donor distances that the smaller metal ion is drawn into the macrocyclic cavity. In so doing the conformation adopted by the macrocycle in (I) appears to be more strained than that in (II), as is indicated by torsion angle calculations. The torsion angle for one of the C–O bonds, for example, is only 133° in (I) compared to an expected value of *ca.* 180° [the corresponding angle in (II) is 177°].

The presence of six donor atoms in the macrocyclic ligand along with two N-bonded thiocyanate groups gives calcium a co-ordination number of 8 in (I), while the co-ordination of strontium in (II) is increased to 9 by a water molecule. The

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for the communication.

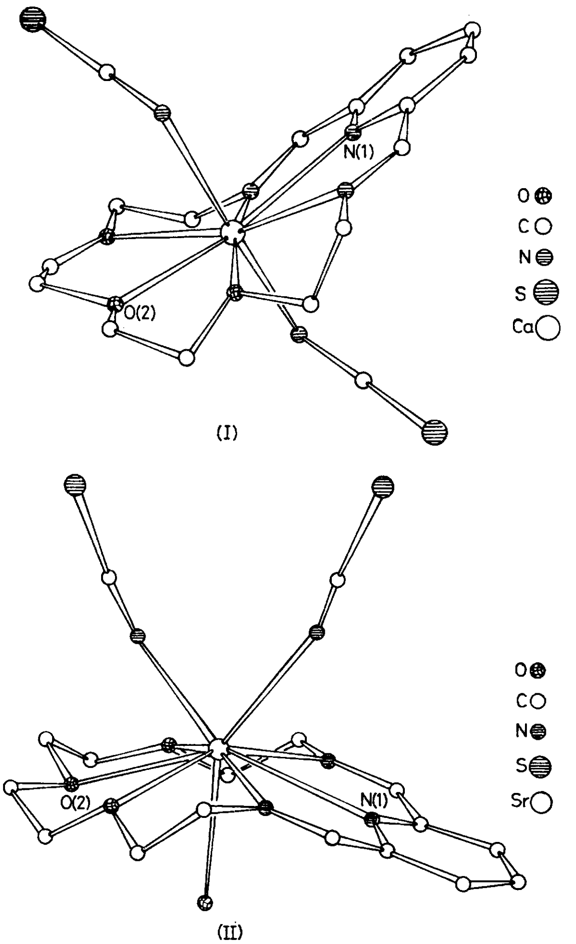

FIGURE. Molecular structures of $Ca(L)(NCS)_2$ (I) and $Sr(L)(NCS)_2.H_2O$ (II).

latter co-ordinates strongly, the Sr–O distance being 2·59 Å, and also gives rise to hydrogen bonding involving a thiocyanate anion from an adjacent molecule. No significant intermolecular interactions are found in the calcium complex.

When the alkaline earth metal complexes are refluxed in aqueous ethanol over lead thiocyanate for *ca.* 10 min a cation exchange process occurs readily to give the previously reported[1] lead complex, Pb(L)(NCS)(SCN), (IV). The reverse reactions do not appear to proceed. In contrast to the metal in (I) and (II), the lead in complex (IV) interacts preferentially with the nitrogen atoms of the macrocycle. Not only is the mean Pb–N(macrocycle) distance of 2·60 Å far smaller than the mean Pb–O(macrocycle) distance of 3·07 Å but it is also significantly shorter than that found for the metal–donor atom distance in (I) or (II). We suggest therefore that this relatively strong affinity of the 'softer' lead for nitrogen atoms of the macrocyclic ligand is the driving force of the observed exchange reactions.

The i.r. spectra of the complexes show different patterns for the thiocyanate CN stretching frequencies: (I), 2065; (II), 2081 and 2073; and (III), 2070 cm^{-1} (broad). Although retrospectively these values may be related to the structural type we have noted that it is not possible to use the i.r. data to predict with certainty the mode of thiocyanate bonding in this general class of complexes. This is in contrast to transition metal thiocyanate derivatives where a defined relationship between $\nu_{C=N}$ and the SCN bonding mode has been established.[2] Further evidence for this difference is exhibited in the i.r. spectrum of (IV) where $\nu_{C=N}$ occurs at 2085 and 2065 cm^{-1}, *i.e.* at comparable values to those found for (II) despite the fact that in (IV) linkage isomerism occurs.[1] The CS stretching and NCS bending modes are obscured by ligand bands.

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[1] D. E. Fenton, D. H. Cook, and I. W. Nowell, *J.C.S. Chem. Comm.*, 1977, 274.

[2] A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, **24**, 69; the ranges quoted for $\nu_{C=N}$ are: 'free' NCS, 2100; S-bonded, 2120—2080, and N-bonded, 2080—2040 cm^{-1}.