Complexes of Lithium Salts with 1,4,8,11-Tetra-azacyclotetradecane

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Summary The cyclic tetradentate secondary amine, 1,4,8,11-tetra-azacyclotetradecane (cyclam) reacts with lithium salts to give complexes of the type $(LiX)_2$(cyclam) when X = Br, I, or ClO_4, and also $LiClO_4$(cyclam).

THE complexation of alkali metals by macrocyclic polyethers has provided a series of compounds of varying stoicheiometry and geometry, depending upon the ring cavity size and the cation included in the complex.[1,2] For some cyclic polyethers bimetallic species may be isolated.[3,4] Complexes of nickel(II) with macrocyclic thioethers[5] and macrocyclic amines[6] also provide examples of complexes in which the ligand incorporates two metal atoms.

1,4,8,11-Tetra-azacyclotetradecane (cyclam) reacted with excess of $LiClO_4$ in methanol to give needles of $LiClO_4$(cyclam). Slow evaporation of the mother liquor gave $(LiClO_4)_2$(cyclam). Reaction of cyclam with an excess of lithium bromide or iodide in chloroform gave crystals of $(LiBr)_2$(cyclam) or $(LiI)_2$(cyclam). Similar experiments with sodium and potassium salts yielded only the starting materials.

As shown in the Table, the i.r. spectra of the 2:1 complexes resemble each other in the region 800—910 cm^{-1}, which has been shown[7] to be diagnostic for *cis*- and *trans*-isomers of octahedral complexes. Comparison of the values with those for transition-metal complexes indicate that the ligand is similar to, but not identical with, the *trans*(III)-form† as determined by *X*-ray structure analysis of $NiCl_2$(cyclam),[8] or the *trans*(IV)-form.[9] The changes observed are probably imposed by the steric requirement of tetrahedral co-ordination for the lithium cation. The spectra are also different from that of free cyclam, showing that conformational changes occur on ligation. A single sharp band (ν_{NH}) is observed at 3295 cm^{-1} for $LiClO_4$(cyclam) and at 3250 cm^{-1} for $(LiBr)_2$(cyclam) or $(LiI)_2$(cyclam) in contrast to the two bands observed at 3260 and 3185 cm^{-1} in free cyclam. For $(LiClO_4)_2$(cyclam) the sharp band is observed at 3275 cm^{-1} together with a broader band at 3155 cm^{-1}. The broad band is probably a manifestation of hydrogen bonding from the secondary amine to the perchlorate anion.

Preliminary *X*-ray crystallographic results confirm the stoicheiometries. The 2:1 complexes $(LiClO_4)_2$(cyclam) and $(LiI)_2$(cyclam) are triclinic with one of these formula units in the unit cell. $(LiClO_4)$(cyclam) is body-centred tetragonal with only two formula units per unit cell so that all the nitrogen atoms are crystallographically equivalent (consistent with one ν_{NH} band in the i.r. spectrum) and probably tetrahedrally arranged about a lithium ion. In this complex the nitrogen compound contrasts with the lithium salt complexes of 16-membered macrocyclic polyether rings, for which the 1:1 stoicheiometry was attributed[4] to equimolar crystallisation of 2:1 complex and free ligand.

TABLE

I.r. spectra in the 800—910 cm^{-1} *region*

cis-[Co(cyclam)Cl_2]Cl[a]			890w	872s	859s	841w	824w	808s
trans-[Co(cyclam)Cl_2]Cl[a]		906s	888s					818s
trans-[Ni(cyclam)Cl_2][b]		894w	875s					800w
$(LiBr)_2$(cyclam)	909w	900w	888w			848s		805s
$(LiI)_2$(cyclam)	909w	904w	884w			843s		806s
$(LiClO_4)_2$(cyclam)	909w		884w			860s		817s
$LiClO_4$(cyclam)		909s				852m		810s
cyclam	909w	893w	880w			830s		

[a] From ref. 7. [b] From ref. 10.

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† The forms of the ligand are those described in ref. 9.

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