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NOVEL LITHIUM CATION COMPLEXANTS

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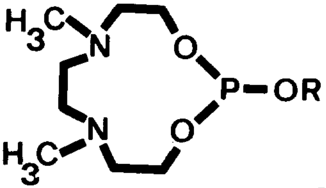
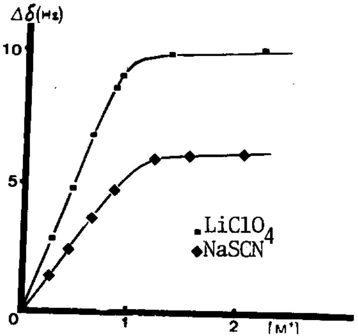
Two of us have recently prepared[1] new derivatives of 1,10-dioxa-4,7-diaza-11-phosphacycloundecane (1).

We report here the complexing aptitude of these crowns 1,2 towards alkali metal cations. Complexation induces downfield shifts of the proton resonances measured with a Varian T-60 spectrometer (Fig.) (Table).



1 R : CH_3, C_2H_5



Using the observed 1:1 stoichiometry, we have extracted[2] from the data in acetonitrile solution at 35°C the stability constants K and the limiting chemical shift δ_B in the bound form. The K values obtained from the best fits of the theoretical curves to the experimental points indicate strong binding of the lithium cation ($K > 300\ M^{-1}$), while the sodium ($K = 8\text{-}10\ M^{-1}$) and potassium ($K = 5\ M^{-1}$) complexes of these 11-crown-5 analogs (1) are rather weak. Several lithium complexes with crown ethers[3-6], cyclic decapeptides[7] and cryptands[8] have been characterized. But such a selectivity towards lithium as we find here has only been reported with 12-crown-4[4], 14-crown-4[3,5], and the (2.1.1) cryptand[8]. With a diameter of ca.

R	salt	resonance	$\delta_B(\mathrm{Hz})^a$	$\Delta\delta(\mathrm{Hz})^b$	$K(M^{-1})^c$
C_2H_5	$LiClO_4$	NCH_3	143.6	10.1	> 300
C_2H_5	$NaClO_4$	NCH_3	137.7	4.2	10
C_2H_5	NaSCN	NCH_3	139.9	6.4	8
CH_3	NaSCN	NCH_3	139.9	6.2	9
CH_3	NaSCN	OCH_3	208.7	9.9	8
C_2H_5	KSCN	NCH_3	136.3	2.8	5
a) ± 0.4 Hz, downfield from TMS			b) ± 0.6 Hz		c) at 35°C, ± 15%

Table : summary of the results.

1.2 Å, the lithium ion can fit into a cavity of 1.2-1.6 Å [3]. Strong interactions with Li^+ are indeed observed with 11-crown-5, 12-crown-4, 14-crown-4, and the (2.1.1) cryptand, whose hole dimensions are within this range.

The lithium-complexing avidity of (1) should be extremely useful for synthetic purposes. A number of important alkylation reactions have rates and/or products very much dependent upon the structure of the lithium ion pairs present[9]. Derivatives of this type could be used, in conjunction with 12-crown-4[10], to drive such reactions towards formation of specific products.

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