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N-BRIDGED HETEROCYCLES PART IV. METAL COMPLEX FORMATION WITH N-BRIDGED HETEROCYCLES AND TWO SIMPLE 'YES-NO' TESTS FOR COMPLEXABILITY OF CROWN ETHERS AND RELATED SYSTEMS

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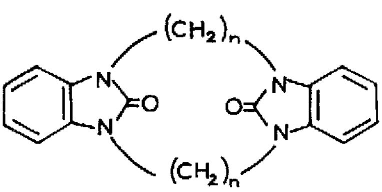
The synthesis of a new range (1-13) of N-bridged benzimidazolones, quinoxalin-2,3-diones and uracils were described in Part III[1]. All these compounds contain highly negatively polarised carbonyl oxygen atoms as well as, in some cases, ether oxygens, which suggest the possibility of complex formation with cations. We now report the isolation of such stable, crystalline complexes and two simple, rapid 'yes-no' tests for complexation.

Because of the lack of such simple tests for complexability, we have evolved two tests, both relying on the ability of crown ethers to solubilise cations in organic solvents. The first involves dissolution of the precipitated inorganic salt (from a solution in methanol by dropwise addition of toluene) by addition of a small amount of the crown ether[2]. The second relies on the recently reported ability of crown ethers to render the deep-red Meisenheimer complexes of trinitrobenzene soluble in non-polar organic solvents[3]. We dissolved trinitrobenzene and the crown ether in chloroform and observed the colour of the solution on addition of the inorganic salt. The results are summarised in the Table and are compared with 18-crown-6 as a standard. Although the two tests do not give the same results throughout, they do show the trend of complexability and a good result in both tests is strongly indicative of efficient complex formation.

Some of the results are particularly noteworthy. Thus the total specificity of the dimer (2; m.p. 211°) for calcium ions is remarkable and was supported by the isolation of a 1:1 calcium thiocyanate complex as a stable crystalline solid, m.p. 243°. Similarly we have isolated a stable 1:1 potassium thiocyanate complex (m.p. 272-5°) of the crown ether (8; m.p. 117-8°).



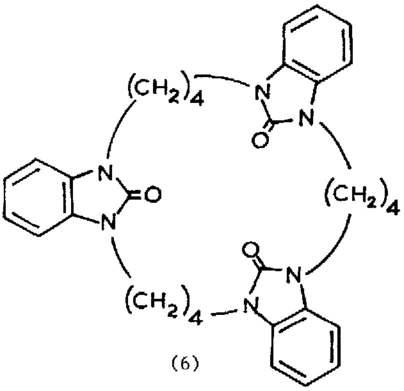
(1) n=5

(2) n=6

(3) n=7

(4) n=8

(5) n=10



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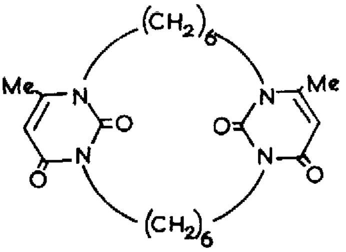

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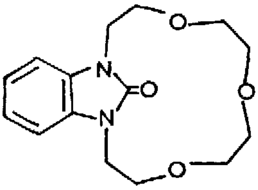

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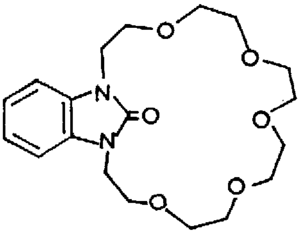

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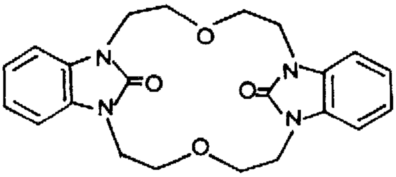

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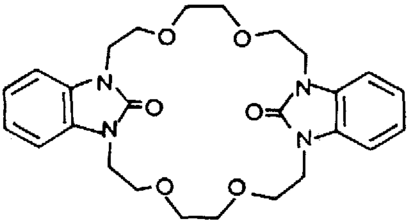

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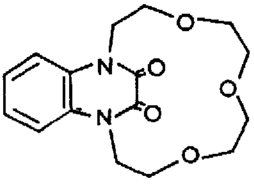

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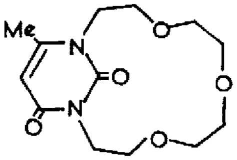

(13)

Metal salt[a] / Test / Compound	Mg^{2+}		Li^+		Na^+		Ca^{2+}		Sr^{2+}		K^+		Ba^{2+}		NH_4^+		Cs^+	
	I^b	II^f	I^d	II^f	I^b	II^e	I^c	II^f	I^b	II	I^b	II^e	I^d	II^f	I^d	II^e	I^c	II
18-crown-6	√	√	√	√√	√√	√√	√√	X√	√√	-	√√	√√	√	√√	√√	√√	√√	-
1	X	X	√√	X	X	X	√√	X	√√	-	X	X	√	X	√	X	X	-
2	X	X	X	X	X	X	√√	√√	X	-	X	X	X	X	X	X	X	-
3	X	X	√	X	X	X	X	√√	X	-	X	X	X	X	X	X	X	-
4	X	X	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X	-
5	X	X	X	X	X	X	X√	X	X	-	X	X	X	X	X√	X	X	-
6	X	X	X	X	X	X	√√	X	√√	-	X	X	X	X	X	X	X	-
7	X	X	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X	-
8	X	X	√	X	√	X	√√	X	√√	-	√√	√	X	X	X	X	√√	-
9	X	√	√	√√	√	√√	√	√√	√√	-	√	√√	√	√	X	X	√√	-
10	√	X	√√	X	√√	√√	X	√√	√	-	X	X	√	√√	X	X	X	-
11	√	X	√√	X	√√	X	X√	X	√√	-	X	X	√	X	√	X	X	-
12	√	X	X	X	X	X	X	X	X	-	√	√√	X	X	X	X	√	-
13	X	X	X	X	X	X	X	X	X	-	X	√√	X	X	√	X	X	-

[a] the salts used are placed in order of their ionic radii.

[b] bromide; [c] chloride; [d] iodide; [e] carbonate; [f] hydroxide salt used.

Test I is the dissolution test; Test II is the colour test.

The ticks and crosses refer to the rate of achieving dissolution (in test I) or colour (in test II). The double tick (√√) indicates immediate change; one tick (√) indicates a positive result; the (X√) symbol indicates the test only occurs on standing or shaking.

In both cases complexation is accompanied by a decrease in the infrared carbonyl stretching frequency (nujol mull) (from 1710 to 1680 cm^{-1} in the former and 1705 to 1695 cm^{-1} in the latter complex). This property allows another method of monitoring complexation in our series and will be reported fully elsewhere.

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References

1. M. M. Htay and O. Meth-Cohn, Tetrahedron Letters, 1975, in press.
2. This test was first suggested to us by Dr. P. Plesch of Keele University for testing the efficiency of complexations of various crown ethers with potassium ions employing potassium iodide.
3. A. R. Butler, J. Chem. Soc. Perk. 1, 1975, 1557.