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CRYSTALLINE COMPLEXES OF CYLINDRICAL MACROCYCLIC POLYETHERS. DIDECALINO- AND DECALINO-BENZO-18-CROWN-6

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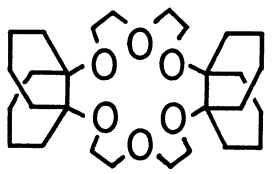
Didecalino- and decalino-benzo-18-crown-6 have been found to form 1:1 (crown ether:cation mole ratio) complexes in stoichiometry with NaNCS, KNCS, RbNCS, CsI_3, and/or H_3OClO_4 without any formation of sandwich-type complexes.

Although the formation of sandwich-type complexes is a common feature in the complexation of crown ethers with alkali metal cations, especially with cations that are too large to fit with the macrocyclic cavity,[1] little is known about the influence of topological change of the ligand on the complex stoichiometry. In previous paper,[2] we revealed that a new type of cylindrical crown ether, didecalino-18-crown-6 (1), exhibited the excellent complexing ability toward alkali metal cations because of the remarkable embedding effect of decalin moieties which were oriented perpendicular to the ring plane of crown ether. In this paper, we wish to report the conspicuous effect of decalin moiety on complex stoichiometry in the complexation of 1 and decalino-benzo-18-crown-6 (2) with those cations.



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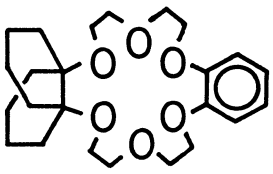

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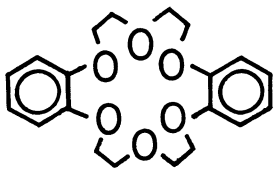

3

Crystalline complexes of 1 were prepared with Pedersen's or Bartsh's procedure,[3,4] as shown in Table 1. Concerning the formation of sandwich-type complexes, it was previously reported that dibenzo-18-crown-6 (3), being a flat molecule, formed 1:1 complexes with KNCS and RbNCS, 2:1 sandwich ones with RbNCS and CsNCS, and 3:2 club-sandwich one with CsNCS.[3] Interestingly, 1:1 crystalline complexes were gained without exception even with larger cations such as Rb^+ and Cs^+ in the presence of twice the excess of 1. In addition, the similar results

Table 1. Crystalline complexes of 1 with NaNCS, KNCS, RbNCS, CsI_3, and H_3OClO_4

Crystalline[a] complex	Crown ether:cation mole ratio		Mp/°C	Yield/%
	Reactants	Complex[b]		
Didecalino-18-crown-6			178-179	
NaNCS	1:1	1:1	197-199	60
KNCS	1:1	1:1	282-284	78
RbNCS	1:1	1:1	261.5-262.5	85
	2:1	1:1	262-263	68
CsI_3	1:1	1:1	160.5-162	78
	2:1	1:1	157-158	84
H_3OClO_4		1:1	118-119	45

a) No crystalline complex was obtained with CsNCS.

b) Elemental analyses were within 0.40% theory.

were obtained in the case of 2. Melting points of 1:1 complexes obtainable are as follows: KNCS complex 222-224 °C, RbNCS 183-185 °C, and CsI_3 147-148 °C. No crystalline complexes were given with NaNCS and CsNCS.

These results definitely suggest that the introduction of decalin moiety into crown ether prominently makes inhibition of approach of additional crown ethers to 1:1 complex already formed in the system.

The determination of the crystal structures of the title crystalline complexes by X-ray analysis is now in progress.

References

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