Communications

Stability Constants of 4,5 : 13,14-Dibenzo-6,9,12-trioxa-3,15,21-triazabicyclo[15.3.1] heneicosa-1(21),17,19-triene-2,16-dione with Alkali Metal Ions in DMF

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The aza-crowns have complexation properties that are intermediate between those of the all-oxygen crowns and those of the all-nitrogen cyclams. These aza-crown ethers have received considerable attention in recent years because of their ability to selectively bind cations[1]. Despite their potential interest as selective complexing agent, very few compound where amide group replaces oxygene have been prepared[2,3], and thus their chemistry has not been extensively studied.

We now describe a new macrocyclic amide which is easy to prepare and has somewhat different matal binding properties from other crown ethers.

Macrocyclic amide was prepared by the reaction of dipicolinic acid dichloride with 1,5-bis(2-aminophenoxy)-3-oxapentane using the high dilution technique, and the synthetic route is outlined in Scheme 1, and the starting materials were prepared according to the literature[4]. The reaction of dichloride with diamine was carried out as follows: separate solution of 25 mmol of dichloride in 250 m*l* of benzene and of 50 mmol of diamine in 250 m*l* of benzene were added dropwise at same rate to 1000 m*l* of rapidly stirred benzene for 10 hrs. The diamine hydrochloride was filtered off and benzene was allowed to slowly evaporate under reduced pressure. White needle was formed and were isolated before the solution was completely evaporated: mp. 236-237℃; IR (KBr) 3410, 2900, 1680, 1600, 1530, 1490, 1450, 1260, 1140,
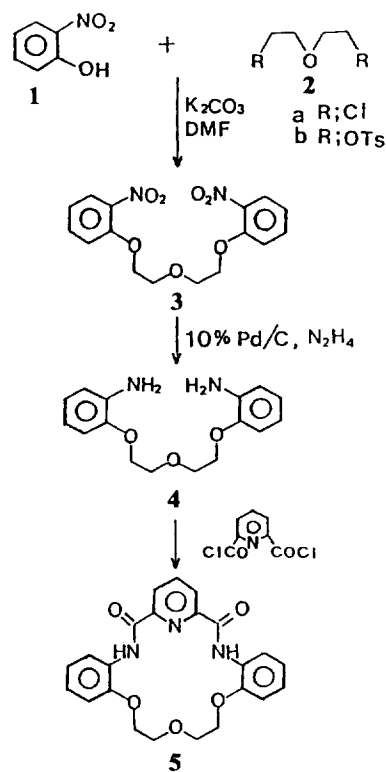
Scheme 1

750 cm^{-1}; NMR (CDCl$_3$) δ 3.85 (m, OCH$_2$), 4.2 (m, O-OCH$_2$), 6.8 (m, benzen), 7.9 (m, pyridine), 9.68 (s, NH); MS, m/e (% relative intensity) 419.35 (M$^+$ 100), 134.15 (63), 77.10 (42), 52.20 (32), 120.15 (28).

The stability constants (K_s) for alkali metal ions with the title compound have been determined conductometrically on a Barnstead Model PM-70CB, which had a stated accuracy of ± 0.1% of the bridge reading. A Toa-CG 511C conductance cell was used and the cell constant was 0.1083 cm^{-1}. N,N-dimethylformamide (DMF) and alkali metal perchlorates were purified by literature method[5]. The specific conductivity of DMF was 6×10^{-7} ohm^{-1}cm^{-1}, and the concentration of alkali metal perchlorate and ligand were 5×10^{-4} M and 1×10^{-2} M respectively.

The experimental procedure to obtain the stability consta-

Table 1. Stability Constants (log K_s) for Complexes of Alkali Metal Perchlorates and Macrocyclic Amide and DB18C6 in DMF at 25℃

Compound	Li⁺	Na⁺	K⁺	Rb⁺	Cs⁺
DB18C6[8]	3.0	3.4	3.6	3.5	3.5
Cyclic amide	2.3	2.0	2.5	2.4	2.7

Table 2. The Ionic Diameters and Charge Densities of Alkali Cations, and the Hole Size of the 18C6 (Å)[10,11]

Cation	Ionic diameter	Charge density$\times 10^{20}$ (Coulomb/Å³)	Polyether	Hole size
Li⁺	1.36	12.1		
Na⁺	1.94	4.46		
K⁺	2.66	1.62	All	2.6-3.2
Rb⁺	2.94	1.18	18-crown-6	
Cs⁺	3.34	0.79		

nts of macrocyclic amide complexes with alkali metal ions was just the same as that described in a paper of Cho and Chang[6]. From the measurement of conductance a plot of equivalent conductance against [crown]/[salt] was obtained for each amide-salt system. For small values of K_s a smooth curve was obtained and from this curve the complex stability constants K_s were calculated. The actual K_s values are calculated by a nonlinear least-squares analysis using Marquardt regression algorithm[7].

The stability constants for the macrocyclic amide-alkali metal complexes are shown in Table 1 together with those of DB18C6 in DMF at 25℃.

Macrocyclic amide has two possible binding sites for metal ions, the nitrogens and the ether oxygens. Keeping these structural features in mind, several interesting trends can be gleaned from the stability constant data.

The stability constant sequences of the alkali metal ions with DB18C6 in DMF at 25℃ are K⁺>Rb⁺+>Cs⁺>Na⁺> Li⁺. For macrocyclic amide, they are Cs⁺>K⁺>Rb⁺>Li⁺> Na⁺. Of all the alkali metal ions, the K_s value of K⁺ are larger than the others in each ligand except for Cs⁺ in macrocyclic amide. The ability of the alkali metal ion to form complexes with DB18C6 is dependent on the ionic diameter, as can be seen in Table 2. Pedersen[9] has observed that complexing power can be expected to be weak when the hole of the polyether is too small or too large for the cation, because the salt-polyether complexes are formed by ion-dipole interaction between the cation and the dipole of oxygen formed by ion-dipole interaction between the cation and the dipole of oxygen atoms symmetrically arranged in the polyether ring.

However, the selectivity tendency of macrocyclic amide for cations is completely inconsistent with the size-fit concept. This may be attributable to the fact that macrocyclic

amide has three nitrogen atoms, more rigid structure, and amide groups. The special stability of the Cs⁺ complex may be explained by the theory "hard and soft acids and bases" and/or additional interaction between Cs⁺ and the amide oxygens in the cyclic amide. Because the ligand has three nitrogen atoms, which make the cyclic amide have soft character, and the charge density of cesium cation is the least (Table 2).

Moreover, ionic diameter of cesium cation much larger than the cavity size of ligand will cause cesium cation to interact with the amide oxygens pointing away from the ring of ligand. Newkone and Kawato[12] had reported that the amide carbonyl group in polyfunctional azacrowns coordinates strongly to Eu³⁺. On the other hand, the possible reason for relatively high stability of the Li⁺ complex of the macrocyclic amide complexes can be explained by its structure that three nirogen and three oxygen atoms occupy separately in the ligand ring. If the smallest lithium cation can be leaned to one side of two species of atom groups in the more rigid ring, lithium cation will be fitted effectively to a side of the macrocyclic cavity.

Since the structure of the complexes studied are not yet known, the binding sites of the ligand cannot be predicted with certainty. For the explanation to these unusual behaviors, the thermodynamics of these complexations should be studied further. The properties of this and other pyridine-containing multihetero-macrocycles are under active investigation, and an analysis of such data will be given in a future publication.

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