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COMPLEXATION OF ALKYLAMMONIUM SALTS BY MACROCYCLIC POLYETHER - DIESTER COMPOUNDS (1)

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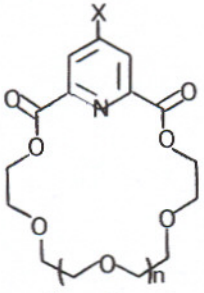
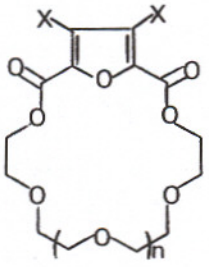
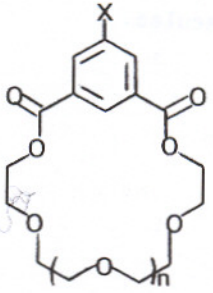
We have reported the preparation of a variety of macrocyclic polyether-diester compounds (2). Some of these compounds form strong complexes with metal cations in methanol (3,4). We have also published a preliminary communication of the complexation of compounds 1-9 with certain alkylammonium cations (5). We now wish to more fully report the complexation of alkylammonium salts not only by compounds 1-9 but 10-15 and 16-21 as well.



1 - 9
X = H, Cl, OCH_3
n = 1-3



10 - 15
X = H, OCH_3
n = 1-3



16 - 21
X = H, NO_2
n = 1-3

Compounds 1-21 complex with various alkylammonium cations as shown by significant chemical shift changes in their ^1H n.m.r. spectra in methylene chloride - D_2. These chemical shift changes are most impressive for the benzylammonium perchlorate complexes of compounds 12(X=H, n=3), 15(X=OCH_3,

n=3), 18(X=H, n=3) and 21(X=NO_2, n=3). In each case, the hydrogens on the carbons next to oxygen are separated into six distinct peak patterns at δ2.96 to δ4.60. The temperature dependencies of the ^1H n.m.r. spectra for the complexes were examined. Calculations of the free energies of activation ($\Delta G^{\ddagger}$) for the dissociation of the complexes show that the eighteen-membered ring containing a pyridine unit (1, 4, and 7, all n=1) formed the most stable complexes (5). In those cases, the 4-methoxy ligand (7, n=1) formed the strongest complex while the 4-chloro ligand formed the weakest.

The alkylammonium perchlorate complexes of the benzo and furano ligands (10-21) were unusual in that complexes of the twenty-four - membered ring ligand (n=3) were the most stable. CPK models and spectral data suggest that complexation involves the oxygens on the polyether bridge most removed from the benzo or furano moieties.

REFERENCES AND NOTES

1. The authors wish to thank Dr. J.F. Stoddart for his many helpful discussions and for the alkylammonium salts used in this study.

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