THE PREPARATION OF MACROCYCLIC POLYETHER-DIESTER LIGANDS CONTAINING THE PYRIDINE SUBCYCLIC UNIT, THEIR COMPLEXES AND THEIR REDUCTIVE DESULFURIZATION TO THE PYRIDINO-CROWN ETHERS.

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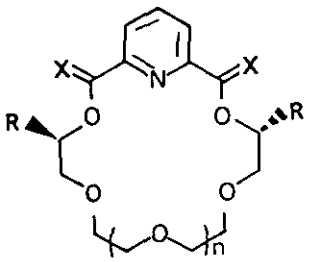
We have reported the synthesis and cation complexing properties of a variety of macrocyclic polyether-diester ligands including those containing pyridine (1) and furan (2) subcyclic units. Chiral macrocyclic ligands containing the pyridine subcyclic unit exhibited enantiomeric recognition when complexed with chiral alkylammonium salts (3). We now report the synthesis and complexing properties of new thionodiester-crown ligands (1-5) and their reductive desulfurization to the pyridino-crown compounds (6-10).

Thionomacrocycles 1-5 were prepared in good yields by treating O,O'-dimethyl 2,6-pyridinedicarbothioate with the appropriate glycol in the presence of methoxide ion in benzene. The methanol by-product was removed by molecular sieves. These macrocycles formed stable complexes with alkali metal salts. Thionomacrocycles 1-5 were desulfurized by Raney Ni (4) to give pyridino-crowns 6-10.

Enantiomeric recognition by ligands 5 and 10 for certain chiral alkylammonium salts has been studied by titration calorimetry in CH_3OH and temperature dependent ^1H NMR spectroscopy in CD_2Cl_2. Both (S,S)-5 and (S,S)-10 exhibited chiral recognition for the hydrogen perchlorate salts of (R)-α-(1-naphthyl)ethyl amine and (R)-methyl phenylalanate over the corresponding (S)-forms.



1 n=0, R=H, X=S
2 n=1, R=H, X=S
3 n=2, R=H, X=S
4 n=3, R=H, X=S
5 n=1, R=CH_3, X=S

6 n=0, R=H, X=H_2
7 n=1, R=H, X=H_2
8 n=2, R=H, X=H_2
9 n=3, R=H, X=H_2
10 n=1, R=CH_3, X=H_2

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