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Synthetic methods were developed for the preparation of macrocyclic and macrobicyclic hosts containing Lewis acidic tin atoms. Anion binding occurred in solution and in the solid state. Complexation of anions by the hosts was studied by NMR spectroscopy and X-ray crystallography. Size selective anion complexation was achieved with macrobicyclic hosts. Mechanistic studies related to the primary synthetic reactions used for the production of the macromolecular skeletons were conducted.					
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FINAL REPORT

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Macrocycles Containing Tin.

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June 1, 1989

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PROJECT SUMMARY

--The main theme of the project has been the development of macromolecular compounds that contain Lewis acidic tin atoms and the application of these compounds as hosts for the complexation of anions and neutral donors.

Alkyl
Synthetic procedures were developed for the production of the macromolecular species. A general approach for the production of macrocycles containing tin atoms was reported in Technical Report 1. *2,6*-Distanna-alkanes were prepared and activated for reaction with a di-Grignard reagent to give macrocyclic compounds containing two or four tin atoms, and the products were purified by preparative reverse phase chromatography (Technical Reports 3, 4). Macrobicyclic skeletons were created by reaction of a macrocycle containing two tin atoms with a di-Grignard reagent (Technical Reports 5, 10). The creation of a Lewis acidic host species was accomplished by selective cleavage of a phenyl group from each tin atom in the macromolecule by reaction with HCl or HBr (Technical Reports 6, 10).

Tin
Methods for observing and quantifying binding of anions by the Lewis acidic hosts were developed. The most useful method involved ^{119}Sn NMR spectroscopy (Technical Report 8, 10, 11, 12). X-ray crystallography was employed to characterize the hosts (Technical Report 5) and complexes (Technical Report 12). Solid state ^{119}Sn NMR spectroscopy has also been employed to characterize the free hosts and complexes with anions (Technical Report 12). *Macrobicyclic Compounds*

The macrocyclic hosts were found to bind halide with poor selectivity (Technical Report 6, 8). However, size selective binding of chloride by macrobicyclic hosts was found (Technical Report 10). Size selectivity was also apparent in one host that was so small that it could only complex the small fluoride anion (Technical Report 11). That the anions were complexed within the cavity of the hosts was demonstrated by solid state studies (Technical Report 12).

Related studies involved mechanistic investigations of the primary reactions employed for the production of the carbon-tin bonds in our hosts. Thus, reactions of tin anionoids with alkyl bromides were studied from the mechanistic point of view (Technical Report 2). These studies were concerned, in part, with the possibility that the reactions occur by an initial electron transfer process, and alkyl halide "mechanistic probes" were employed. The interest in mechanistic probes led to an evaluation of previous applications of these substrates, and we concluded that the fundamental chemistry in the reactions was poorly understood. Eventually, we made an important contribution to the use of mechanistic probes in general when we uncovered radical chain isomerization reactions of the probes (Technical Report 7, 9).

The project is continuing under ONR grant N00014-89-J-1214, R&T Code 4135009.

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TECHNICAL REPORTS

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