Multi-Podands. Ag(I) Complexation with Mono- to Quadru-Podands Having Sulfur Donor

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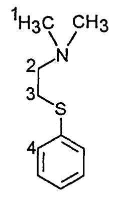
A series of mono- to quadru-podand having same arms were synthesized and thermodynamic parameters for the complexation with Ag(I) in methanol have been determined. All of the podands except mono-podand form 1:1 complexes with Ag(I) definitely and the complexation was enthalpy driving. Binding characteristics were also examined by NMR and solvent extraction.

Acyclic synthetic ionophores behave very similar to cyclic species and thus should be useful additions to the available crown ethers and cryptands. Furthermore, acyclic oligoethers, called podands, could be obtained simply and cheaply.[1] Some acyclic ionophores having oxygen and sulfur as the binding sites have been studied in connection with the extraction of precious metal ions.[2] More recently C-pivot tripode ligands were reported to exhibit higher selectivity for alkali metal cations than did N-pivot analogs.[3]

Little attention, however, has been given on the relationship between number of arms and cation selectivity for the multi-armed podands.[4] We here wish to report a series of new multi-armed podands that has essentially same arm, but has different number of arms to reveal the complexation characteristics, especially with Ag(I) in solution state.



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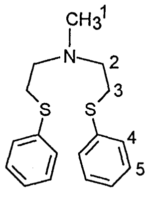

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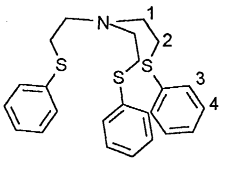

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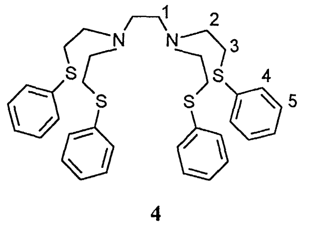

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All of the podands were obtained in good yield by the reaction of corresponding chlorides with aromatic thiol in the presence of KOH in ethanol under reflux condition. Column chromatography on silica-gel with hexane/ethylacetate gave the pure products.[5]

To determine the stability constant, log K, of complexes with Ag(I) in methanol, potentiometric titration[6] was done by Ag(I)-ISE shown as in Figure 1. In spite of different structures due to the number of arms, all of the podands except **1** form the 1:1 stoichiometric complexes with Ag(I) definitely and the non-linear fitting program, Kinfit4 gave the quite accurate results in calculation of log K.[7a] The magnitude and the sequence of stability constant is, **4** (12.43 ± 0.22) > **3** (9.29 ± 0.16) > **2** (7.02 ± 0.12) > **1**[7b]. As results, two or three orders of magnitude in log K as every number of arms increased.

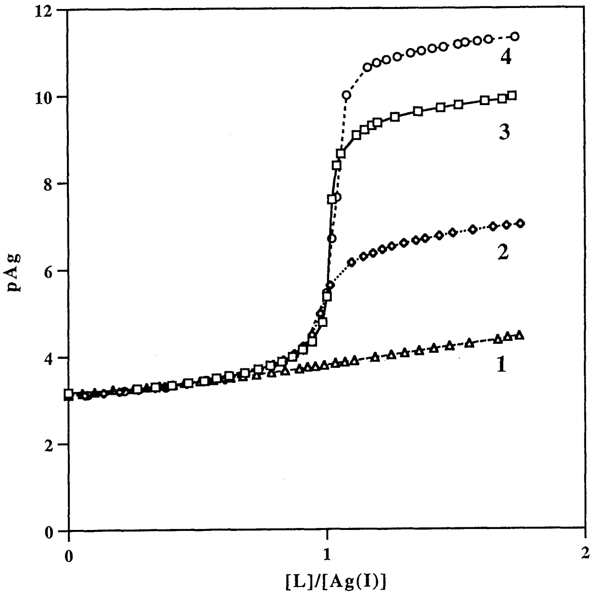

Figure 1. Potentiometric titrations of Ag(I) with podand **1**-**4** in methanol at 25.0 °C.

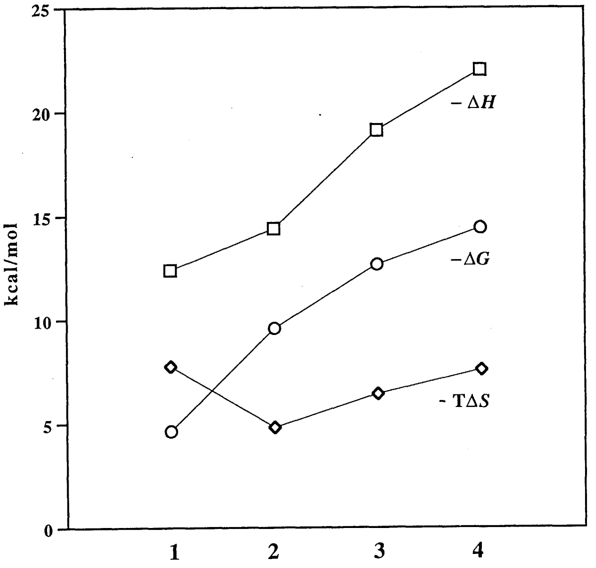

Figure 2. Thermodynamic parameters of Ag(I) complexation with podand **1**-**4** in methanol at 25.0 °C.

The enthalpies of same reaction were evaluated from the calorimetric titration by using the precise solution calorimeter.[6b,8] The corresponding ΔH, ΔG and TΔS variation for Ag(I) complexation with the podands are plotted in Figure 2. These results are noteworthy because apparently the quite difference of framework of ligands, lead to small changes in entropy but large differences in enthalpy terms. A survey of the

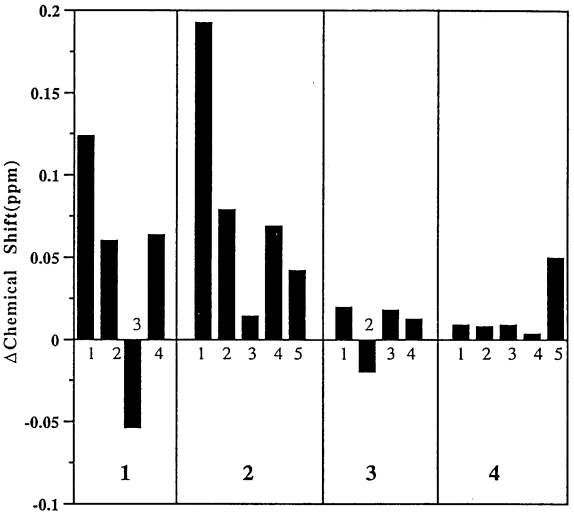

Figure 3. Difference of ^{1}H chemical shift for podand **1**-**4** by complexation with Ag(I).

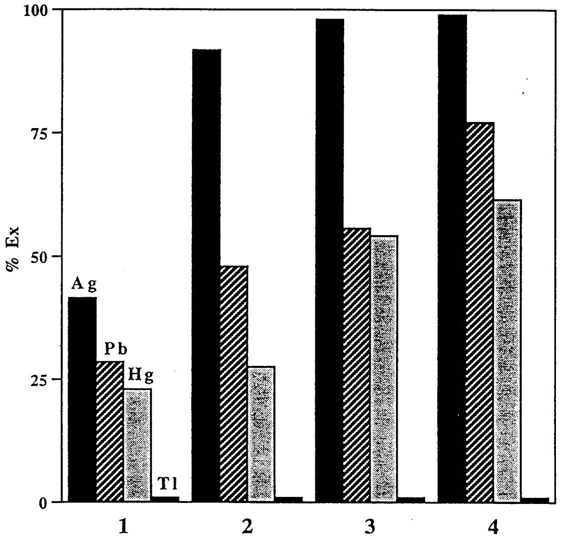

Figure 4. Extractability of metal ions as picrates into chloroform at 25.0 °C by podand **1**-**4**.

data shows that the complex stability of the podands is entirely enthalpic origin, accompanied by unfavorable decrease of entropy with similar quantities.

The ^{1}H NMR spectra of the podands and the complexes with Ag(I) have been measured to get information concerning the binding site and structural changes.[9] For comparison, the changes of chemical shift ($\delta_{complexed}$ - δ_{free}) for each proton are plotted in Figure 3. Most resonances are shifted downfield, consistent with nitrogen and sulfur coordination to Ag(I). Apparently, the magnitude of chemical shift changes for podands is $\mathbf{2} \geq \mathbf{1} > \mathbf{3} \geq \mathbf{4}$, and in case of ^{13}C NMR study for the identical system same result was observed.[10] This is a reverse of the expected order and serves to illustrate that other factors may override the degree of chemical shift on complexation. Such behavior may reflect the occurrence of the tighter space filling of larger podands on complexation than smaller one. So this behavior which is deduced from the higher field shift cancel the ion induced shift to the lower field. Otherwise the partial stacking of the aromatic rings[11], as found for closely related complexes was not observed in this case.

In our previous work[11], we found the podands extract metal cations from aqueous to organic phase by ion-pairing mechanism as well as crown ethers.[12] Figure 4 shows the %*Ex* of some soft metal cation picrates by the podands as extractants. As the number of arms increased, the %*Ex* increased for every cation except Tl(I).

It is known that Ag(I) and Hg(II) (d^{10}) show the preference for linear coordination. But as we can see from the data, the large increase of log *K* for 1:1 complexation as the number of arm increased is due to the increase of favorable enthalpy changes. So, all of the sulfur atoms in each arm probably participate in the coordination to the Ag(I).

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References and Notes

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5 **1**: IR 3017, 2950, 1590, 1100 and 730 cm^{-1}; ^{1}H NMR 7.42-7.10 (m, 5H, aromatic), 3.15-3.05 (t, 2H, -NCH$_2$), 2.60-2.50 (t, 2H, -SCH$_2$), 2.89 (s, 6H, -NCH$_3$); ^{13}C NMR 136.4 (α), 125.7 (o), 128.8 (m), 129.1 (p), 58.5 (-NCH$_2$), 45.1 (-SCH$_2$), 30.2 (CH$_3$). **2**: IR 3017, 2900, 1595, 1100 and 745 cm^{-1}; ^{1}H NMR 7.40-7.15 (m, 10H, aromatic), 3.10-3.01 (t, 4H, -CH$_2$), 2.75-2.65 (t, 4H, -SCH$_2$), 2.30 (s, 3H, -NCH$_3$); ^{13}C NMR 136.3 (α), 126.0 (o), 128.9 (m), 129.1 (p), 56.5 (-NCH$_2$), 42.1 (-14$_2$), 31.3 (-CH$_3$). **3**: IR 3060, 2950, 1590, 1150 and 740 cm^{-1}; ^{1}H NMR 7.40-7.20 (m, 15H, aromatic), 3.10-3.00 (t, 6H, -NCH$_2$), 2.75-2.65 (t, 6H, -SCH$_2$); ^{13}C NMR 136.3 (α), 126.0 (o), 128.8 (m), 129.2 (p), 53.5 (-NCH$_2$), 31.7 (-SCH$_2$). **4**: IR 3010, 2960, 2815, 1582, 1100 and 735 cm^{-1}; ^{1}H NMR 7.32-7.10 (m, 20H, aromatic), 3.02-2.89 (t, 8H, -NCH$_2$), 2.80-2.65 (t, 8H, -SCH$_2$), 2.52 (s, 4H, -NCH$_2$); ^{13}C NMR 136.3 (α), 126.0 (o), 128.9 (m), 129.2 (p), 53.8 (-NCH$_2$), 52.8 (-SCH$_2$), 31.6 (-NCH$_2$).

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7 a) L. Dye and V. A. Nicely, *J. Chem. Edu.*, **48**, 443 (1971); b) If we assume that the stoichiometry for **1**-Ag(I) system is 1:1, the value of log *K* is 3.4 ± 0.3.

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