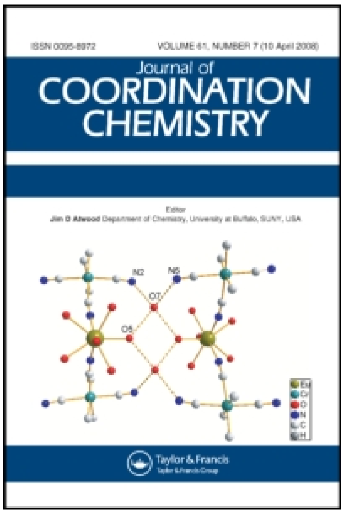

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New Bis- and Tris- Benzo-Crown Ether Receptor Molecules Containing Respectively Ter-Anisyl and Tren Bridging Linkages

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NEW BIS- AND TRIS- BENZO-CROWN ETHER RECEPTOR MOLECULES CONTAINING RESPECTIVELY TER-ANISYL AND TREN BRIDGING LINKAGES

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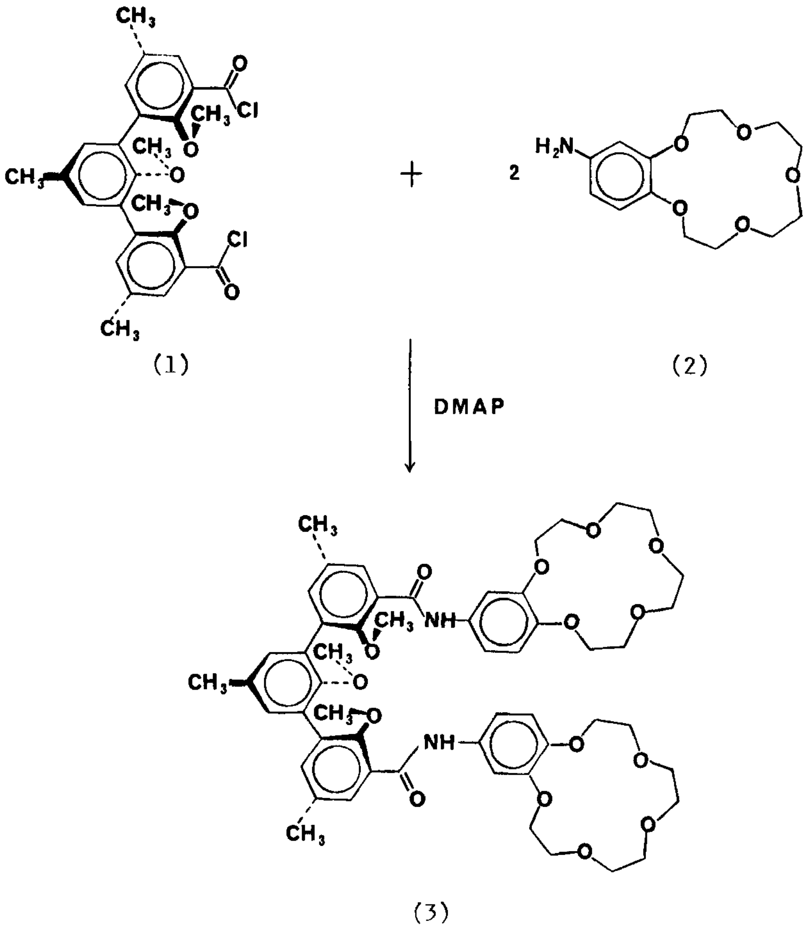
Abstract New bis- and tris- benzo-crown ether receptor molecules containing respectively a rigid ter-anisyl bridge and a Schiff base tren linkage have been prepared. Preliminary coordination studies of these ligands with potassium, sodium and copper guest cations have led to the formation of mono-metallic and hetero-polymetallic complexes.

Keywords: Ter-Anisyl, Tren Bridging Linkages, Schiff base condensation

The design and synthesis of macropolycyclic molecules containing more than one recognition site for binding several guest species is of considerable current interest in the chemical literature.[1-5] These multisite receptors may exhibit allosteric properties[6,7] by binding sequentially two or more guest metal cations in close proximity to one another. The resulting polynuclear complexes may facilitate electron transfer studies and serve as models of relevance to biological redox processes.

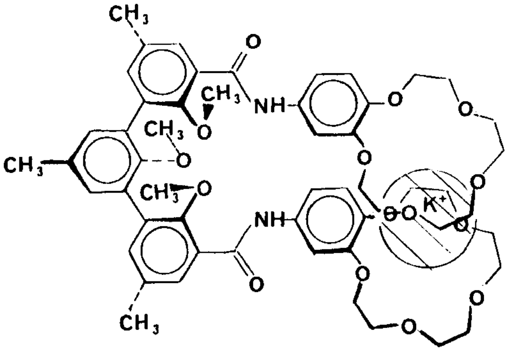
We report here the preparation of a bis(benzo-crown ether) ligand (3) containing a rigid ter-anisyl linkage and the first tris(benzo-crown ether) (7) constructed using a tren bridging moiety.

The condensation of 2,2',2"-trimethoxy-5,5',5"-trimethyl-[1,1':3',1"-terphenyl]-3,3"-dicarbonyl dichloride[8] (1) with two moles of 4-amino-benzo-15-crown-5[9] (2) in the presence of triethylamine and DMAP gave the bis(benzo-crown ether) (3) as a white crystalline solid (60% yield, m.p. 110-111°C). Scheme 1. Its structure was verified by elemental analysis, mass spectrometry and ^{1}H and ^{13}C n.m.r. spectroscopy.



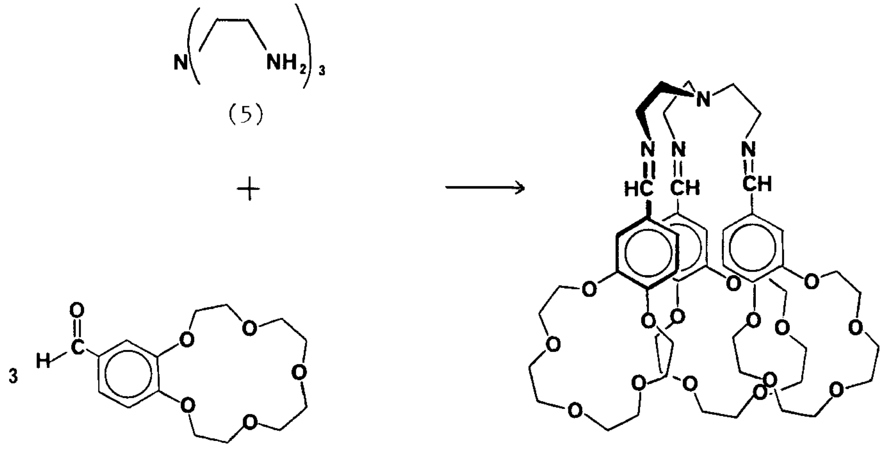
Scheme 1

^{13}C N.m.r. spectroscopy was used initially to investigate the complexation of (3) with the alkali metal cation guest potassium. The stepwise addition of potassium nitrate to a methanolic solution of (3) led to considerable shifts of the OCH_2 carbons of the benzo-15-crown-5 units. The stoichiometry of (3) to guest potassium cation was found to be 1:1 suggesting the formation of an intramolecular hemispherand type sandwich complex (4). No evidence, from subsequent ^{13}C n.m.r. (4)-potassium titrations, for the complexation of a second potassium guest cation at the anisyl binding site was found. Complexation studies of (3) with lithium, sodium, and cesium are currently under investigation.



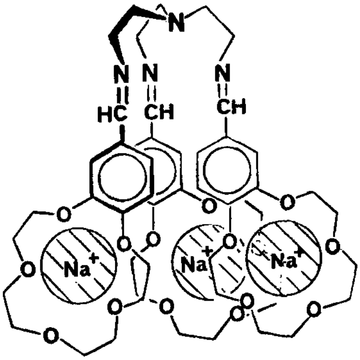
(4)

The tris(benzo-crown ether) (7) was synthesised in excellent yields (98%, m.p. 83-85^{o}C) by reacting tren (5) and three moles of 4-formyl-benzo-15-crown-5[10] (6). Scheme 2.



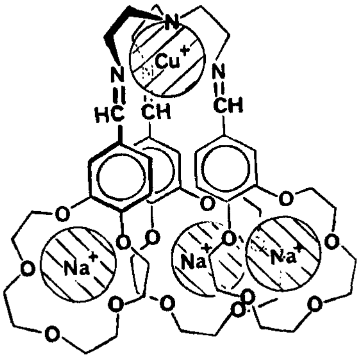
Scheme 2

Four recognition sites are present, the Schiff base tren function for binding a transition metal ion and three crown ether subunits for binding alkali metal guest ions. The stoichiometry of (7) to sodium was found to be 1:3 indicating the three benzo-15-crown-5 units of (7) are acting independently of one another, each one complexing one sodium cation (8).



(8)

The reaction of Cu(I)PF_6 with (7) led to the successful isolation of the [Cu(I)(7)]PF_6 complex as a pale yellow solid. Subsequent titration with sodium gave the hetero-polymetallic complex (9).



(9)

We are currently extending our studies to preparing related (3)-alkali metal and (7)-transition metal-alkali metal polymetallic complexes of catalytic interest.

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