

Adamantane as a Building Block in the Construction of Crown Ethers and Cryptands: Synthesis, Structure and Properties

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Several new adamantane- and oxadamantane-containing crown ethers and cryptands have been synthesized, and their ability to complex metal cations has been studied. In molecules of this type, the adamantane moiety functions as a rigid spacer that lowers the conformational mobility of the host molecule and also affects the size and shape of the host cavity relative to the corresponding parent non-substituted system. The results of the extraction experiments combined with the molecular modeling studies of the corresponding K^+ complexes showed, that pre-organization in given host-molecules exerts a dramatic influence upon that molecule's ability to interact effectively with guest metal ions to form corresponding host-guest complex.

Keywords: Adamantane-crown ethers, oxadamantane-crown ethers, extraction experiments, cation complexation, cation transport

Introduction

In the last twenty years, research in the area of supramolecular chemistry has led to the development of an impressive number of new molecules and new assemblies. Following the canonical definition of *J. M. Lehn*, that "a supramolecular system is formed by the interaction with binding and selection of substrate by a given receptor system",¹ the molecular receptor plays a key role, and its design is a major challenge for the realization of supermolecules.

Ones prepared supermolecule could form other organized assemblies or supramolecular devices. Also, a supermolecule can adopt various functions, e.g., it can be used for **recognition** (important for different types of sensors), **transformation** (e.g., as a catalyst system) and **translocation** (e.g., as carrier species). Crown ethers were one of the first receptors that have been used as alkali metal or transition metal complexants and to perform supramolecular functions such as selective catalysis, recognition and translocation of ionic or neutral organic species across natural or so-called bulk membranes.

Since the first discovery of the crown ethers in 1967² there has been an explosion of interest in the study of their ability to function effectively as metal cation complexants.^{1,3} Subsequent development of crown ether chemistry was driven by efforts to increase both binding strength and ion specificity.⁴

Incorporation of a rigid adamantane moiety into crown ethers and cryptands affects their conformational mobility and their ability to serve as complexing ligands by partially rigidifying the host system. In addition, incorporation of a lipophilic polycyclic moiety should increase the solubility of the crown ethers in nonpolar solvents with concomitant

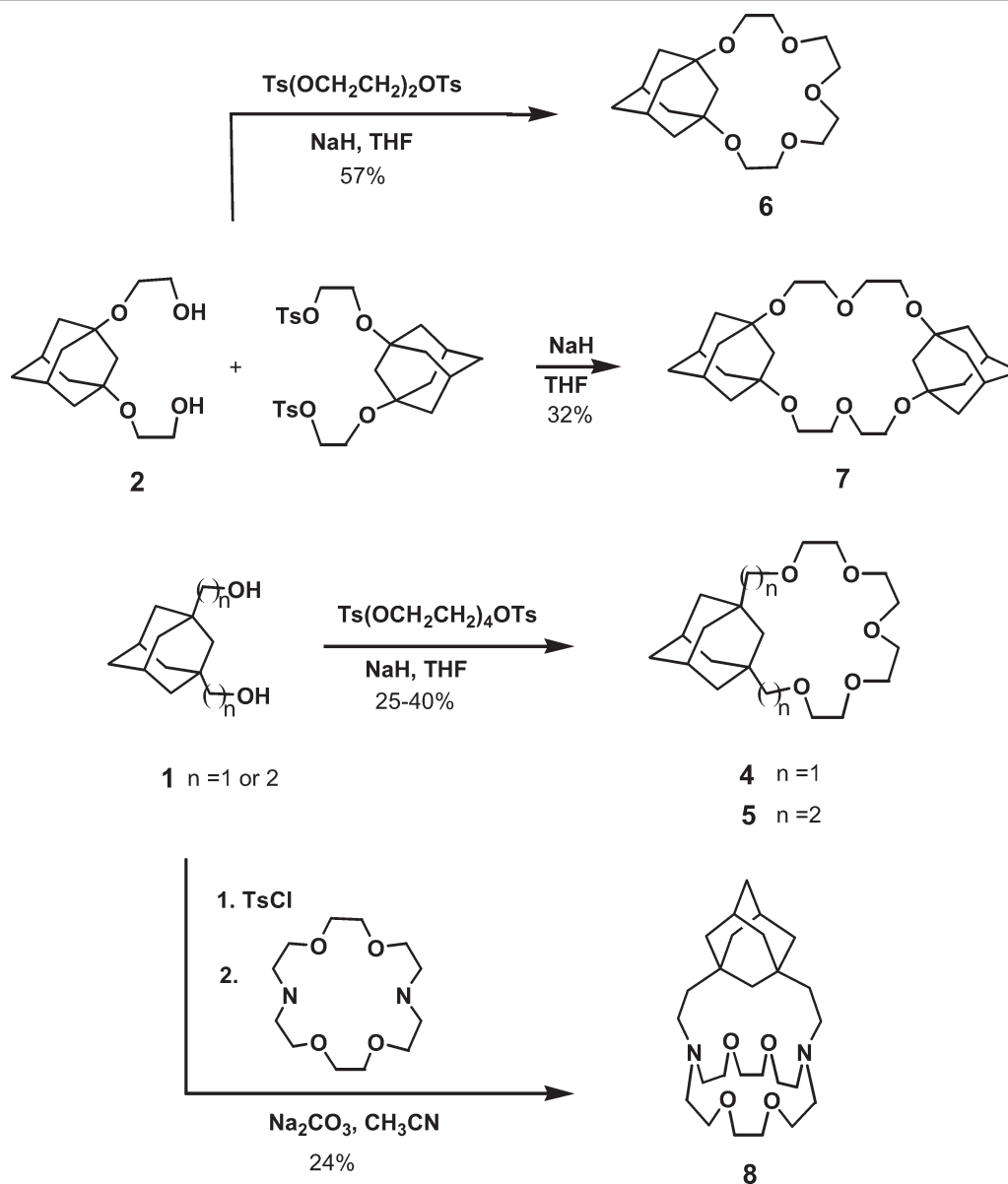
increase their ability to perform selective ion extraction and ion transport *via* complexation with metal ions. Also, various atomic positions in the adamantane moiety can serve as branch points at which additional ligating groups can be introduced.

As part of an extensive program that involves the synthesis and chemistry of novel adamantane-containing macrocyclic molecules,^{5–17} we have prepared several adamantane- and oxadamantane-crown ethers and cryptands. We have also studied their ability to complex metal cations by the host-mediated extraction experiments from aqueous solution into chloroform or methylene chloride. Compounds of this type are of interest as members of new class of host systems for the study of host-guest interactions.

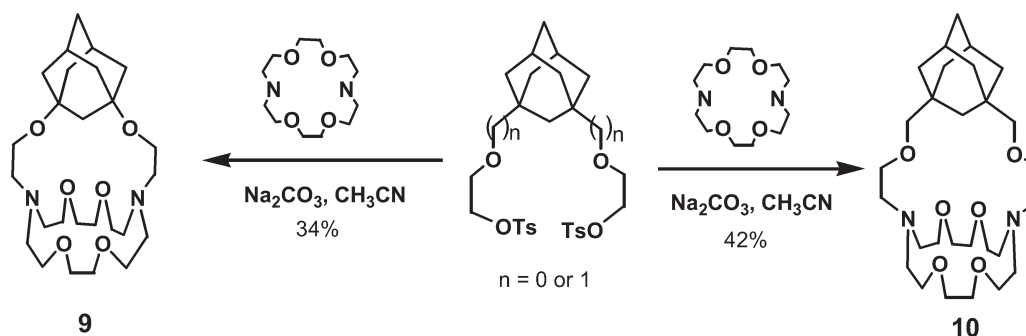
Results and Discussion

Synthesis of adamantane- and oxadamantane-annulated crown ethers and cryptands

Adamantane derivatives **1**, **2**, and **3** were employed as starting materials for the preparation of a wide variety of adamantane-annulated host systems, as shown in Schemes 1, 2, and 3. Thus, crown ethers **4** and **5** were prepared from **1** ($n = 1$ or 2) by using Na^+ templated Williamson syntheses. Reaction of the conjugate base of diol **1** with the corresponding ditosylate resulted in the formation of **4** and **5**, which possess 18-crown-5 and 20-crown-5 systems, respectively. The same approach has been employed to prepare adamantane-annulated 16-crown-5 and diadamantane-annulated 20-crown-6 (i.e., **6** and **7**, respectively, Scheme 1).⁷



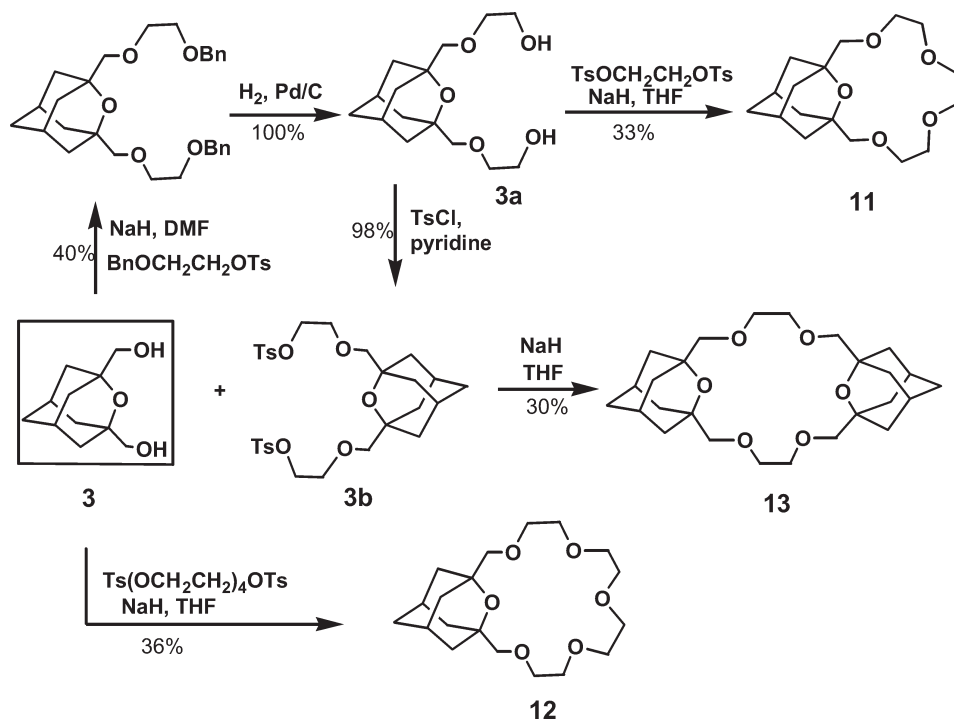
Scheme 1



Scheme 2

Adamantane derivatives **1** and **2** also proved to be useful as the linking agents for the synthesis of adamantane-containing cryptands (Schemes 1 and 2). First, adamantane derivatives **1** and **2** were converted into the corresponding ditosylates and then were subjected to Na^+ templated base promoted reactions with diaza-18-crown-6 to produce the corresponding cryptands **8**, **9**, and **10**, respectively.⁸

Oxaadamantane-containing crown ethers have been prepared by using an approach that is closely analogous to that shown above for the synthesis of corresponding adamantane-containing crown ethers. Several examples in this regard are shown in Scheme 3. Thus, NaH promoted reaction of the oxaadamantandiol **3** with 1-tosyloxy-2-benzyloxyethane in DMF, followed by hydrogenation afforded



Scheme 3

diol **3a** which was converted subsequently into the corresponding tosylate **3b** via a standard procedure that employed TsCl-pyridine. Then, **3b** was coupled with diol **3** to give crown ether **13**. The Na⁺ templated reaction of the conjugate base of diol **3a** with ethylene glycol ditosylate resulted in the formation of crown ether **11**. By using the same conditions, condensation of diol **3** with tetraethylene glycol ditosylate afforded crown ether **12** in 36 % yield.⁷

However, 1,3-bis(hydroxymethyl)-2-oxadamantane (**3**) has not yet been reported in the literature at that time; thus, it was necessary for us to develop the synthesis of **3**. A suitable oxadamantane precursor was prepared in several synthetic steps by starting with 1,3-dibromoadamantane.^{9,10}

Synthesis of *N*-adamantylaza-crown ethers

Attachment of an adamantane moiety to aza-18-crown-6 can be performed either by using an amide bond (**14**, **15**, **18**, **19**) or through an intervening methylene group (**16**, **17**, **20**, **21**). In the former, the C=O linkages should impose rigidity and thus should serve to preorganize the receptor. However, introduction of a C=O group is likely to reduce greatly the binding properties of the nitrogen atom in the macrocyclic ring. In the latter case, introduction of a methylene group would preserve the complexation ability of the macrocycle, but the resulting ligand is likely to be more flexible and, hence, less highly preorganized.

The synthetic strategy used to prepare compounds **14–21** was based on the coupling reactions of the corresponding acylchloride [i. e.; 1-(2-tosyloxyethyl)adamantane (**26**), 1-(3-tosyloxypropyl)adamantane (**27**), 1,3-bis(2-tosyloxyethyl)adamantane (**28**), 1,3-bis(3-tosyloxypropyl)adamantane (**29**)] with aza-18-crown-6 (Scheme 4).¹¹

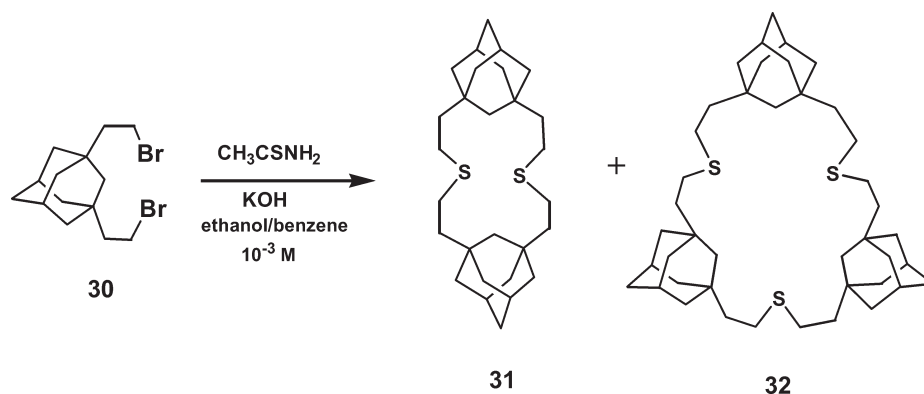
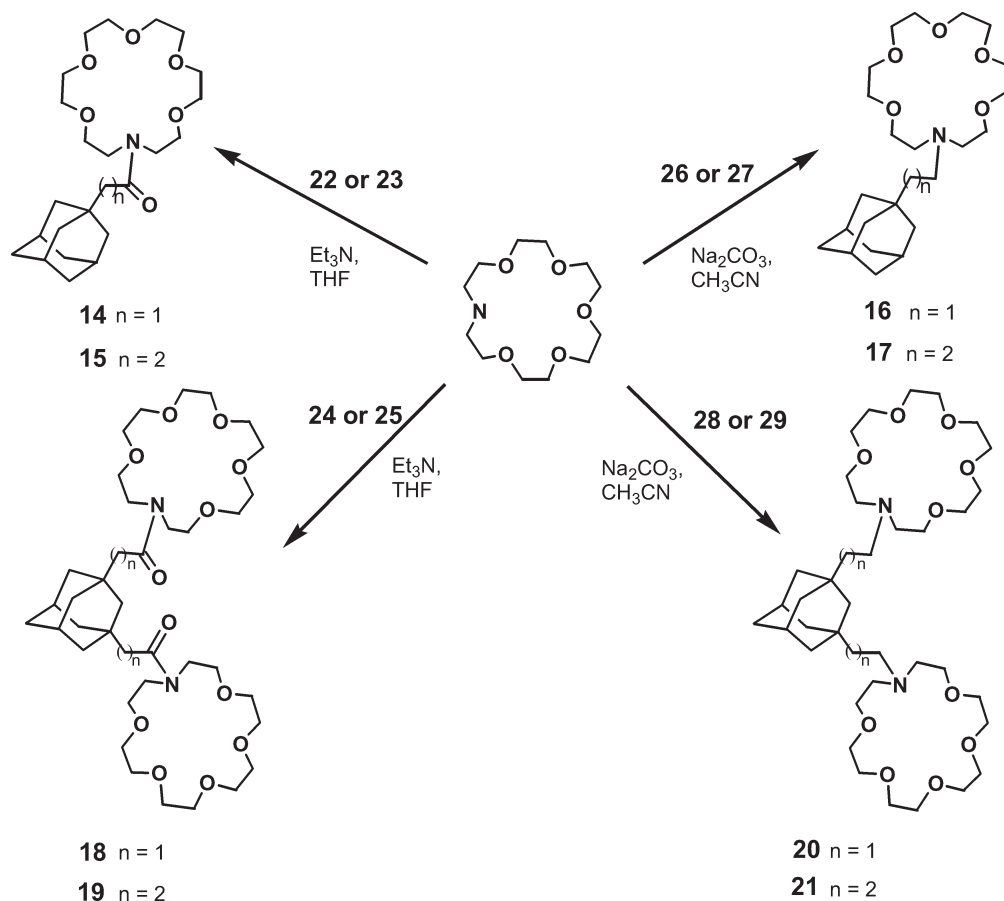
Synthesis of adamantane-containing thiocrown ethers

Thiocrown ethers have been a source of continuing interest because of their ability to complex heavy transition metal cations, such as Ag⁺ and Hg²⁺. Also, thiocrown ethers have high resistance to degradation under acidic conditions; thus, they are well suited for selective removal of Hg²⁺ ions from aqueous acidic media.

As a part of our studies in this field, we have prepared a series of novel macrocyclic thiaethers that contain 1,3-bridged adamantyl moieties¹² as well as other macrocyclic thiaethers that contain an attached spiroadamantane.¹³ The methods employed for this purpose are shown in Schemes 5 and 6.

The syntheses of macrocyclic thioethers **31** and **32** were achieved via intramolecular cyclization of 1,3-bis(bromomethyl)adamantane (**30**) with thioacetamide by using a high dilution technique. The reaction proceeded smoothly when performed by using a 10⁻³ mol L⁻¹ solution of dibromide in the mixture of absolute EtOH-benzene (1:1). In this way, **31** and **32** were obtained in 52 % yield (molar ratio $r_{31/32} = 3:1$; however, the product ratio obtained depends upon the concentration of reagents used).

The structures of **31** and **32** were determined via spectroscopic measurements and subsequently were confirmed by application of single crystal X-ray structural analysis.¹² Molecular structure of dimer **31** was shown to have sulfur atoms oriented exodentate to the ring. The exodentate orientation of sulfur atoms was also found in macrocyclic thioether **32**.^{12,14} Adamantane units in both structures adopt the expected geometry, and the molecule possesses high symmetry. The structure of the macrocyclic ring in **31** can be described in terms of the structure of tetrat-



hia-12-crown-4 thioether (12S4) where two sulfur atoms are replaced by two adamantane units.

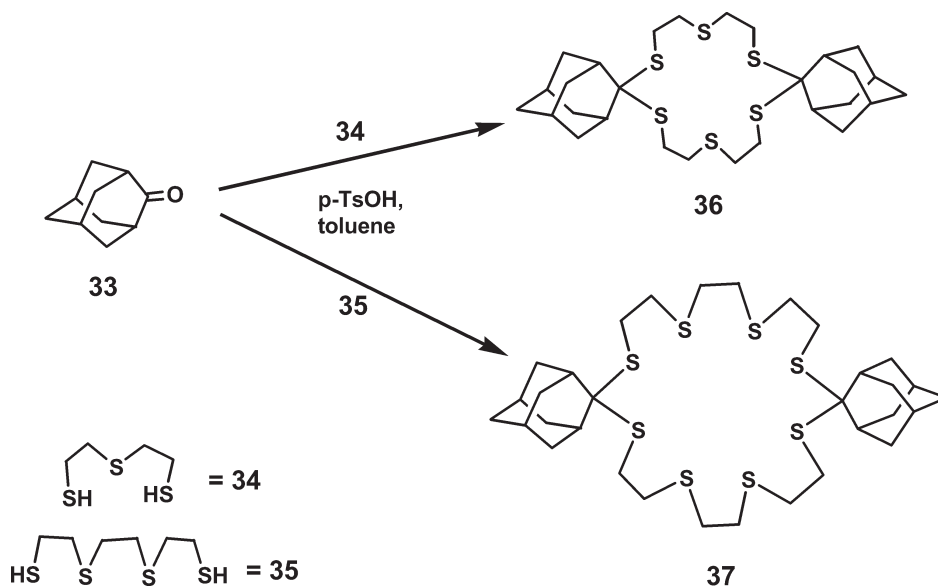
The nonbonding distance between sulfur atoms in **31** (S...S) is 8.389 Å (0.8389 nm), while the macromolecular cavity is small. The distance between nearest hydrogen atoms at adamantane-C5 and C13 is less than 3 Å (0.3 nm), which implies that **31** may not be a suitable complexant for large transition-metal cations, such as Hg²⁺. Therefore, we decided to turn our attention to the synthesis of macrocyclic thiaethers with attached spiro-adamantane units (see Scheme 6).

Acid catalyzed condensation of adamantane-2-one (**33**) with dithiols **34** or **35** afforded spiroadamantane thia-

crown ethers **36** and **37** in 81 % and 59 % yield, respectively.¹³

The molecular structure of thiacycrown **36** possesses C₂-symmetry. Two sulfur atoms are oriented away from the center of the macrocyclic cavity (i.e., they are exodentate with respect to the macrocyclic ring), and the adamantane units are mutually *trans*. The internuclear distances between S-atoms are 7.514 Å (S6-S14), 6.449 Å (S1-S9) and 6.257 Å (S3-S11), which implies that thiaether macrocycle **36** possesses a cavity that may be suitable for complexation of transition metal cations, such as Ag⁺ or Cu⁺.¹⁵

Thiacycrown ethers **36** and **37** display very limited solubility in alcohols or in water, a fact that renders them potentially



very useful as a new class of water-insoluble agents for environmental remediation. However, homogeneous CHCl_3 or CH_2Cl_2 solutions of, both, host compounds and the metal-ion salts could be prepared readily. Thus, thiacycrown ethers may serve as potential extracting agents for soft- and heavy metal ions, e.g. Cu^{++} , Ag^+ , Cd^{++} , and/or Pb^{++} .

Summary of results of extraction experiments

Binding properties of adamantane oxa- and aza-crown ethers and cryptands were studied by using alkali metal pi-

crate extraction experiments, which were carried out via solvent extraction of the metal picrate from aqueous solution into chloroform. The results thereby obtained were compared with the corresponding results obtained by using three model host systems, i.e., 18-crown-6, aza-18-crown-6 and diaza-18-crown-6. Alkali metal (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) picrate extractions were performed by using 5 mmol L^{-1} solutions of host systems in CHCl_3 and were examined by comparing the absorption intensities. In each case, relative extraction efficiencies toward alkali metal picrates were compared with the results of the corresponding model compound at the same concentration (Table 1). The extraction technique used in this

Table 1 – Extraction of Alkali Picrates with CHCl_3 Containing Crown Ethers

Ionophore	Extractability w/%				
	Li^+	Na^+	K^+	Rb^+	Cs^+
diaza-18-crown-6	1.7 ± 0.3	13.5 ± 0.3	14.5 ± 0.2	13.6 ± 0.7	13.6 ± 0.4
8	11.2 ± 0.4	22.4 ± 0.6	46.7 ± 0.5	25.4 ± 0.7	22.1 ± 0.7
9	16.2 ± 0.6	21.9 ± 0.2	19.2 ± 0.5	21.1 ± 0.7	18.1 ± 0.6
10	3.0 ± 0.5	16.9 ± 0.6	46.0 ± 0.6	53.5 ± 0.8	44.2 ± 0.6
18-crown-6	1.5 ± 0.4	4.0 ± 0.6	73.7 ± 0.2	61.3 ± 0.4	34.7 ± 0.5
11	1.3 ± 0.7	6.8 ± 0.6	8.2 ± 0.8	3.4 ± 0.7	3.1 ± 0.9
12	< 1	9.8 ± 0.3	64.0 ± 0.7	61.0 ± 0.1	41.9 ± 0.5
13	17.5 ± 0.5	21.7 ± 0.3	88.1 ± 0.2	86.8 ± 0.1	69.4 ± 0.4
aza-18-crown-6	11.6 ± 0.3	35.5 ± 0.6	42.9 ± 0.6	37.0 ± 0.6	39.8 ± 0.5
16	2.2 ± 0.2	24.7 ± 0.7	52.8 ± 0.5	44.3 ± 0.6	28.3 ± 0.4
17	< 1	18.7 ± 0.3	34.9 ± 0.6	29.8 ± 0.3	21.6 ± 0.2
20	4.7 ± 0.3	32.4 ± 0.3	79.0 ± 0.5	66.2 ± 0.3	40.9 ± 0.4
21	5.4 ± 0.3	31.0 ± 0.5	69.2 ± 0.3	57.2 ± 0.4	35.7 ± 0.6

^a Defined as mass fraction of picrate extracted into organic phase. General experimental conditions: 5 mmol L^{-1} CHCl_3 solution of host (0.5 mL) and 5 mmol L^{-1} aqueous solution of alkali metal picrate (0.5 mL). Each value is the average of three or five independent extraction experiments.

study has been described elsewhere.^{7,11,18} In the case of thiacycrown ether **36**, the ability of this host to complex transition metal cations (introduced as Cu^{2+} , Ag^+ , Cd^{2+} and Pb^{2+} nitrates) was studied by extraction experiments that employed 10^{-3} mol L^{-1} solutions of **36** in CH_2Cl_2 . The results obtained via these extraction experiments are shown in Table 2. The extent to which metal cations were thereby extracted was assessed via atomic absorption spectroscopy.¹⁶

Consideration of the results of the extraction experiments led to the following observations.

Adamantano-crown ethers **4–7** as well as the lariat crown ether **14**, **15**, **18** and **19** showed almost negligible extraction capability toward any of the alkali metal cations. Complexation properties of crown ethers **12** and **17** and cryptand **9** are comparable to those of 18-crown-6, aza-18-crown-6 and diaza-18-crown-6, respectively. However, crown ether **13** showed enhanced extractability for all cations but lower selectivity compared to 18-crown-6. Among the lariat crown ethers studied, **16**, **20** and **21** proved to be the best alkali metal picrate extractants. This crown ethers displayed significant levels of avidity towards complexation with K^+ and Rb^+ and enhanced K^+/Na^+ selectivity.¹¹

We also studied the K^+ transport ability of ionophores **11–13** across a bulk liquid membrane. Here, we observed a linear increase in concentration in the receiving phase through the first 7 hours, which enabled us to calculate transport-rate of K^+ . It was found that bis-2-oxadamantano-18-crown-6 (**13**) displayed diminished ability to transport K^+ vis-à-vis either mono-oxadamantane-18-crown-6 (**12**) or 18-crown-6. Since crown ether **13** is an excellent K^+ extractant (88 %), this suggests that cation-release may be responsible for the relatively low transport rate.⁷

In order to understand the remarkable difference between the complexation abilities of the oxadamantane ionophore **13** and its fairly low transport ability, we resorted to molecular modeling to investigate the corresponding complex with K^+ .¹⁹ Two low-energy conformations of bis-oxadamantano-crown were obtained via these calculations (see Fig. 1).

The conformation that possesses a C_{2h} symmetry was found to be more stable by 7.95 kJ mol^{-1} (1.9 kcal mol^{-1}) than the corresponding conformation that adopts a C_i -conformation.¹⁷ These results differ from those obtained for the parent 18-crown-6, which indicated that the lowest free energy conformation in *vacuo* corresponds to the structure with C_i symmetry.²¹ This suggests that bisoxadamantano-18-crown-6 (**13**) is favorably preorganized for complexation.

We also found that the size and shape of the cavity in bis-oxadamantano-crown-6 (**13**) is ideal for K^+ complexation (Fig. 2). One of the two bulky oxadamantane-units is below and the other is above the approximate plane of the macrocyclic ring. Additionally, they effectively sequester K^+ within the cavity, thereby hindering release of this cation into the organic layer upon extraction from the aqueous medium. This accounts for the observed low rate of K^+ transport by **13**.⁷

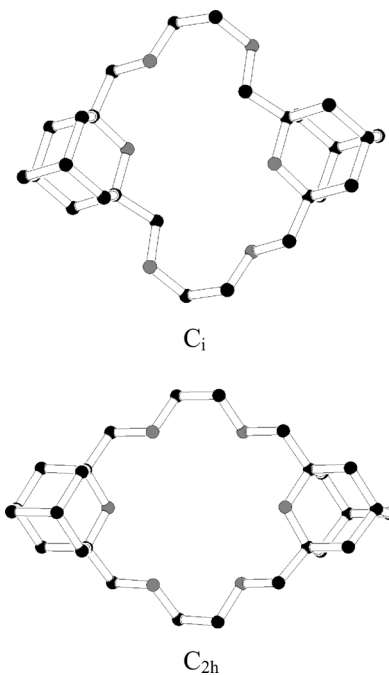


Fig. 1 – Two low-energy conformations of bis(oxadamantano)-18-crown-6 (**13**)

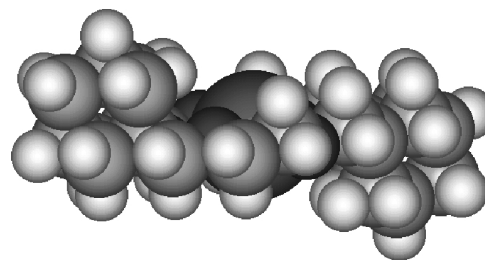


Fig. 2 – Computational CPK model of the K^+ -complex of bis(2-oxadamantano)-18-crown-6 (**13**)

Cryptands **8** and **10** (Scheme 1, Table 1) display both high avidity and high selectivity toward extraction of K^+ picrate. However, cryptand **9** showed very similar ability to extract alkali picrates as parent diaza-18-crown-6, despite the fact that **9** contains two additional oxygen atoms that should participate in K^+ complexation.

Computationally-derived CPK-models of adamantane-containing cryptands **8–10** in coordination with K^+ , are shown in Fig. 3. Here, it can be seen that K^+ in host molecule **8** is buried inside the lipophilic core, whereas in the corresponding K^+ complex of ligand **9**, two oxygen-atoms do not participate in complexation. Moreover, these two oxygen atoms are oriented outside the cavity of ligand **9**, and an adamantane methylene group further interferes with complexation. However, when the third bridge was enlarged by the addition of two CH_2 groups as in cryptand **10**, sufficient flexibility is introduced into the macrocycle that permits the two oxygen-atoms to become oriented toward the cavity, thereby permitting them to participate in coordination with the K^+ guest. As a consequence, ligand **10** extracts large cations very effectively.

In Table 2, the results obtained via $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , $\text{Cd}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ extraction experiments performed by using thiacycrown ether **36** are compared with the

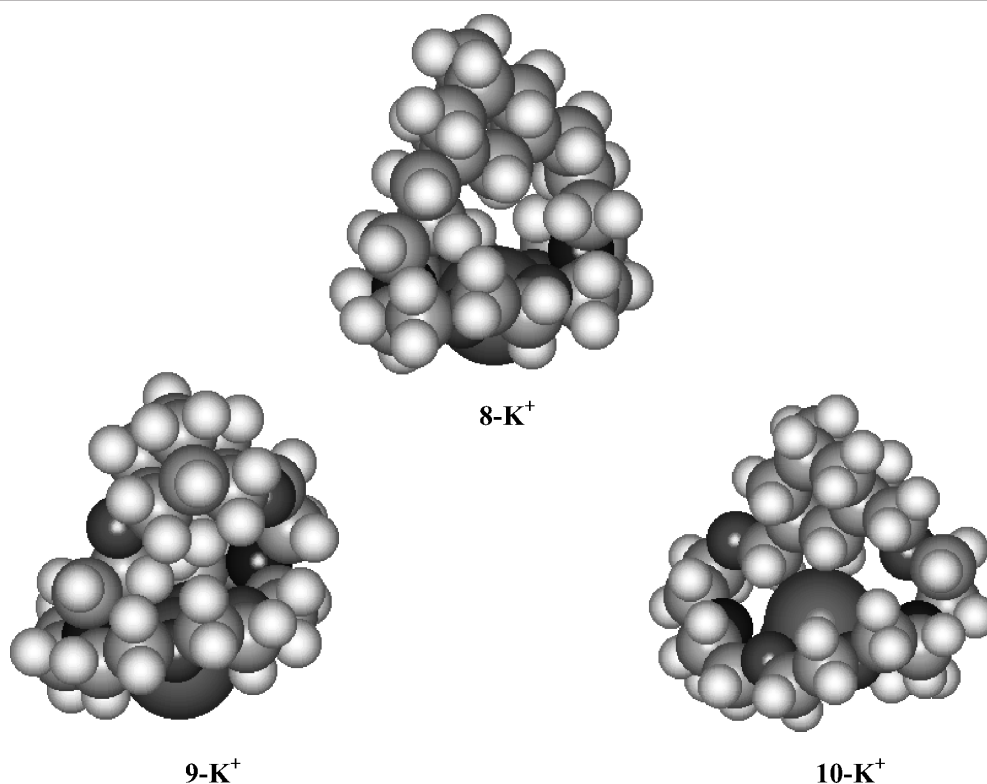


Fig. 3 – Computational CPK models of host-guest complexes **8-K⁺**, **9-K⁺**, and **10-K⁺**

Table 2 – Extraction of Cu^{2+} , Ag^+ , Cd^{2+} and Pb^{2+} with CH_2Cl_2 Containing Crown Ethers

Ionophore	extractability, w/% ^a			
	Cu^{2+}	Ag^+	Cd^{2+}	Pb^{2+}
16-crown-S-6	3.2±0.2	13.5±0.4	1.1±0.2	2.5±0.3
36	8.6±0.2	44.0±0.3	3.2±0.3	6.5±0.3

^a Defined as mass fraction of M-nitrates ($M = \text{Cu}^{2+}$, Ag^+ , Cd^{2+} , Pb^{2+}) extracted into organic phase. General experimental conditions: 1 mmol L⁻¹ CH_2Cl_2 solution of host (1 mL) and 1 mmol L⁻¹ aqueous solution of M-nitrate (1 mL). Each value is the average of five independent experiments.

results obtained for the corresponding parent thiacycrown-6 (Table 2). Thiacycrown ether **36** is more than twice as avid as the parent thiacycrown-6 toward extraction of Cu^{2+} , Cd^{2+} and Pb^{2+} nitrates. However, **36** displays considerably higher avidity toward extraction of Ag^+ nitrate than does the parent thiacycrown-6 (see Table 2).

After extraction of AgNO_3 had been completed and the solvent was removed, a white powder remained. Elemental analysis of this material suggested that it is a 1:1 host-guest complex. However, we were unable to obtain suitable crystals of this complex for single crystal X-ray structural analysis.

Next, proton NMR spectroscopic studies were undertaken in an effort to obtain further structural information concerning this 1 : 1 complex. Thus, an incremental quantities ($\chi = 10, 25, 50, 75, 100, 150,$ and 200 mole %) of a solution of AgBF_4 in CD_3CN were added to a solution of ligand **36** in CDCl_3 . We noted that the ¹H NMR spectra changed

continuously until one equivalent of AgBF_4 had been added. No further change in the appearance of the ¹H NMR spectrum occurred with continued addition of AgBF_4 , thereby indicating that a 1:1 **36**- Ag^+ complex had been formed. This experiment clearly demonstrates that spiro-adamantano-16-crown-6 **36** is a highly suitable Ag^+ complexant.

The results obtained in these studies indicate clearly that the most highly preorganized systems, e. g. oxaadamantano-crown ethers **12** and **13**, lariat crown ethers **16** and **20**, and bis(adamantano)-crown thiaether **36**, function most efficiently as host systems for the selective complexation of K^+ and Rb^+ or Ag^+ , respectively. Furthermore, our results demonstrate that addition of polycyclic molecules affects the size and shape of the binding cavity in crown ether, alters the electronic properties of the binding portion of the host, and also affects the overall conformational mobility of the macrocycle. Incorporation of polycyclic molecules increases the lipophilicity of the parent host molecule and thereby improves the overall performance of the host as a metal cation extractant.

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SAŽETAK

Adamantan kao ugradbena jedinica u pripravi krunastih etera i kriptanada: sinteza, struktura i svojstva

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Pripravljeni su novi adamantanski i oksaadamantanski krunasti eteri i kriptandi te je ispitivana njihova sposobnost kompleksiranja s metalnim kationima. U tom tipu spojeva adamantanska molekula služi kao kruti dio koji smanjuje konformacijsku pokretljivost cijele molekule, a utječe i na dimenziju i oblik šupljine makrocikličkog prstena u odnosu na osnovni nesupstituirani sustav.

Rezultati eksperimenata ekstrakcije te rezultati molekuskog modeliranja odgovarajućih K⁺ kompleksa pokazali su da preorganiziranost molekule-domaćina ima znatan utjecaj na sposobnost molekule za interakciju s metalnim ionima i stvaranje kompleksa.

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