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Alfred Werner's expanded legacy: Anion and metal ion coordination in an unsymmetrical, octaamido cryptand

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Dedicated to Alfred Werner on the 100th anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

An unsymmetrical cryptand host, **1**, was synthesized by a simple three-step strategy using two basic building blocks, tren and 2,6-diacetylpyridine, with ethylenediamine as a connecting fragment. The cryptand, originally synthesized as a host for anions, binds both anions and metal ions as observed crystallographically for the chloride, dihydrogen phosphate, and nickel(II) complexes. The host consists of two bridges containing a single diamidopyridine group plus a third, longer bridge containing two diamidopyridine groups linked through the ethylene spacer. In the chloride complex, the anion is held within the relatively planar simple tetraamidopyridine macrocyclic unit by four hydrogen bonds. In the dihydrogen phosphate complex, the host is diprotonated, and the two single diamidopyridine spacers fold so that the pyridines stack with π–π interactions. The longer tetraamido dipyridine bridge forms a rounded "handle" in the opposite direction with a tetrameric cluster consisting of two linked dihydrogen phosphate ions and two water molecules inside the circular handle. The new host shows only moderate binding affinity toward most of the anions tested in DMSO-d_6. In its doubly deprotonated form, the cryptand forms a nickel(II) complex, in which the metal ion is held in a pincer-like fashion by one of the diamidopyridine units in the longer chain.

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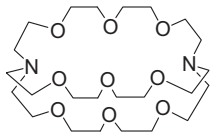
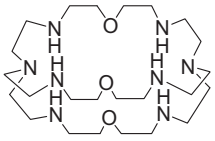
1. Introduction

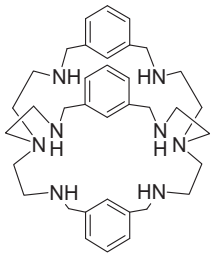
Anion coordination is now a vibrant field of supramolecular host–guest chemistry [1–6], with hosts varying in dimension and complexity from simple acyclic to more complex patterns, including totally organic monocycles, bicycles, and higher order molecular architectures, as well as metal-based hosts such as scaffolds. Historically, bicyclic cryptands have been especially appealing since they can engulf an anion within their cavity. These receptors have figured prominently in supramolecular chemistry since the first introduction of the diaza polyoxa macrobicycles as hosts for alkaline earth and alkali metal ions by Lehn and co-workers in 1969, **C[1]** [7,8]. The early cryptands morphed in the late 1970s into the polyaza cryptands, **C[2]** [9–11]. While the first aza cryptands were synthesized to bind two metal cations [9], they were later found to bind halides and the linear azide ion quite effectively [10,11]. In subsequent work a number of researchers explored cryptands with the same tris(2-aminoethyl)amine (tren) bridgeheads and various aliphatic, aromatic or heterocyclic units as spacers, **C[3]** [12–14].



C[1]



C[2]



C[3]

While our group also examined polyaza cryptands in the mid to late 1990s [15–22], in the early 2000s, we shifted focus to amide-based hosts [23]. The rationale for this was their lessened sensitivity to degree of protonation, their solvent preferences (more amenable to mixed solvent separations applications), and last but not least, their analogy with the naturally occurring amide hosts in protein systems [24]. As part of this examination of polyamide hosts, we designed and synthesized the corollary to the aza cryptands, bicyclic polyamide cryptands (with six amide binding sites), **C[4]** [25–28]. To our knowledge this new cryptand framework represented only the second example of tren-based amide cryptands, the first being

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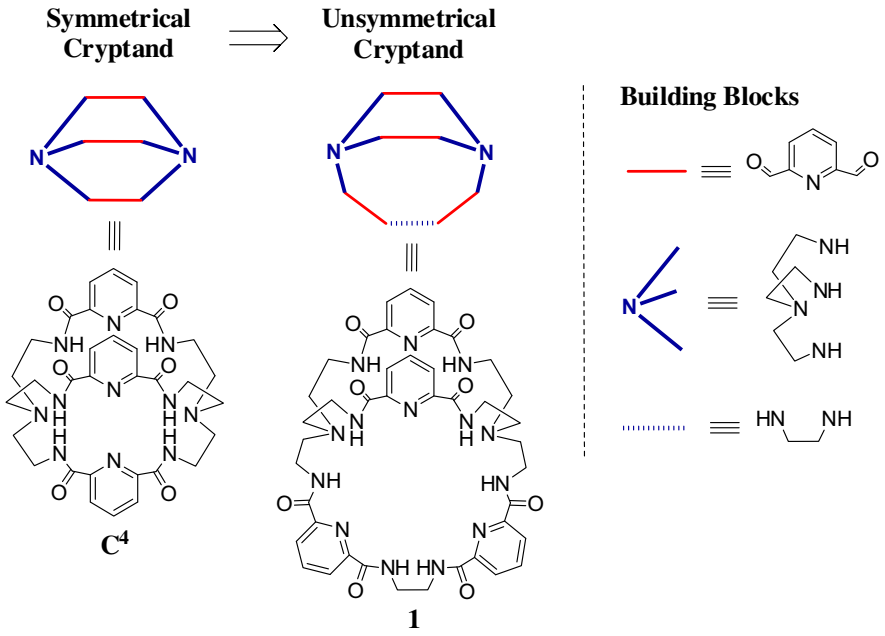


Scheme 1. Design strategy for expanding the hexaamide cryptand $\mathbf{C^4}$ by elongating a spacer.

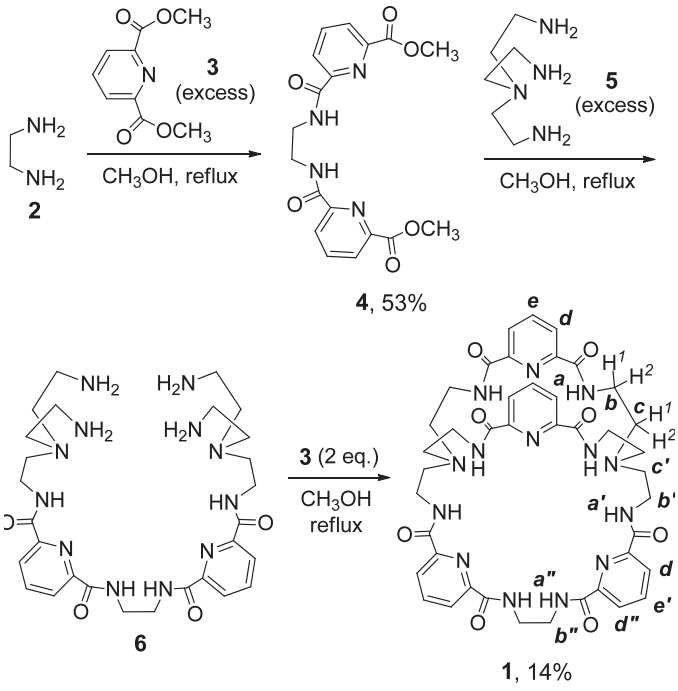
the elegant catechol systems of Raymond and co-workers, used as mimics of the iron-loving siderophores [29–31]. Interestingly, while the aza cryptands were first synthesized as metal ion hosts, followed by an exploration of anion binding [9–11], for the non-catechol-based amide cryptands, the history is reversed. Only recently have transition metal complexes been reported by Nocera and Cummins, in what promises to be seminal work in probing the dimetallic chemistry of these ligands [32–35]. These authors have also reported a stabilized, cryptand-sequestered O_2^{2-} complex, obtained by reversible reduction of O_2 [36], that provides an indication of future applications for this class of ligands.

In an effort to expand on amide-based cryptand chemistry, we decided to lengthen one of the cryptand chains by incorporating an additional diamidopyridine unit (Scheme 1). Unsymmetrical cryptands are rather rare, and most of those reported are unsymmetrical by virtue of mixed heteroatoms [37–42]. Here we report the dual binding capabilities of this new ligand, both for anions and metal ions, with binding data for a variety of anions and crystal structures of the chloride, dihydrogen phosphate, and nickel(II) complexes. Structural similarities and differences and the role of the anion/cation on the conformation of the flexible cryptand will be described.

2. Results and discussion

2.1. Synthesis

The expanded cryptand **1** was synthesized by a simple three-step strategy (Scheme 2). The extra ethylenediamine fragment (**2**) was first reacted with excess dimethyl 2,6-pyridinedicarboxylate (**3**) in methanol at reflux to give fragment **4** in 53% yield after purification by column chromatography. Fragment **4** was further reacted with excess tris(2-aminoethyl)amine (**5**) in methanol at reflux temperature, and the crude product **6** was obtained without further purification after removal of the solvents and excess tris(2-aminoethyl)amine under reduced pressure. The final macrocyclization between **6** and two equivalents of dimethyl 2,6-pyridinedicarboxylate (**3**) in refluxing methanol gave the expanded cryptand host **1** in 14% yield after purification by column chromatography. No other products were characterized although oligomeric or polymeric products would have probably remained on the column. The new cryptand was fully characterized by mass spectrometry (MS), ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallography. This step-wise strategy allows for sequential incorporation of different structural units into the cryptand skeleton and thus provides an efficient synthetic routine for a class of cryptand-like hosts with structural diversity.



Scheme 2. Three-step synthesis of the expanded cryptand **1**.

2.2. Crystal structures

2.2.1. $[Et_4N^+][\mathbf{1}\cdot Cl^-]\cdot 4.28H_2O$

The chloride complex crystallizes in the triclinic space group, $P\bar{1}$ as the tetrahydrate, although a fifth water molecule with 0.28

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