

Molecule of the Month

Cryptatium, the First "Elementoid"

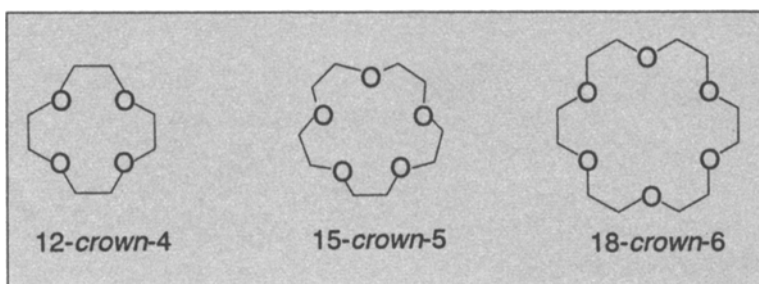
Uday Maitra

Electrochemical reduction of a cryptate yielded a neutral species with the properties of an *expanded* atom.

Most of the 92 elements, excluding the transuranium elements, were discovered by the turn of the nineteenth century. The early part of the twentieth century witnessed the discovery of the transuranium elements, but most of them were largely of academic interest because of their high radioactivity, and relatively short half-life. Thus, the search for the heaviest element (or metal?) became rather difficult to pursue.

As a matter unrelated to the discovery of elements, towards the end of the sixties, a rather novel metal ion complexing agent was serendipitously discovered by Charles Pedersen. He found that cyclic polyethers were able to complex alkali metal ions, by providing a cavity in which the charged alkali metal cation can sit comfortably in a *sea* of electrons donated by the oxygen atoms! In a sense this is similar to the hydration of a metal ion in water, except that the stabilization is done by oxygen atoms made available in a cyclic molecule. These crown ethers show high selectivity in complexing alkali metals, since the size of the cavity (which is determined by how big the ring is, it can be 12, 15, 18, 21.. membered) can be made just optimum to match the

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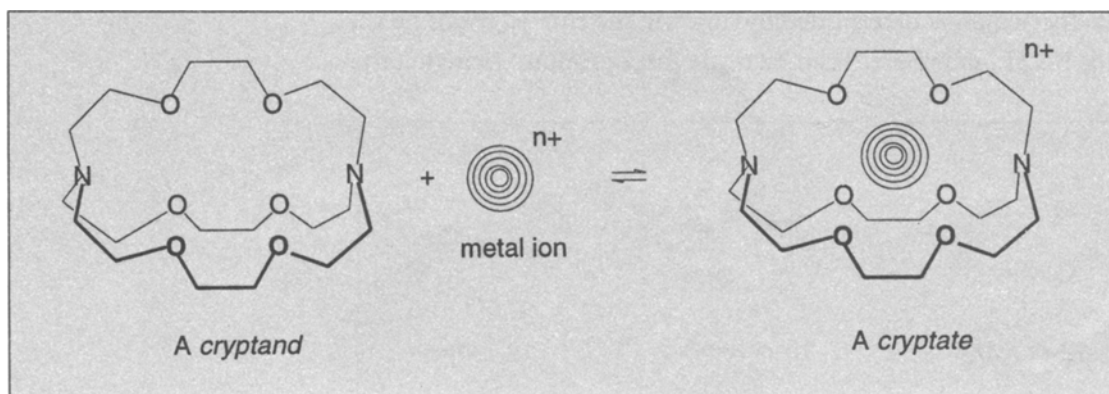


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ionic radius of the alkali metal ion. Thus, 12-crown-4, 15-crown-5 and 18-crown-6 have been found to be selective for binding Li^+ , Na^+ and K^+ , respectively. The ability of the crown ethers to complex alkali metal ions selectively has led to many applications – one of the most important being the solubilization of inorganic salts in organic solvents in the presence of crown ethers. One can, for example, dissolve KMnO_4 in benzene in the presence of a crown ether to give a purple solution!

Just when Pedersen was investigating crown ethers, Jean-Marie Lehn was busy creating a three dimensional *cage* for metal ions. His idea was to construct a *cryptand* (Latin *crypta* means cavity; and Greek *kryptos* means hidden) for efficient complexation of alkali metal ions. If a crown ether could be considered as a disk like object, the cryptand is a spherical object, which should be capable of capturing a metal ion more effectively. Indeed, Lehn had found that cryptands formed *cryptates*, alkali metal ion complexes of exceptional stability.

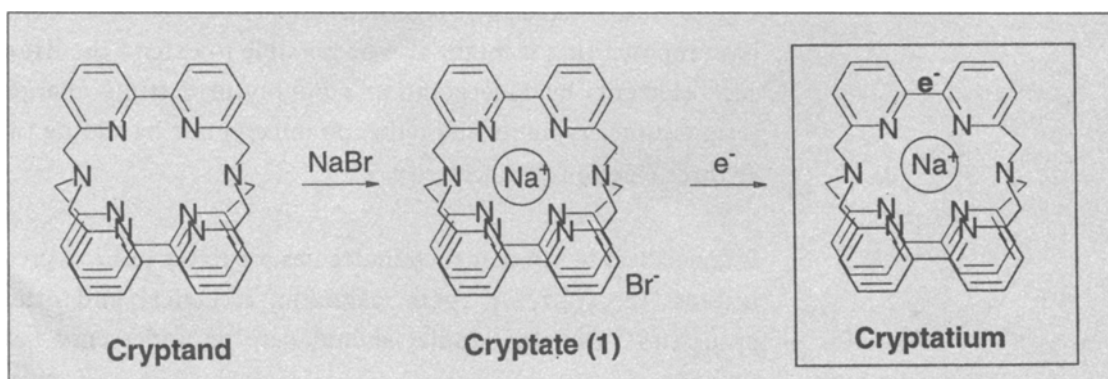
Cryptates can be regarded as *expanded atoms*, where the positive charge of the metal ion has spread over many atoms. One interesting property of such metal complexes is that they interact very weakly with anions or with solvent molecules, since the metal ion is well stabilized inside the cage having a number of oxygen and nitrogen atoms which can donate electron pairs to it! As a result, such (almost) spherical metal complexes can be



regarded as *super-heavy* alkali-metal ions (compare the ionic radius of Cs^+ (1.65\AA) with that of the cryptate shown in the previous page which is about 5\AA)! If that is so, then it is interesting to think what would happen if an electron is added to a cryptate. Where will it go? Such systems have actually been made by Lehn, and are considered to be salt-like species with the electron as the anion (an *electride*). Such a species can also be thought of as a large alkali metal with a very small ionization potential (more like the Rydberg state of an atom). We therefore see two extremes: a true metal atom where the valence electron is in a metal orbital, or an electride (electron added to a cryptate) where the electron is at a very large distance from the metal cation. Lehn has considered another possibility in between, in which the *valence* electron will be associated with a ligand orbital. The cryptand shown above does not have a vacant low energy orbital for adding an electron, but one can certainly design another cryptand capable of accommodating an electron on its surface..

The addition of an electron to a cryptate can produce a species behaving like the Rydberg state of an atom.

The cryptand shown below essentially has three bipyridine (bpy) units arranged as the three blades of a propeller, with the two ends of each of the three units being linked to a pair of nitrogen atoms. Bipyridyl units have been used extensively for the complexation of metal ions (many of you have probably seen the blood-red color of the bpy complex of ferrous ion, $\text{Fe}(\text{bpy})_3^{2+}$).



The cryptatium represents a neutral species somewhere in between an atom, and an electride. It can also be regarded as a molecular element.

The bipyridine unit also has a relatively low-energy vacant orbital in which an electron can be added. How does one add an electron to a cation? This is nothing but a reduction process. Normal reducing agents can often create problems, because of the byproducts formed from them. A method which is commonly used for the generation of reactive metals is electrochemical reduction (readers may recall that reactive metals such as Na, K, Ca etc. are always manufactured this way). Indeed, this was the method employed by Lehn and coworkers for adding an electron to cryptate 1. Upon electrochemical reduction of 1, they observed the formation of air-sensitive blue-violet crystals on the cathode. Using special techniques necessary for the handling of air-sensitive solids, they were able to get an X-ray crystal structure of this blue-violet crystal. Unlike the crystal structure of a related cryptate bromide salt, the crystals of this blue-violet solid did not show any anion in between the cryptate units – suggesting that this species is electroneutral. This would be possible if the negative charge, *i.e.*, the electron is residing in the molecule itself, and naturally the most likely site for it is the ligand orbital. Support for this hypothesis comes from the observation that in the crystal structure, the Na⁺ ion is closer to one bipyridine unit. This is because the bipyridine unit with the extra electron draws the counter ion closer to it. Lehn and coworkers termed this compound *sodio-cryptatium*, and have suggested that this species may be described as an expanded atom, or as a radical contact ion pair. The cryptatium therefore represents a *neutral* species somewhere in between an atom, and an electride. It can also be regarded as a *molecular element*. Lehn has proposed that it might also be possible to extend the list of such elements by incorporating a doubly or a triply charged cation in the cryptand, and reducing the cryptate by adding two or three electrons, respectively.

It is needless to say that such molecules are likely to be of great interest for studying their magnetic, electrical and other properties. Detailed studies should help us understand how

exactly the electron gets delocalized over the three bpy units. Lehn has also envisaged a *fullerium* species, which can be considered to be a fullerene, such as C_{60} , containing a metal ion M^{n+} in its internal cavity, and n electrons delocalized on the carbon framework!

We can perhaps conclude that the search for the heaviest (molecular) element is still on!

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Fractals

