

Engineered Organic Compounds for Refining Rare Earth Metals

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Abstract

Rare Earth metals are a set of intermediate-atomic number elements which are important for both industrial and strategic reasons. The current techniques of refining and purifying these materials are inefficient and highly polluting, because they rely on solvent exchange methods which often involve strong mineral acids. Organic Chemistry and Biotechnology may allow the development of low-cost methods capable of replacing the current Rare Earth refining industries. The generic term for the relevant chemicals is “ligands”, which describe organic substances capable of binding to metal ions in solution. Examples include substances such as Crown Ethers, Aza-Crown Ethers, Porphyrins, and Chlorins. The central proposal is to develop organic ligands which have high specificity to bond with, for example, Neodymium.

Introduction

The primary idea of this paper is to engineer organic molecules such that they have extremely specific affinity for the ions of certain elements, while having relatively low affinity for other elements. The most important such element is Neodymium.

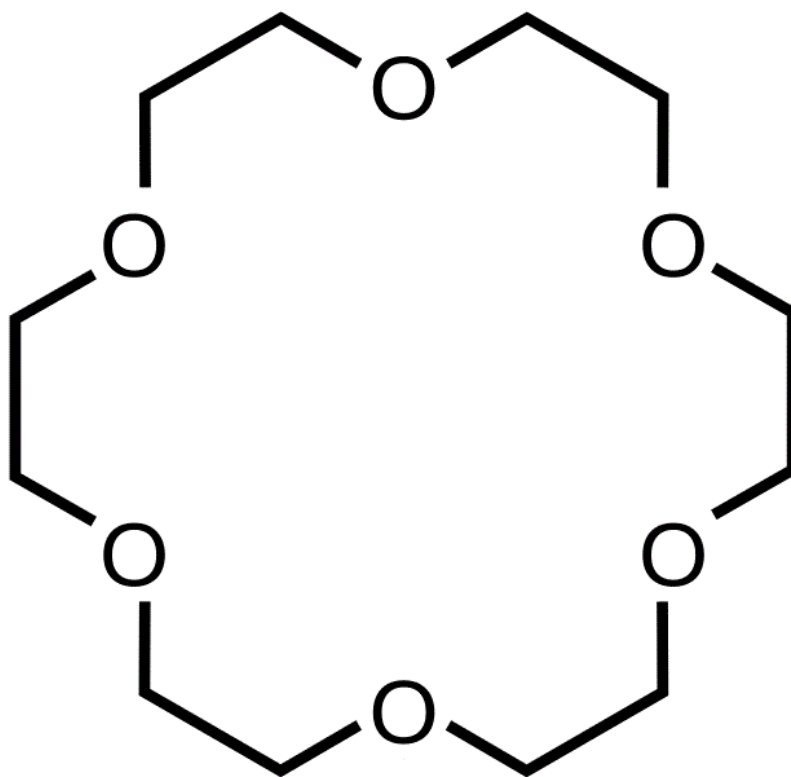
The secondary idea of this paper is that such organic molecules should be engineered to have a high binding energy with the target ion under acidic conditions, and low binding energy under alkaline conditions. By doing this, we can have a situation in which the organic molecule are put into a water solution of various chlorides, such that they chelate with, say, the Neodymium and nothing else. These organometallic complexes can then be separated from the rest of the material and then turned into Neodymium Oxide by reacting with an alkaline solution such as Sodium Carbonate.

The third idea is that suitable organic molecules could possibly be produced at low cost using biotechnology.

Crown Ethers

Crown ethers [1] are cyclic chemical compounds made of Carbon, Oxygen, and Hydrogen. They consist of a ring containing several ether groups (R–O–R'). The most common crown ethers are cyclic oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e., $\text{--CH}_2\text{CH}_2\text{O--}$.

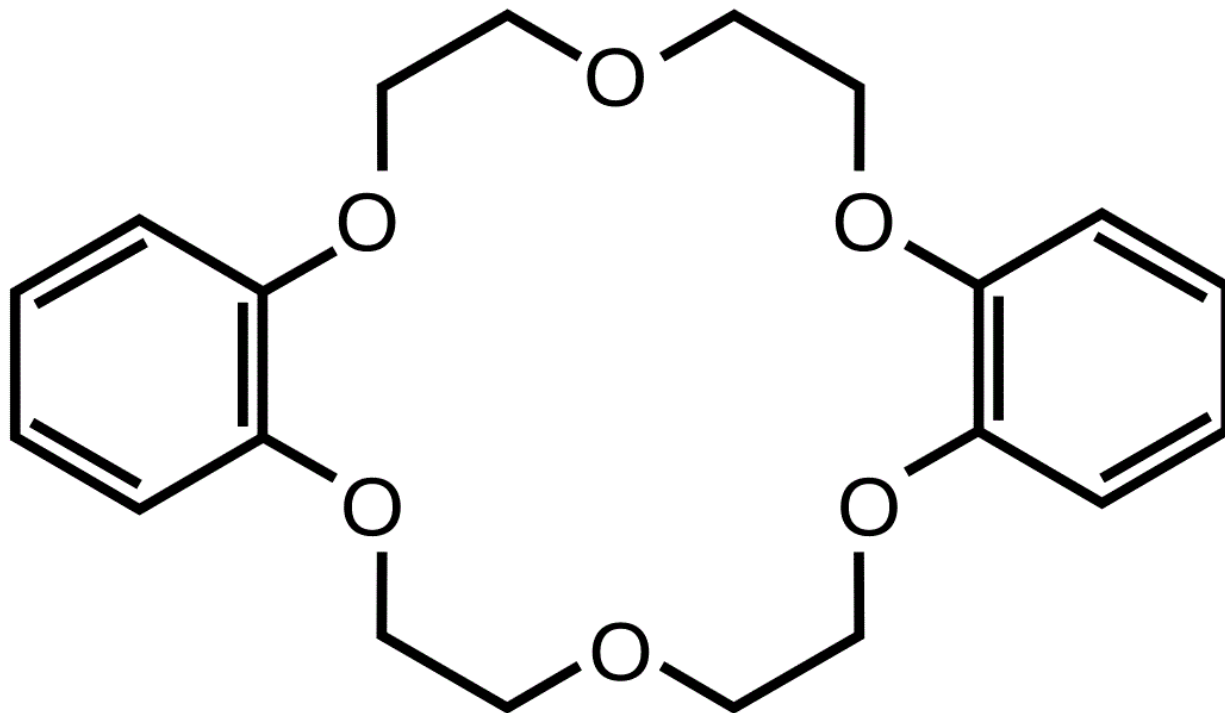
The most common crown ether in the literature is 18-crown-6, which is built of six unit ethers:



Other common members of this series are the tetramer ($n = 4$), the pentamer ($n = 5$), and the hexamer ($n = 6$). The term "crown" refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person's head. The first number in a crown ether's name refers to the number of atoms in the cycle, and the second number refers to the number of those atoms that are oxygen.

Crown ethers are a much broader set than the oligomers of ethylene oxide; an important group are derived from catechol.

For example, Benzo_18_crown_6:



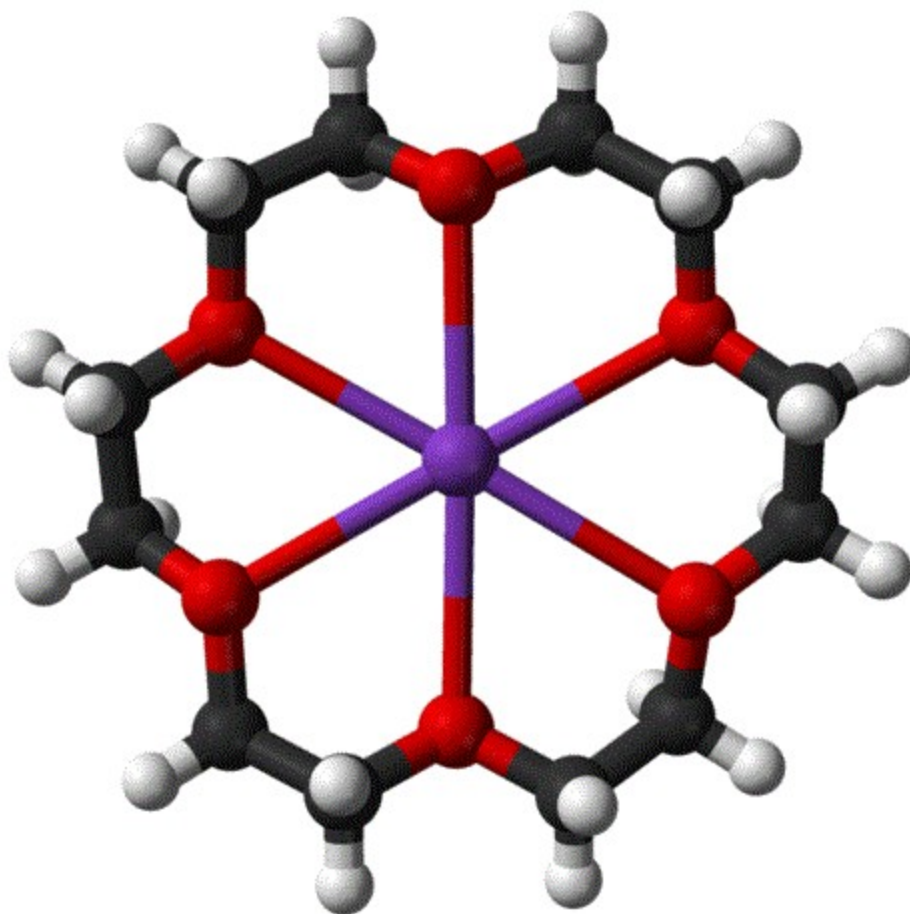
The size of the central hole can be varied by using more complex ring structures, including furan, indol, and phenols.

Also, compounds can be designed with amino groups or carboxylic acid groups, so as to change their shape, depending on the pH.

Crown Ethers and Metal Ions

The paired electrons on the Oxygen atoms of a crown ether are able to make a coordinate bond with metal ions. These bonds typically have 10% of the energy of a covalent bond, which means that metal ions can be attached or detached without the need for high temperatures.

For example, a Potassium ion fits nicely into a #18-6 crown ether:



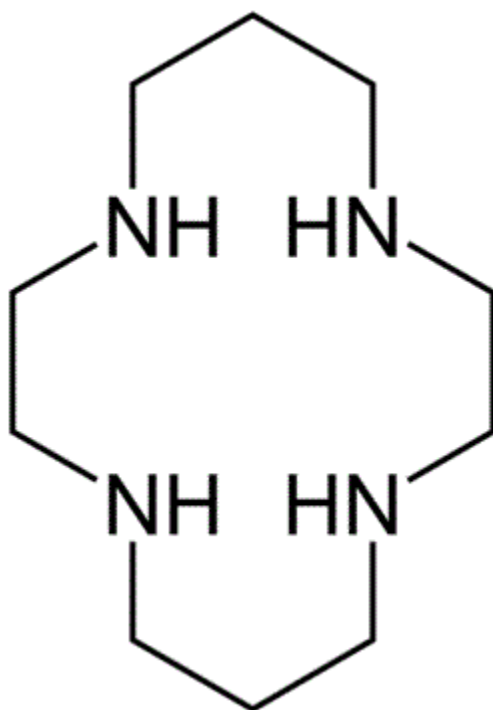
Other common ion/crown ether pairs include [2]:

Crown Ether	Cavity Size, Å	Typical Alkali Ion	Effective Ion Radius, Å
12-crown-4	0.6–0.75	Li ⁺	0.76
15-crown-5	0.86–0.92	Na ⁺	1.02
18-crown-6	1.34–1.55	K ⁺	1.38
21-crown-7	1.7–2.1	Cs ⁺	1.67

Aza-Crown Ethers and Related Compounds

An aza-crown ether is an aza analogue of a crown ether (cyclic polyether). That is, it has a nitrogen atom (amine linkage, -NH- or >N-) in place of each oxygen atom (ether linkage, -O-) around the ring. [3]

For example, the aza equivalent of 12-crown-4 is called aza-12-crown-4:



Note that it is possible to replace half of the Oxygen atoms with Nitrogen.

Note that it is possible to replace the Oxygen atoms with Sulfur.

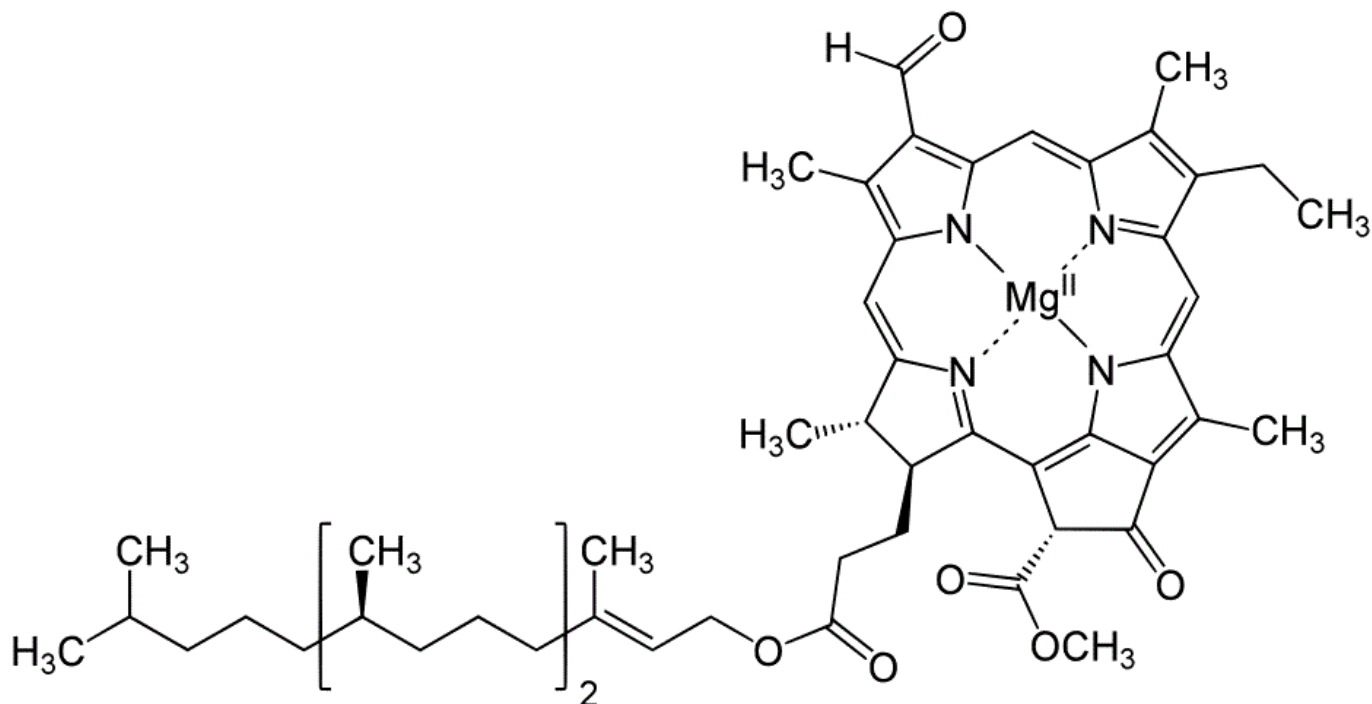
Note that it is possible to replace the Oxygen atoms with Selenium.

The number of possibilities is quite large.

Biological Systems

Metal organic compounds are common in bio-chemistry. Examples include Chlorophyll and Hemoglobin. One interesting advantage of biologically derived ligands comes from the fact that we can use modern techniques of genetic engineering to evolve compounds which are highly selective for individual elements.

Biological compounds which act like crown ethers usually contain Carbon, Nitrogen, and Hydrogen. These are frequently attached to moderately large proteins. For example, Chlorophyll:



In this case, the ligand ring consists of four aromatic rings, each of which contains one Nitrogen atom, which provides the coordinate bond electrons.

One of the major advantages of biological systems for Rare Earth Refining is the fact that modern Bio-Engineering allows us to optimize the behavior of the ligands by evolution.

Proteins

Various groups [4] have published papers on biotechnology-derived ligands which are based on bacterial proteins. While these compounds have excellent Calcium/Lanthanum selectivity, it is not clear whether flexible molecules like protein are well suited for isolating Rare Earths.

Engineering the Ligands for Rare Earth Refining

The goal of designing (or evolving) highly selective ligands for metal ions requires that the molecule bonds strongly with a narrow range of ion sizes. To separate Rare Earths, the ion size range should be on the order of 1% of the ion radius. Since Rare Earth ions have a radius of approximately 0.1 nanometers (1 Å), the tolerance needs to be approximately 0.001 nanometers, or 1 picometer.

The various Rare Earth elements are shown below. The size varies by approximately 13 pm for each step on the size table:

Symbols	4f electrons	unpaired 4f electrons	ionic radius
La	0	0	1.045
Ce	1	1	1.010
Pr	2	2	0.997
Nd	3	3	0.983
Pm	4	4	0.970
Sm	5	5	0.958
Eu	6	6	0.947
Gd	7	7	0.938
Tb	8	6	0.923
Dy	9	5	0.912
Ho	10	4	0.901
Er	11	3	0.890
Tm	12	2	0.880
Yb	13	1	0.868
Lu	14	0	0.861
Sc	0	0	0.745
Y	0	0	0.900

This will require that the ligand structure is rigid, and that it has a non-trivial number of rings. The overall structure of the required chemical would resemble a small RNA molecule.

A secondary design requirement is that the shape of the ligand can be changed easily, for example by varying the pH. This is likely to be done by the use of phenols groups in the aromatic parts of the structure.

In principle, it is possible to construct the necessary chemicals at low cost. It will not be easy.

Appendix A: Packaging and Using the Ligands

The molecules described in this paper could be used in the context of free-floating materials in a solvent. This method would involve recovering the ligand molecules after each attach/detatch cycle, which would involve losses after each cycle.

A better approach is to add some “anchor point” to the molecule, which would allow the ligands to plastic filiaments or tape. These anchor points could be some kind of arcylic group, or it could be some kind of epoxy group. Either way, the ligand molecules would be applied as a coating to some mareial which would act as a mechanical support.

References

- [1] https://en.wikipedia.org/wiki/Crown_ether
- [2] <https://www.britannica.com/science/rare-earth-element/Electronic-structure-and-ionic-radius>
- [3] https://en.wikipedia.org/wiki/Aza-crown_ether
- [4] <https://www.altatech.io/about>