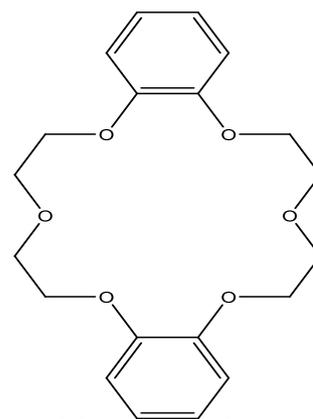
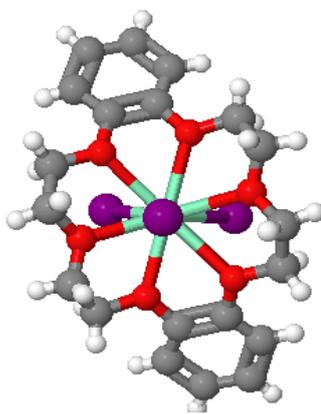


Macrocycles are a type of multidentate ligand that is cyclic with three and over donor atoms. They are much more stable than non-cyclic multidentate ligands and monodentate ligands.



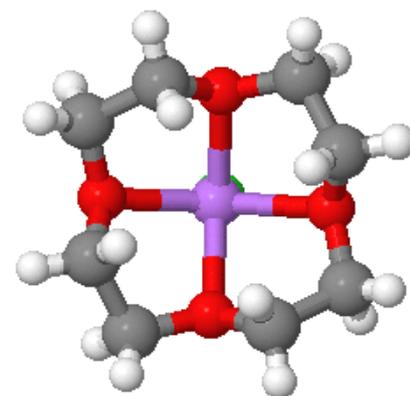
Macrocycle: dibenzo-18-crown-6 attached to SmI_3 NASLOI

Macrocyclic Effect

Different types of ligands form different bond stabilities with transition metals. **Macrocycles > Multidentate Ligands > Monodentate Ligands.** Multidentate ligands are more stable than monodentate ligands because of the **chelation effect**. The effect is caused by the multidentate ligand forming more bonds to the metal centre. More energy is required to break the multiple bonds compared to a single one therefore it is more stable. The more times a multidentate ligand can bind to a metal the stronger it becomes. However, macrocycles form stronger complexes than multidentate ligands. This is because of the **macrocyclic effect**. Macrocycles are more thermodynamically stable because of entropy, it is more favourable to lose multiple multidentate ligands and replace them with one macrocycle.

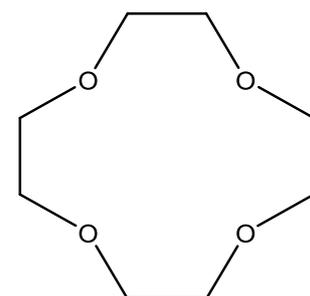
Types of Macrocycle

There are many types of macrocycle due to the nature of ligand bonding. Macrocycles can have many different types of donor atoms and some types even have bridges containing donor atoms across the ring that can bind to the metal. Also there may be many branches and different groups off the macrocycle rings can have. The larger the macrocycle the larger the metal ion that it can fit. Metals bind strongly with the macrocycles which cavity fits its size best. Macrocycles can also contain two or more different types of donor atom.

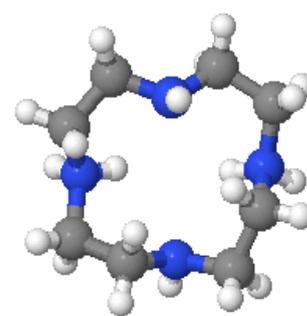
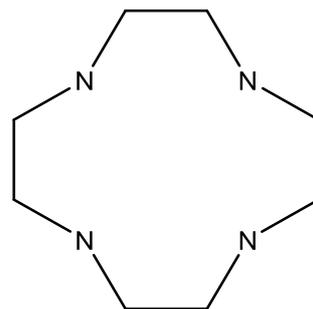
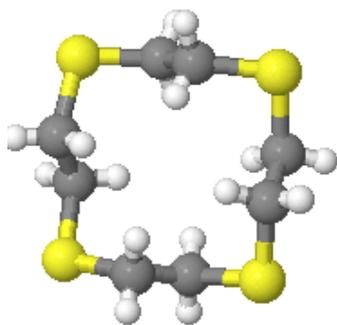
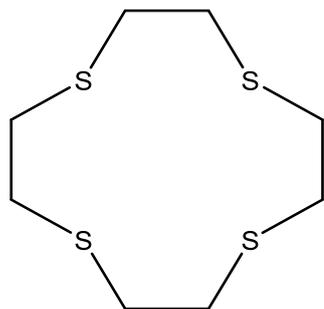


Crown ethers are one of the most common types of macrocycle. They are simply cyclic ethers with multiple oxygen atoms available for binding. They have a simple naming system also, **N-crown-N**, where the first number is the total number of atoms and the final number is the number of binding atoms. See **12-crown-4** example on the left.

Refcode: JOJROP



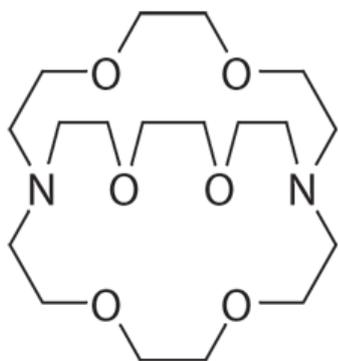
Nitrogen and sulphur can also form crown ether type molecules simply by replacing the oxygen atoms with S and O. There may be many branches and different groups off the macrocycle ring so will not be as simple as the selected examples.



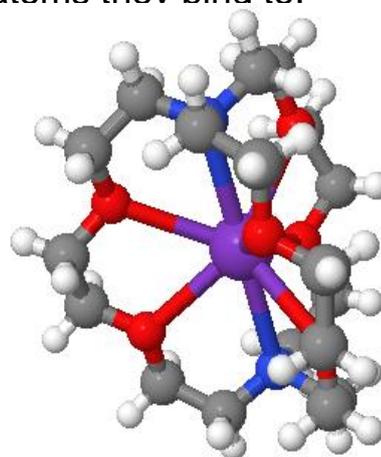
Refcode: FOPCAO or CEFXAM

Refcode: BIBWAL or JIKJUI

Cryptands are a type of macrocycle that are bicyclic or polycyclic caused by bridges with donor atoms across the original macrocycle. Cryptands are more stable than a simple macrocycle due to the fact it has more binding atoms and multiple rings. However, cryptands are hard to make and more selective in the atoms they bind to.



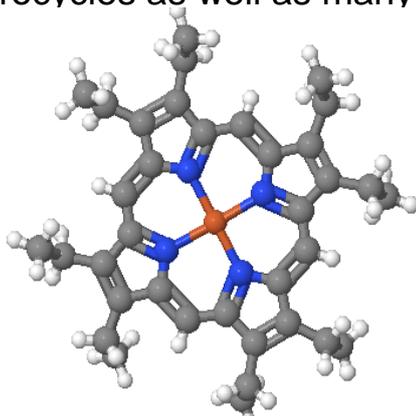
Refcode: KAZXIU



Uses of Macrocycles

Macrocycles have many uses. A first major use of macrocycles was their use in dyes such as phthalocyanine, a blue dye used in the textile and paper dyeing industry. Macrocycles also have use in medicine, their strong affinity for metals means they can be used in chelation therapy to treat heavy metal poisoning along with many other medical applications. Without macrocycles life as we know it would not exist today due to their extensive use in biology. The active site in haemoglobin which binds to Fe is a nitrogen containing macrocycle which is attached to the larger protein, allowing the transportation of oxygen in the body. Chlorophyll the green pigment heavily involved in photosynthesis contains macrocycles as well as many vitamins and other biological molecules.

Refcode: DEDWUE Similar molecule to the active site in haemoglobin



To look at more examples, see the macrocycle table in the 'selected refcodes' sheet.

