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Calixarenes are cyclic phenol-formaldehyde oligomers (see Figure). The number
of monomeric units is designated by a number in square brackets in the name. Thus a
calix[4]arene is made of four phenol derivatives linked by methylene groups. Calixarenes
are often substituted at the para position of the phenol. These substitution can be polar or
non-polar, typically chosen to control solubilities. The most common polar substitution is a
sulfonate group, but the synthesis generally begins with the p-tert-butyl calixarene. The
calixarenes were first synthesized in the 1870's, and since its original structure was
proposed in 1940's their crystal structure was solved in 1979. New chemistry of calixarenes
and their metal complexes is still being discovered today. Calixarenes have
applications in removal of ions from radioactive waste and from sea water. In
addition, metalocalixarenes form three dimensional supramolecular structures.

Aminda Lawrence

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Figure 1

One of the recently discovered applications of calix[4]arenes is catalysis of phosphate
diester transesterification. Mono- and dinuclear zinc complexes are known to catalyze this
reaction. When one, two or three zinc ions are complexed with a 2,6-bis aminomethyl
pyridyl groups attached to the top of the calix[4]arene, the rates of diester transesterification
are dramatically increased. Specifically, the zinc calix[4]arenes increase the rate of cleavage
of an RNA model compound by a factor of 32,000. While these complexes could probably
not be used in vivo, there are in vitro applications of RNA cleavage as well, and a better
understanding of RNA cleavage could lead to gene therapy and anti-viral drugs.

When water-soluble calix[4]arenes pack in the solid state, their interactions are
dominated by hydrophobic interactions. The calixarenes pack "up, down, up, down"
forming a bilayer structure where the sulfonate groups layer with the solvent and counter-ions.
Metal ions can interact with these layers in several ways. They can intercalate between
the layers as hydrated ions, they can bind to one calixarene per metal ion or they can bind to more
than one calixarene per metal ion. All three types are observed.
Several novel structural features of calixarenes have recently been discovered. When certain organic molecules are combined with metal ions and calixarenes, crystalline material containing three dimensional structures such as spheres, tubes and capsules is obtained. For example, when pyridine n-oxide is combined with p-sulfonatocalix[4]arenes along with a lanthanide nitrate, spherical and tubular structures are obtained, depending on the amount of pyridine n-oxide (see Figure 2). In essence, the organic molecule and metal ion allow the calixarenes to pack “up, up,” making curved rather than planar layers. In addition to the spherical and tubular morphologies, remarkable ionic capsules can be produced by the addition of a crown ether and chromium ions to calix[4]arenes. These capsules act as superanions enabling the crystallization of aqua complexes of chromium ions.

![Figure 2](image)

Many possible applications of metallo-calixarenes are suggested by these novel structures. The tubular and spherical structures are large enough to contain molecules, probably with a high degree of specificity. Other applications could include further catalysis, or even more likely medical or engineering applications.

References

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References


Progress Towards More Effective Gold-Based Pharmaceuticals

Kelli M. Harl

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Gold compounds were introduced in medicine when alchemists such as Paracelsus used them as a cure-all for everything from paralysis and fevers to syphilis and alcoholism. In 1890, Robert Koch was the first to note the bacteriostatic activity of gold when he observed K[Au(CN)₂] inhibiting the growth of tuberculosis bacilli. Today, gold(I) thiolate complexes are used as treatment for rheumatoid arthritis. Myochrysin, Solganol, and Allochrysin are injectable gold-containing pharmaceuticals used for this purpose. Ridaura, or Auranofin, is a gold phosphine anti-rheumatic agent taken orally. Auranofin is safer than the injectables, but less effective. In addition to its anti-rheumatic properties, Auranofin also displays anti-tumor activity. Gold complexes are currently being studied as potential therapy for HIV, malaria, asthma, and a host of other maladies in addition to their anti-tumor and anti-rheumatic properties.

The most common oxidation states of gold are +I and +III. The inherent problem of side effects is commonly attributed to gold(III) metabolites generated under the oxidative conditions in inflamed tissue. It is postulated that the active species of the rheumatoid arthritis drugs and anti-tumor drugs are also metabolites of the administered substances, thus explaining the variable clinical responses to gold therapy in terms of side effects and efficacy.

Investigation of the chemistry and anti-tumor properties of gold(III) complexes is one area of active research toward the development of gold-based drugs. Since gold(III) and platinum(II) are isoelectronic, it is plausible that a gold analogue of cisplatin could be developed for chemotherapy. Studies of four coordinate square-planar complexes of gold(III)(damp), where damp = bidentate 2-((dimethylamino)methylene)phenyl, display anti-tumor activity with substituents of acetato or malonato. Anti-tumor activity was also evident in similar complexes containing salicylate and thiosalicylate moieties. It is believed that gold binds to DNA in a fashion analogous to cisplatin, although the varied response from different tumor types suggests a different mechanism of cytotoxicity.

Since the mechanism of gold-drug action and toxicity remains unknown, studies of gold(III) reactions with amino acids, peptides, and proteins are a priority in gold-drug