



INORGANIC (CARBON-FREE) CYCLIC STRUCTURES. COVALENT RINGS AND CYCLIC SUPERMOLECULES

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INTRODUCTION. A PERSONAL NOTE

This mini-review is a tribute to the memory of Professor Candin Liteanu, my mentor and model during undergraduate years. I owe him my interest for inorganic rings. I was a student in my first year (freshman according to American academic terminology) in the Department of Chemistry of the University of Cluj when Professor Liteanu suggested a literature project about inorganic polymers. Coming with the high school knowledge of chemistry, where we learned mostly about the Periodic Table, acids, bases and salts, as well as some organic chemistry, I had no idea about the subject. I started browsing inorganic chemistry treatises and I found what I was looking for: polyphosphates, silicates, silicones, phosphonitrile chlorides (the old name of phosphazenes) but the most interesting and fascinating finding in the literature were some cyclic compounds, containing carbon-free rings. I knew from the organic chemistry about benzene and cyclohexane, but the fact that elements other than carbon can also form cyclic compounds was really something special. At the time inorganic rings (borazine, “phosphonitrilic” chlorides, metaphosphates, sulfur nitride) were treated within the chemistry of individual elements (boron, phosphorus, sulfur), and no unifying view was yet in use. Within this approach some inorganic rings were covered in a series of splendid monographs on boron,¹ phosphorus² and sulfur.³

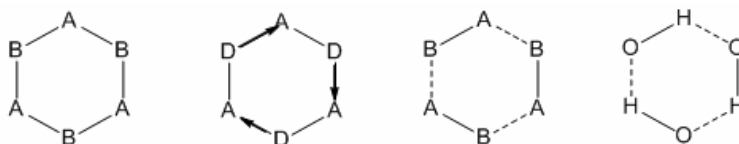
I spent my five years as student with mining the literature for inorganic rings and the result was a monograph entitled “Introduction to the chemistry of inorganic cycles”, published in Roumanian and translated into Polish language.⁴ It was followed a few years later by a two volume monograph published in English,⁵ to which two other volumes⁶ were added later for updating. I believe, these books contributed to establishing the chemistry of inorganic rings as a self-consistent chapter of inorganic chemistry, reflected after 1960 in a series of other unifying monographs.^{7,8} Now, the inorganic rings are legitimized as a self-consistent branch of chemistry by the biannual International Symposia on Inorganic Ring Systems (IRIS) and the interest for inorganic rings is well alive.^{9,10} A relatively recent and comprehensive presentation of inorganic rings is available in Encyclopedia of Inorganic Chemistry,¹¹ and a “hot” treatment of small inorganic rings was just published.¹² Here we will discuss only monocyclic structures, but small inorganic rings can serve as building blocks for various polycyclic architectures.

TYPES OF INORGANIC RING STRUCTURES

Ring structures play an important role in the chemistry of carbon. Cyclic hydrocarbons are very stable and important organic compounds. Partial replacement of carbon by another element (called heteroatom) leads to

a vast area of heterocycles. Full replacement of carbon results in inorganic rings. Some organic chemists even describe these ring as “heteroatom only” rings, implying that they are just an extension of the chemistry of organic heterocycles. In this context a question arises: to what extent other chemical elements can imitate carbon to form rings analogous to cyclic hydrocarbons (“homocycles”) and what sort of element combinations are possible and able to form inorganic heterocycles. Most likely candidates for comparison with organic rings are those formed by non-metals using covalent bonds. As illustrated bellow, a wide diversity of covalent inorganic rings, homo- and heterocycles, are known. A theoretical analysis of the electronic structures of “inorganic benzenes” showed that some homonuclear rings have a moderate aromatic character while in heteronuclear rings the lone pairs of electron tend to localize at the most electronegative atoms.¹³

The formation of inorganic rings is not limited to covalent bonds. The self-assembly of supramolecular structures from molecular units (tectons) associated through various intermolecular non-covalent forces such as dative bonds, secondary bonds, hydrogen bonds, electrostatic interactions, etc. can also produce inorganic (carbon-free) rings. Selected, illustrative examples are presented bellow. No discussion about the preparative methods for inorganic ring compounds is possible here because of space limitations.



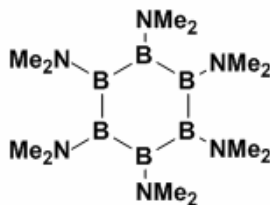
The nomenclature of inorganic rings raised some difficult questions. The IUPAC Commission on Inorganic Nomenclature suggested a system¹⁴ but nobody used it and in this article a common system will be preferred, which is compatible with the nomenclature of organic rings.¹⁵

COVALENT RINGS

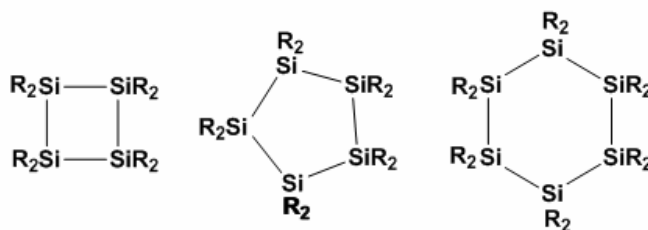
1. Homocyclic ring systems

Homocyclic rings are formed by ring closure of identical catenated atoms, like the carbon atoms in cycloparafins or aromatic hydrocarbons. The inorganic homocycles are illustrated by cyclopolysilanes, their germanium, tin and lead analogues, cyclopolyposphanes and their arsenic, and antimony analogues, by sulfur and selenium allotropes and some others. Less frequent are homocyclic ring formed from boron or nitrogen atoms alone.

An interesting B₆ boron homocycle is found in B₆(NMe₂)₆ where electron back-donation from the dimethylamino substituents probably stabilize the six-membered ring which displays a chair conformation.¹⁶

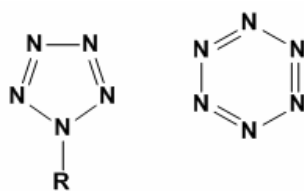


Cyclopolysilane analogues of cycloparafins, (SiH₂)_n with n = 4, 5 and 6,¹⁷ and perchloro derivatives (SiCl₂)_n n = 4-6, as purely inorganic compounds are chemical rarities because of the sensitivity of Si-H and Si-Cl bonds to moisture, oxygen and low thermal stability, but organic substituents make very stable cyclopolysilanes (SiR₂)_n (usually n = 3-6, even higher for R = Me; those with n up to 15 were confirmed by X-ray diffraction).¹⁸ The perphenylated cyclosilanes have n = 4-6.¹⁹ The problem of a hexasilabenzene was much debated in the literature, but there is no similarity with the purely organic ring.²⁰ A remarkable achievement was the synthesis and structural characterization of a tetrasilacyclobutadiene iron complex (RSi)₄Fe(CO)₃, starting from [BrRSi]₄.²¹ A cyclotrisilane ring compound (SiR₂)₃ was obtained with R = mesityl.²²

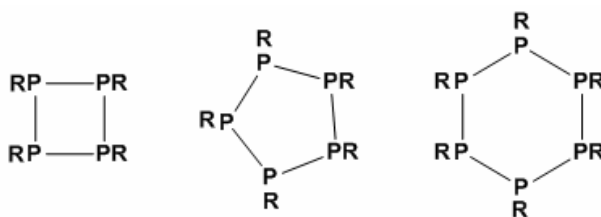


Cyclic polygermanes $(\text{GeR}_2)_n$ with $n = 3-7$,²³ and polystannanes $(\text{SnR}_2)_n$ with $n = 3-9$,²⁴ are also known.

A five-membered nitrogen homocycle is known in the pentazole family as aryl substituted ring derivative, Ar-N_5 , with $\text{Ar} = \text{Ph}$, $p\text{-C}_6\text{H}_4\text{NMe}_2$.^{25, 26} It can be speculated about a six-membered N_6 ring (unsubstituted) but theoretical calculations suggest that it would be unstable towards formation of three N_2 molecules, in spite of the apparent presence of a π electronic sextet in the ring.²⁷ There is much interest in the N_5 ring, in anionic or even cationic form as a potential six-electron donor ligand.^{28, 29}



A rather extensive and interesting cyclophosphine $(\text{RP})_n$ chemistry has been developed³⁰ and also arsenic $(\text{AsR})_n$ homoatomic rings³¹ and antimony $(\text{SbR})_n$ analogues,³² are well known.



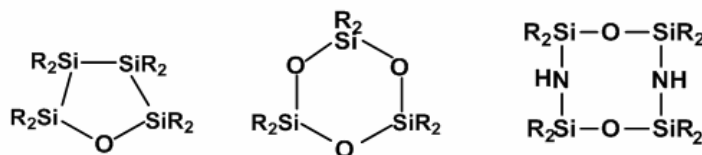
Several cyclic allotropes of sulfur, S_x , with $x = 6-24$ have been identified and most of them were well characterized by X-ray diffractions. Of these the cyclic S_8 is the most common form of elemental sulfur.³³

Heterocyclic ring systems

The covalent inorganic heterocycles contain at least two different elements. There are three different ways to generate inorganic heterocycles:¹¹

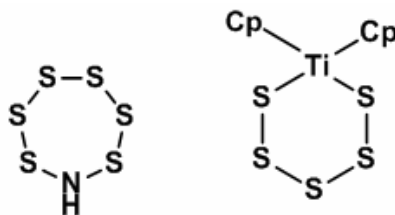
- (a) by insertion of a heteroatom in a parent homocycle, maintaining some bonds between identical atoms; these rings are of general type A_mB_n ;
- (b) by regular alternation of two elements, *i.e.* by a combination of a small number of repeating units; these rings are of general type $(\text{AB})_n$;
- (c) by combining a number of different repeating units; these rings are of type $(\text{AB})_m(\text{A}'\text{B}')_n$.

For the siloxane rings the three types are illustrated.



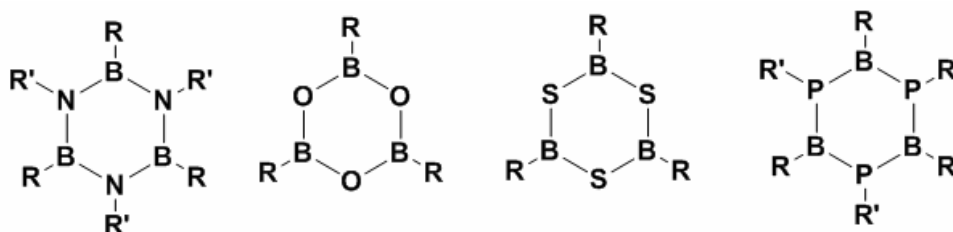
Obviously, the possibilities of ring formations on the basis of these principles are innumerable.

One of the oldest known heterocycle of type (a) is heptasulfur imide (or cycloazaheptasulfane). Several mixed sulfur-selenium rings fall into this category as well as a titanium compound Cp_2TiS_5 .



There are numerous rings formed by regular alternation of two elements. Only a small illustrative selection is discussed here.

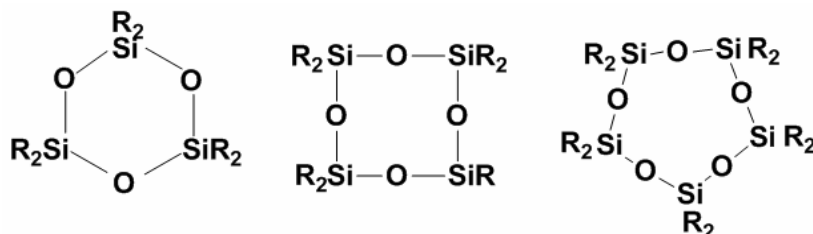
Borazine or cyclotriborazane (HBNH_3), also nick-named as “inorganic benzene”, with its numerous B- and N-substituted derivatives, was known for a long time and, remarkably, its structure was correctly deduced in a time when no X-ray diffraction was in current use. There is some debate about possible aromaticity of this ring which contains six π electrons, all coming from nitrogen. Other boron heterocycles are boroxines (RBO_3)³⁴ and borthianes (RBS_3)³⁵ as well as cyclotri(boraphosphanes) or phosphinoborines (RBPR'_3) and cycloarsaboranes (arsinoborines) (RBPAs'_3). The structures of many borates are also based upon B_3O_3 rings.



These rings are trimers of hypothetical $\text{RB}=\text{ER}'$ monomers. Double bond borazenes, $\text{RB}=\text{NR}'$, can be isolated only with very bulky, sterically demanding organic substituents. Also, double bond monomeric species $\text{RB}=\text{ER}'$ with $\text{E} = \text{P}, \text{As}$, can be isolated only with very bulky R and R' substituents and favored by donor stabilization, as in compounds of the type $(\text{donor})\text{RB}=\text{ER}'$.³⁶ Four-membered ring compounds $(\text{RBNR}')_2$, and eight-membered ring derivatives $(\text{RBNR}')_4$ have also been described.³⁷ With bulky substituents aluminum analogues, *e.g.* $[\text{MesAlNPh}]_2$ (Mes = mesityl) can be obtained.³⁸

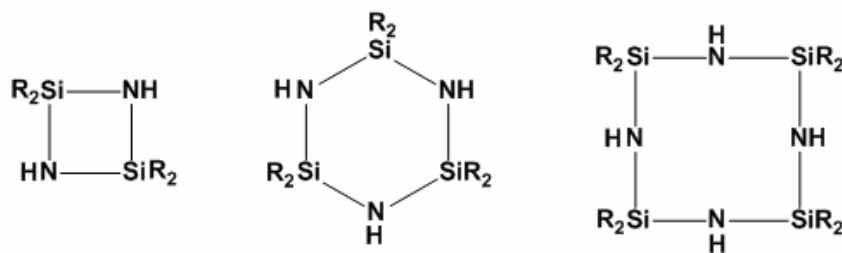
An important family of rings formed by regular alternation is offered by cyclosiloxanes, mainly with organic substituents at silicon, $(\text{R}_2\text{SiO})_n$. In the case of $\text{R} = \text{Me}$, rings with n from 3 to...35 have been characterized,³⁹ and very stable are the phenyl derivatives $(\text{Ph}_2\text{SiO})_n$ with $n = 3$ and 4. Cyclosiloxanes, $(\text{R}_2\text{SiO})_n$, ($n = 3, 4$), are used as ingredients in beauty and personal-care products and are important intermediates in the manufacture of silicone (siloxane) polymers, used as high-performance elastomers and fluids and surface modifiers.⁴⁰ Probably some of these uses will have to be reconsidered in view of the recent reports that cyclosiloxanes produce fatal liver and lung damage in mice.⁴¹

Silicon-oxygen rings also define a class of cyclosilicates, containing the $[\text{SiO}_3]_n^{-2n}$ anions. An interesting finding was the discovery of cyclosiloxanes displaying crown ether-like behavior.^{42,43}



Numerous hetero- and metalla-siloxanes⁴⁴ and some spectacular ferrocenyl-substituted cyclosiloxanes⁴⁵ have been described.

Important heterocycles are the cyclosilazanes $(\text{R}_2\text{SiNR}')_n$ with $n = 2, 3$ and 4.⁴⁶ Cyclosilazanes (as well as borazines) are attractive as precursors of high tech ceramics.⁴⁷

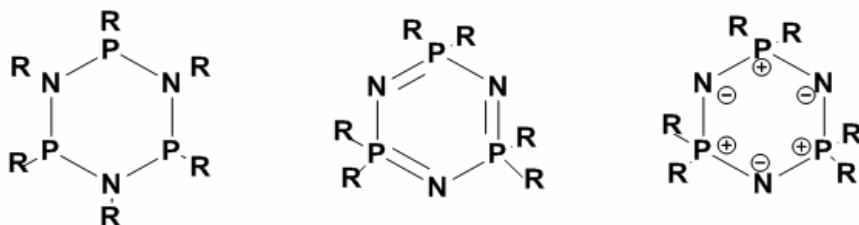


Organogermanium⁴⁸ - and tin-oxygen analogues are also well known.

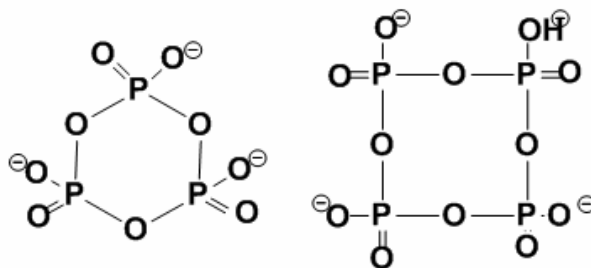
An extensive chapter of inorganic heterocycles based upon phosphorus-nitrogen, phosphorus-oxygen species, with some phosphorus-sulfur and phosphorus-selenium rings is also known.

The phosphorus-nitrogen heterocycles comprise phosphorus(III) derivatives,⁴⁹ *e.g.* cyclotriphosphazanes $(\text{RPNR}')_3$ and phosphorus(V) derivatives, *e.g.* cyclotriphosphazenes $(\text{R}_2\text{PN})_3$. Four- and eight-membered rings based upon PN units are also known, and in the case of cyclophosphazenes the members of a family of $(\text{X}_2\text{PN})_n$ with $\text{X} = \text{F}$ and Cl , and n values from 2 to 35 have been identified.⁵⁰ The cyclophosphazenes are an important class of inorganic ring compounds, underscored by their application as starting materials for polyphosphazene polymers, which are obtained by ring opening polymerization.⁵¹ There is interest on cyclophosphazenes for several applications, such as hydraulic fluids and additives, cores for star polymers or dendrimers, nanostructured materials, water repellents, non-flammable fibres, foams, fuel pipes and metal ion conductors in batteries.⁵² The cyclophosphazenes can also be used as multi-site coordination ligands in coordination metal complexes.⁵³

Although formulated with an alternation of single and double bonds, and experimentally shown to have bond lengths intermediate between single and double, thus suggesting aromaticity, it seems that a better description of the electronic structure of cyclotriphosphazene is the one using polar P-N bonds.⁵⁴ Arsenic analogues are also known.

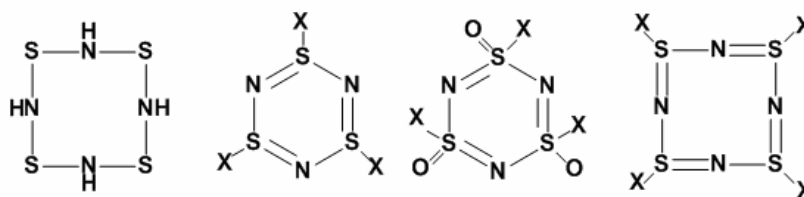


Phosphorus-oxygen rings occur in cyclophosphates (mostly known as metaphosphates), with tri-, tetra- and hexamers $[(\text{O})\text{PO}(\text{O}^-)]_n$, $n = 3, 4, 6$, even 8 and 10, well characterized.⁵⁵

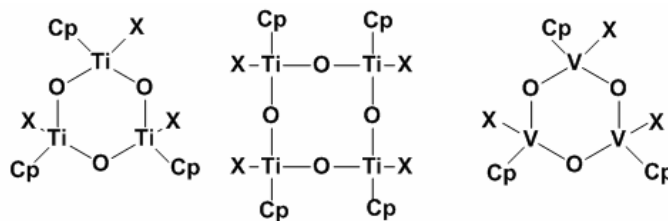


Sulfur trioxide exists in a trimeric cyclic form, containing a S_3O_3 ring. Selenium-oxygen six-membered Se_3O_3 and Se_4O_4 rings are also known.⁵⁶

Paired with nitrogen, sulfur forms a remarkable variety of rings, due to the fact that it may occur in several oxidation states.⁵⁷ Selected examples are tetrasulfur tetranitride, S_4N_4 , cyclotetrathioimide $(\text{SNH})_4$, cyclothiazenes $(\text{XSN})_{3\text{ and }4}$ and oxocyclotrithiazenes $[\text{X}(\text{O})\text{SN}]_3$, to name only a few. Some were described as “electron rich” aromatic rings.⁵⁸



In rare cases transition metals also form inorganic heterocycles, mainly in organometallic oxides, based upon inorganic M_nO_n rings.⁵⁹ Due to the large number of transition metals it can be expected that the potential of this chemistry will be more used in the future. As examples, titanium-oxygen and vanadium-oxygen rings are illustrated (Cp = η^5 -cyclopentadienyl).



The borazine-phosphazene hybrid cations, which are inorganic heterocycles formed by skeletal substitution reactions,⁶⁰ illustrate the third type of inorganic rings, made by combining differing building units.

CYCLIC SUPERMOLECULES

Formation of cyclic structures is possible through various types of intermolecular associations, in which a small number of molecules are connected through non-covalent bonds. This process is known as self-assembly⁶¹ and belongs to the field of supramolecular chemistry. Supramolecular chemistry is “the chemistry of molecular assemblies and of the intermolecular bond” and deals with “organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces”.⁶² The structures obtained when a few, well-defined, discrete molecular species undergo intermolecular association are defined as supermolecules. This is the case of some cyclic species. A large, undefined number of molecules associated through intermolecular forces, determine the formation of supramolecular arrays, often described simply as polymers. It should be added that “any molecule whose interactions are dominated by particular associative forces that induce self-assembly of an organized network” is called tectons.⁶³

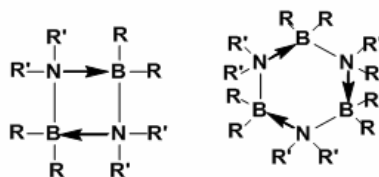
The associative forces which may lead to intermolecular self-assembly are quite varied and include dative bonds, secondary bonds, hydrogen bonds, and even electrostatic (ionic) interactions.

1. Rings formed through dative bonds

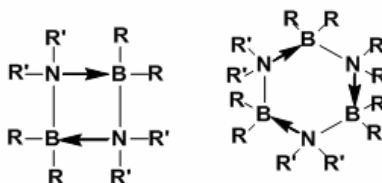
Molecules that contain both donor and acceptor sites may associate through intermolecular dative bonds. Although the dative (donor-acceptor) bond is formed through a pair of electrons (donated from one atom to another) differs from the covalent bond which is formed by one electron from each connected atom to form the electron pair. Thus, a distinction between the two type of bonds should be taken into account.⁶⁴

A classical example is that of aminoboranes, $R_2B-NR'_2$ which can exist in monomeric form only when the substituents R and R' are bulky organic groups. With less sterically demanding substituents the aminoboranes will self-assemble into cyclic dimeric, trimeric or tetrameric supermolecules, sometimes also into supramolecular polymeric arrays.⁶⁵ Thus, diisopropylaminoborane and dicyclohexylaminoborane exist as monomers due to the steric requirements of the alkyl group but other aminoboranes which are not sterically hindered enough to be monomers in solution, exist as a mixture of monomers and dimers.⁶⁶ The

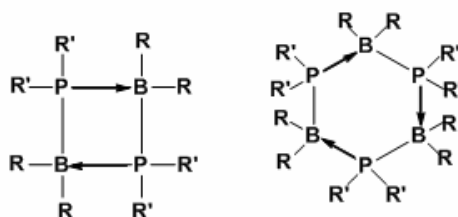
unsubstituted aminoborane⁶⁷ forms rings up to the pentamer $[H_2B-NH_2]_n$ ($n = 2-5$). Macrocyclic species $[MeNH-BH_2]_x$, with $x = 10-15$, along with linear ones $MeHN[H_2B-NHMe]_yH$ with $y = 10-36$, by oligomerization and, respectively, polymerization of the reactive monomer $MeHN-BH_2$ were generated from $MeNH_2 \cdot BH_3$ in solution.⁶⁸



Alternatively, these structures can be written without arrows, with polar bonds, as suggested recently for dative bonds.⁶⁹



Phosphinoboranes, $R_2B-PR'_2$, can exist in monomeric form or as cyclic dimeric, trimeric or tetrameric supermolecules, or as polymeric supramolecular arrays.⁷⁰



In a similar manner, organoaluminum amides, R_2Al-NR_2 , self-assemble into cyclic supermolecules.⁷¹ Thus, an equilibrium between dimeric $[H_2Al-NMe_2]_2$ and trimeric $[H_2Al-NMe_2]_3$ rings was observed,⁷² whereas the isomeric dimethylaluminum derivative forms cyclic trimers $[Me_2Al-NH_2]_3$. Organoaluminum alkoxides and thiolates form dimeric and trimeric cyclic supermolecules,⁷³ and aluminum-phosphorus analogous rings⁷⁴ were also described, *e.g.* trimeric $[Me_2Al-PMe_2]_3$ even in gas phase.⁷⁵ Similarly, gallium, indium and thallium compounds with nitrogen, phosphorus, arsenic and antimony donors form cyclic supermolecules.⁷⁶ Several gallium and indium alkoxides (useful as metal oxide precursors) are cyclic dimers.⁷⁷

In organometallic fluorides the fluorine atom can act as a donor, producing cyclic supermolecules through fluorine-metal dative bonds.⁷⁸ Four-membered Cu_2Cl_2 , six-membered Cu_3Cl_3 and eight-membered Cu_4Cl_4 rings demonstrate the ability of chlorine donor to produce inorganic rings.⁷⁹

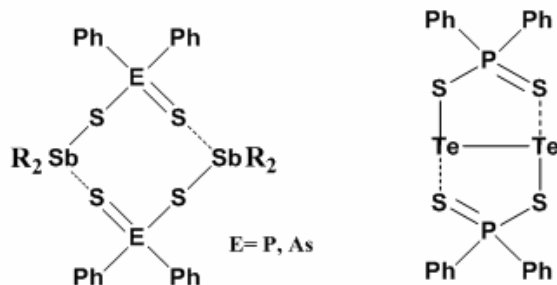
Eight-membered ring supermolecules are formed with phosphinato ligands, *e.g.* dimeric $[Me_2AlOP(O)Ph_2]_2$ ⁸⁰ and $[Bu^t_2GaOP(O)Ph_2]_2$,⁸¹ and cyclic tetrameric $[Me_3SnOP(O)Ph_2]_4$ ⁸² and hexameric $[Ph_3SnOP(O)P(OMe)]_6$,⁸³ as well as tetrameric cupferronate $[Me_3SnONPhNO]_4$,⁸⁴ all through dative bond association.

Formation of inorganic rings through dative bonds is a common feature in metal amide, alkoxide, thiolate and selenolate chemistry.⁸⁵ Coinage metal pyrazolates form trimeric nine-membered rings with M_3N_6 ($M = Cu, Ag$)⁸⁶ and tetrameric twelve-membered Au_4N_8 rings.⁸⁷

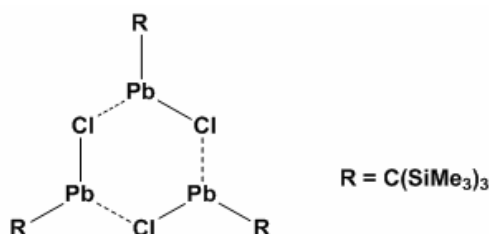
2. Rings formed through secondary bonds

Secondary bonds are “interactions characterized by interatomic distances larger than single covalent bonds but shorter than the sum of Van der Waals interatomic distances”.⁸⁸ Supramolecular self-assembly through secondary bonds may lead to cyclisation, with formation of inorganic (carbon-free) ring structures. This is a quite extensive event in supramolecular organometallic chemistry⁸⁹ and can be well illustrated with

dimerization of several compounds of phosphorus- and arsenic-based thioacids and oxo analogues,⁹⁰ Among these can be cited the soft metal phosphor- and arsenic-1,1-dithiolates, like $[\text{Bi}(\text{S}_2\text{PMe}_2)_3]_2$,⁹¹ and $[[\text{Bi}(\text{S}_2\text{AsMe}_2)_3]_2$,⁹² organometallic dithiophosphinates $[\text{MeHg-S}(\text{S})\text{PPh}_2]_2$,⁹³ and $[\text{Ar}_2\text{Sb-S}(\text{S})\text{PPh}_2]_2$ (Ar = Ph, *p*-tolyl),⁹⁴ In all these, eight-membered rings (described as “pseudoheterocycles” are established. Several inorganic rings are formed in tellurium-sulfur compounds.⁹⁵ An interesting case is that of $\text{Te}_2(\text{S}_2\text{PPh}_2)_2$ which contains five-membered rings due to the presence of a homoatomic Te-Te bond.⁹⁶



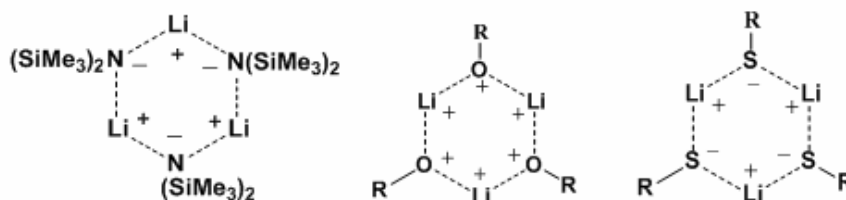
Six-membered rings formed through secondary bonding interactions are present in the trimer $[(\text{Me}_3\text{Si})_3\text{C-PbCl}]_3$.⁹⁷



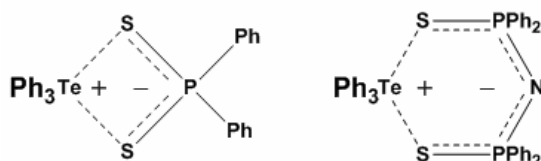
In many cases secondary bonding leads to polymeric supramolecular arrays, and in similar compounds the nature of organic substituents favor one type or another (cyclic *vs* polymeric) structure, without possible anticipation.

3. Rings formed through ionic (electrostatic) interactions

Cyclic self-assembly may occur in the case of some polar compounds, like alkali metal and alkaline earth amides, alkoxides and thiolates, even phosphides, where the bonding in the ring structure is essentially ionic (electrostatic). As illustrative examples six-membered cyclic lithium bis(trimethylsilyl)amide,⁹⁸ a lithium alkoxide $[\text{ROLi}]_3$ (R = $\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2$ -2,6-Me-4), also cyclic hexameric $[\text{NaOBU}]_6$ and nonameric $[\text{NaOBut}]_9$ can be presented.⁹⁹ A lithium thiolate is also trimeric $[\text{LiSR}(\text{THF})]_3$ (R = $\text{C}_6\text{H}_2\text{Bu}^t$ -2,4,6).¹⁰⁰ Usually, ring formation requires bulky organic groups, otherwise polymeric supramolecular arrays are formed.¹⁰¹

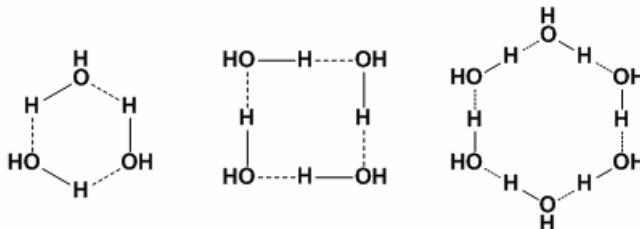


Probably in the chelate rings of triphenyltelluronium cations with dithiophosphorus anions¹⁰² a cooperative ionic and secondary bonding lead to ring formation.

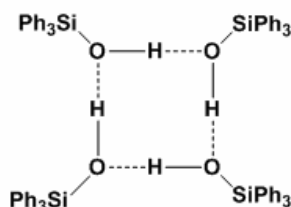


4. Rings formed through hydrogen bonds

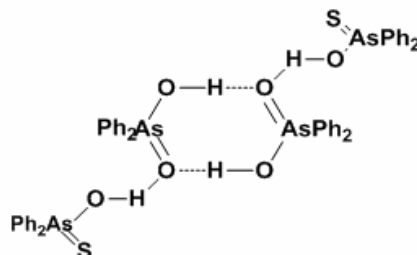
The simplest rings formed through hydrogen bonds occur in the so-called “water clusters”, known as dimers, trimers, tetramers, hexamers and more intricate polycyclic structures, many of which have been identified as guests trapped in the crystal structures of organic and coordination compounds.^{103, 104}



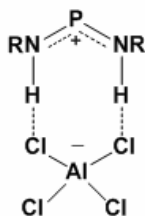
Alcohols are known to associate through hydrogen bonds to form cyclic dimers, trimers or tetramers, based upon inorganic rings formed through hydrogen bonds. Similar cyclic structures are formed by silanols, and there is a great variety of carbon-free cyclic skeletons containing (O-H...O)_n rings.¹⁰⁵ Such rings formed through hydrogen bonds have been found in numerous organometallic compounds containing OH groups.¹⁰⁶



A rather unusual hydrogen bond cyclic structure was discovered in a dimeric adduct of diphenylthioarsinic-diphenylarsinic acids.¹⁰⁷

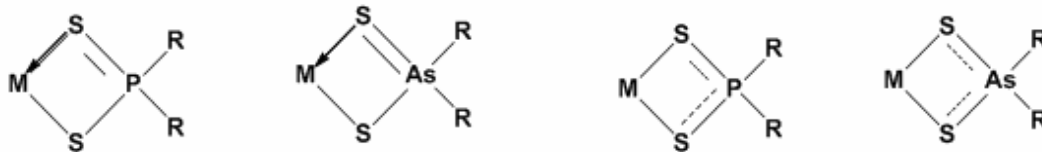


In the diaminophosphenium tetrachloroaluminate [RN-P-NR]⁺[AlCl₄]⁻ with R = 2,4,6-Bu^t₃C₆H₂) an electrostatically enhanced hydrogen bonding leads to formation of a cyclic structure.¹⁰⁸

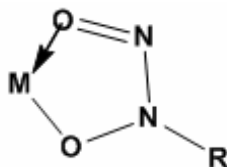


INORGANIC (CARBON-FREE) CHELATE RINGS

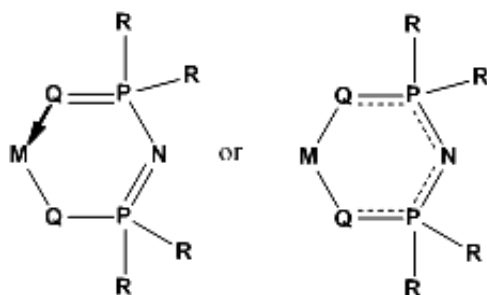
The most popular chelating agents used in coordination chemistry are bidentate organic species, such as ethylenediamine, diphosphines or acetylacetonate, but there are compounds with inorganic skeletons, able to act as chelating agents and to form inorganic (carbon-free) chelate rings.¹⁰⁹ Among these are 1,1-dithiolates (dithiophosphates, dithiophosphinates, dithiophosphonates, dithioarsinates),¹¹⁰ which form four-membered chelate rings.



Cupferron, an old analytical reagent, and other diazeniumdiolates form five-membered chelate rings with several metals.^{111, 112}

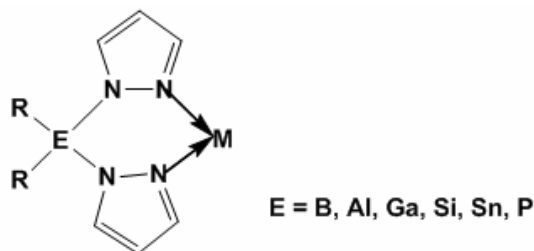


An extensive family of six-membered chelate rings is produced by anionic dichalcogenoimidodiphosphinates as ligands $[QR_2PNPR_2Q]$, where $Q = O, S, Se, Te$.¹¹³ These compounds are now focusing much interest as single-source precursors for the production of thin films of semiconducting metal chalcogenides.¹¹⁴



$Q = O, S, Se, Te$

Very popular chelating ligands which form inorganic chelate rings are the poly(pyrazolyl)borates.¹¹⁵ More recently, poly(pyrazolyl)aluminates,¹¹⁶ poly(pyrazolyl)silanes¹¹⁷ and related gallium, germanium and tin analogues,¹¹⁸ as well as poly(pyrazolyl)phosphine oxides¹¹⁹ emerged as similar reagents.



$E = B, Al, Ga, Si, Sn, P$

There are some other short chain molecules with inorganic backbones and terminal donor atoms able to form inorganic chelate rings. Nice examples are diphosphinoaminosilanes, $R_2P-NR'-SiR_2-NR'-PR_2$,¹²⁰ and bis(diphenylphosphine)sulfide, and $R_2P-S-PR_2$.¹²¹ This is a field with an immense synthetic potential.

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