CLUSTERS AND POLYNUCLEAR COMPOUNDS

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Summary

The synthesis, structures, bonding properties and applications of clusters, cage and polynuclear compounds of p- and d-block elements are briefly presented, highlighting some historical examples and most recent achievements. For p-block elements particular emphasis is on the chemistry of boranes and carboranes for their fascinating structures involving multicenter bonding, whose interpretation challenged chemists for years and opened the way to understand also transition metal clusters. For the d-block elements, the emphasis is on metal carbonyl clusters for the explosive developments experienced by their chemistry in the last four decades and the stirring effect they had and are having in the development of other classes of clusters belonging to all elements of the Periodic Table.

1. Introduction

The ubiquity of cluster and polynuclear compounds in the Periodic Table and the relationships between molecular compounds and condensed phases.

Clusters and polynuclear compounds have perhaps been regarded for a long time as fascinating chemical oddities. The exponential growth of their chemistry has been made possible by the advent of X-ray crystallography and many other spectroscopic techniques. The term "metal atom cluster" was introduced in 1964 by F. A. Cotton to designate a finite group of metal atoms held together mainly, or at least to a significant extent, by metal-metal bonds. That was necessary in order to differentiate this emerging class of compounds from polynuclear complexes in which the metal centers are held together exclusively or mainly by bridging ligands. In this overview of clusters and polynuclear compounds, which can by no means be exhaustive, owing to the enormous vastness of the field and the many facets of their chemistry, the classical definition of metal atom clusters will be extended to all elements of the periodic table, regardless of their metallic or non-metallic nature. Moreover, finite groups of atoms describing simple or fused polygons or polyhedra, either bare or in a ligand shell, and held together mainly or to a significant extent by homonuclear bonds will be considered as clusters. Within this definition, one can trace clusters in all groups of the Periodic Table, beginning from the alkali metals and ending with the group of chalcogens. Clusters are being prepared and studied both by physical and chemical methods. In physical methods, a plasma of an element is prepared by electric discharge, or by bombardment of a target with energetic ions, e.g. Xe^+, or laser desorption. The plasma contains clusters of all sizes, which are charged both as positive or negative ions. The cluster ions are size-selected by a quadrupol mass spectrometer (QMS) and a beam of clusters of selected size can be cooled with helium and allowed to interact with a rarefied atmosphere of a ligand, e.g. CO. The resulting carbonylated $[M_n(CO)_m]^{+\text{ or }-}$ positive or negative cluster ions can be then filtered and analyzed by a second QMS. If the produced beam is sufficiently intense, spectroscopic studies can also be carried out. Although the above methods produce tiny amounts of each sample, very important information regarding the nature of clusters can be and has been gathered. In general, the abundance of M_n clusters in the original plasma decreases smoothly as a function of n. In the particular case of carbon, C_n species with specific n values showed exceptional abundances. These observations triggered an enormous amount of experimental and theoretical studies, which brought to the isolation, characterization and application of now familiar species like C_{60}, C_{70} and, eventually, carbon nanotubes.

Going back to chemistry, we wish the reader could get rid, right from the beginning, of the belief that clusters and polynuclear compounds are fancy chemical oddities. These species fill the gap between single atoms, simple molecules or Werner-type coordination compounds, on one side, and solid state chemistry, on the other side. Countless examples of close relationships between molecules or molecular ions and condensed phases can be made. We shall make here only a few examples, since reference to these close relationships is made throughout the text. As a first example, consider the octahedral $[B_6H_6]^{2-}$ closo-borane and the $M^{II}B_6$ (M = Ca, Sr, Ba, Eu, Yb) hexaboride. The latter display a cubic CsCl-type lattice in which chloride ions are replaced by B_6^{2-} octahedral moieties linked together by B-B bonds in all six orthogonal directions to give rise to an open framework. This lodges the alkali-earth or rare-earth ions in its centers. As a second example, notice that sub-oxides, sub-chalcogenides, sub-halides of early transition metals and lanthanides and their ternary phases are often based on M_6X_{12} or M_6X_8 octahedral moieties linked, condensed or fused in a wide variety of ways. Molecular ions such as $[M_6X_{12}L_6]^{n+}$ (M = Nb, Ta; X = Cl, Br; L = X^-, H_2O; *n* = 2-4) and $[M_6X_8L_6]^{n+}$ (M = Mo, W), which are building blocks of the above condensed phases have been isolated and characterized.

As a final thinking, consider that hydrolysis of a generic M^{n+} aquo complex to the corresponding sparingly soluble hydroxide or oxide will occur through formation of a series of μ-hydroxo and μ-oxo polynuclear compounds of increasing complexity, which eventually give rise to the final condensed-phase lattice. Possible examples are $[Sn_3(\mu\text{-OH})_3(\mu_3\text{-OH})]^{2+}$ and $Sn_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$. Even unraveling of a few involved species is not an easy task, due to chemical complexity of the above mixtures and lack of diagnostic spectroscopic techniques. As the size and disperse distribution of clusters or polynuclear compounds contained in solution increases, the solution will change into a colloidal mixture and will eventually separate the corresponding condensed phase.

Owing to the above situation, even the thousands of clusters and polynuclear compounds, which have been so far individuated and characterized, represent only the tip of the iceberg. In the following sections, a few representative classes of these molecular species will be described with the exclusive underlying intention to give some flavor of their chemistry. The material is organized so to distinguish between clusters and polynuclear compounds, according to the extended definition given at the beginning of the introduction.

2. Clusters of the p-block Elements

2.1. Clusters of p-block Elements in a Ligand Shell: Boron Hydrides

Boron hydrides display a very rich chemistry which has been extensively studied since the pioneering Stock's work in 1912. The importance of boranes stems from three factors: 1) the completely unsuspected structural principles involved; 2) the growing need to extend covalent MO bond theory considerably to cope with the unusual stoichiometries; 3) the emergence of a versatile and extremely extensive reaction chemistry which parallels but is quite distinct from that of organic and organometallic chemistry. As a direct consequence of the central role of boranes in the development of chemistry, the 1976 Nobel Prize has been awarded to W. N. Lipscomb "for his studies of boranes which have illuminated problems of chemical bonding". Since then, the chemistry of boron hydrides has known an increasing interest for both theoretical and practical reasons.

As a starting point, we can consider the fact that boron is a non-metal (*i.e.* an element which tends to form covalent bonds) but it is electronically poor. Thus, the most simple boron-hydrogen compound, *i.e.* BH_3, is electronically unsaturated and exists only as a dimer, B_2H_6 (diborane). This molecule (Figure 1) contains classical 2-centre 2-electron (2c-2e) B-H bonds, and delocalized 3-centre 2-electron (3c-2e) B-H-B bridges.

Diborane can be obtained in a laboratory scale from the reaction of $NaBH_4$ with oxidants or acids:

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

$$2NaBH_4 + 2H_3PO_4 \rightarrow B_2H_6 + 2NaH_2PO_4 + 2H_2$$

On an industrial scale, it can be obtained from the direct reduction of gaseous BF_3 with NaH at 180 °C:

$$2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$$

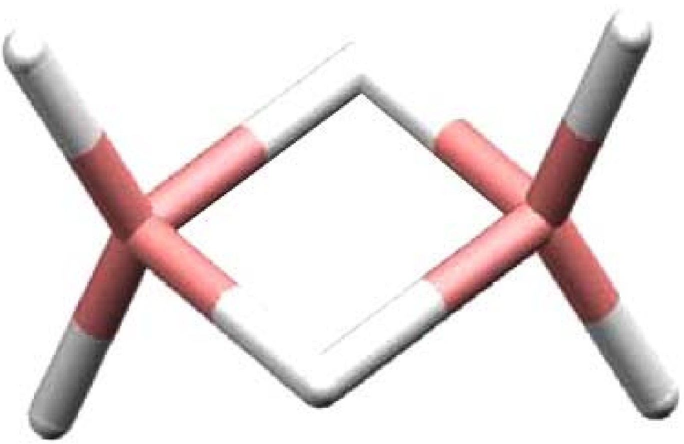

Figure 1: The structure of B_2H_6

B_2H_6 is the usual starting material for the preparation of other higher nuclearity boranes. A convenient route is represented by the controlled pyrolysis of diborane to give B_4H_{10}, B_5H_{11}, B_5H_9, B_6H_{10}, B_6H_{12} and higher boranes, culminating in $B_{10}H_{14}$ as the most stable end product, together with polymeric materials BH_x and a trace of icosaborane $B_{20}H_{26}$. Careful control of temperature, pressure, and reaction time enables the yield of the various intermediate boranes to be optimized.

$$2B_2H_6 \rightarrow B_4H_{10} + H_2 \text{ (at 25 °C for 10 days)}$$

$$2B_4H_{10} + B_2H_6 \rightleftarrows 2B_5H_{11} + 2H_2$$

Alternatively, boranes can be obtained by oxidation of $NaBH_4$ by carefully controlling the stoiciometric ratio of the reagents ("the anionic route"):

$$9NaBH_4 + 4I_2 \rightarrow NaB_9H_{14} + H_2 + 8NaI$$

$$11NaBH_4 + 5I_2 \rightarrow NaB_{11}H_{14} + 15H_2 + 10NaI$$

Finally, boron hydrides can be used as starting materials for the preparation of new boranes. For instance, the deprotonation of a polyborane B_nH_{n+m} $(m = 4, 6)$ results in the formation of the anions $[B_nH_{n+m-1}]^-$ or $[B_nH_{n+m-2}]^{2-}$ by removal of one or two protons from a BHB 3c-2e bridge with formation of a B-B single bond. Cluster expansion with a BH_3 unit, usually offered as diborane in diethyl ether or tetrahydrofurane, produces borane anions $[B_{n+1}H_{n+m+2}]^-$ or $[B_{n+1}H_{n+m+1}]^{2-}$, and, after protonation, the neutral polyboranes $B_{n+1}H_{n+m+3}$. The latter, only rarely are stable, but more often loses H_2 to give $B_{n+1}H_{n+m+1}$, and the overall reaction can be considered the addition of a BH fragment to the starting B_nH_{n+m} borane.

Boron hydrides can be classified into 5 series, even though examples of neutral or unsubstituted boranes themselves are not known for all 5 classes.

- Closo-boranes: $B_nH_n^{2-}$ $(n = 6\text{-}12)$. The neutral B_nH_{n+2} are not known.
- Nido-boranes: B_nH_{n+4}, $[B_nH_{n+3}]^-$, $[B_nH_{n+2}]^{2-}$.
- Arachno-boranes: B_nH_{n+6}, $[B_nH_{n+5}]^-$, $[B_nH_{n+4}]^{2-}$.
- Hypho-boranes: B_nH_{n+8}. No neutral boranes has yet been definitely established in this series, but several adducts are known to have hypho-structures.
- Conjuncto-boranes: B_nH_m. They result from the interconnection of boranes, *via* the sharing of a single B atom (*e.g.* $B_{15}H_{23}$), the formation of a direct 2c-2e B-B bond (*e.g.* B_8H_{18}, $B_{10}H_{16}$, $B_{20}H_{26}$, $[B_{20}H_{18}]^{4-}$), fusion of two clusters via 2B atoms at a common edge (*e.g.* $B_{13}H_{19}$, $B_{14}H_{18}$, $B_{18}H_{22}$), fusion of two clusters via 3B atoms at a common face (*e.g.* $(MeCN)_2B_{20}H_{16}$), or more extensive fusion involving 4B atoms in various configurations (*e.g.* $B_{20}H_{16}$, $[B_{20}H_{18}]^{2-}$).

From a structural point of view, closo-boranes contain only terminal 2c-2e exo B-H bonds (which point outside the boron framework) and they have complete closed polyhedral clusters of *n* boron atoms. The boron skeleton of closo-boranes is actually based on deltahedra, which are polyhedra with all faces that are equilateral triangles. The deltahedra from *n* = 4 to *n* = 12 are tetrahedron (4), trigonal bipyramid (5), octahedron (6), pentagonal bipyramid (7), bis-disphenoid (dodecahedron) (8), tricapped trigonal prism (9), bicapped square antiprism (10), octadecahedron (11) and icosahedron (12). The dodecahydro-closo-dodecaborate $[B_{12}H_{12}]^{2-}$ can be obtained from the reaction of $NaBH_4$ with diborane:

$$2BH_4^- + 5B_2H_6 \rightarrow [B_{12}H_{12}]^{2-} + 13H_2$$

The $[B_{12}H_{12}]^{2-}$ ion is a regular icosahedron of atoms, each of the twenty faces being an equilateral triangle. All of the hydrogen atoms are external to the boron icosahedron and are attached by terminal B-H bonds. The icosahedron itself involves a resonance hybrid of several canonical forms, and both 2c-2e B-B and 3c-3e B-B-B bonding are involved. An icosahedral framework of boron atoms is of considerable importance in boron chemistry; three forms of elemental boron as well as several nonmetal borides contain discrete B_{12} icosahedra.

Similar structures are displayed by the other closo-boranes, once the appropriate deltahedron is considered. Conversely, the structure of a n vertices nido-borane can be obtained from the n+1 closo-borane by removing a B atom, leaving in this way a cup-like or nest-like structure (nido). Nido-boranes contain extra hydrogen atoms in bridging positions (3c-2e B-H-B) in order to "sew up" the loose valences around the opening. Similarly, a n vertices arachno-borane can be formally obtained by removing two B atoms from a n+2 closo-borane and adding extra hydrogen atoms. These are of three types: 1) terminal exo B-H 2c-2e; 2) bridging B-H-B 3c-2e; 3) terminal endo B-H 2c-2e (lying close to the framework). Thus, starting from the closo-$[B_{12}H_{12}]^{2-}$ removal of one boron results in the nido-$[B_{11}H_{13}]^{2-}$ cluster and removing a further B atom the arachno-$[B_{10}H_{14}]^{2-}$ is formed. The complete relationships among the closo, nido and arachno species are shown in Figure 2.

The bonding in all the boron hydride clusters can be described considering four different constituting units: 1) terminal 2c-2e B-H bonds; 2) bridging 3c-2e B-H-B bonds; 3) direct 2c-2e B-B bonds; 4) delocalized 3c-2e B-B-B bonds. Full molecular orbital calculations demonstrate that in a regular deltahedron having n vertices, there are n+1 bonding molecular orbitals. Thus, we can expect that a closo-borane possesses 2n + 1 bonding molecular orbitals, n + 1 coming the boron deltahedron and n for the n B-H bonds (Wade's rules). Let consider the closo-$[B_{12}H_{12}]^{2-}$ anion. This possesses 12 × 3 + 12 × 1 + 2 = 50 valence electrons (3 for each boron atoms, one for each hydrogen atom and the two negative charges); these can fill 25 MO, in keeping with the $2n + 1 = 2 \times 12 + 1 = 25$ rule. If there are two more electrons, one bonding MO and one vertex must be used for these extra electrons rather than for a framework atom, and a nido structure with a missing vertex results. Thus, for such a cluster we expect to have $2n + 2$ bonding MO.

	nido-B_2H_6	nido-$[B_9H_{12}]^-$	nido-$[B_{11}H_{13}]^{2-}$
Valence electrons			
Boron	2 × 3	9 × 3	11 × 3
Hydrogen	6 × 1	12 × 1	13 × 1
Negative charges		1	2
Total	12	40	48
Bonding orbital $2n + 3$	6	20	24

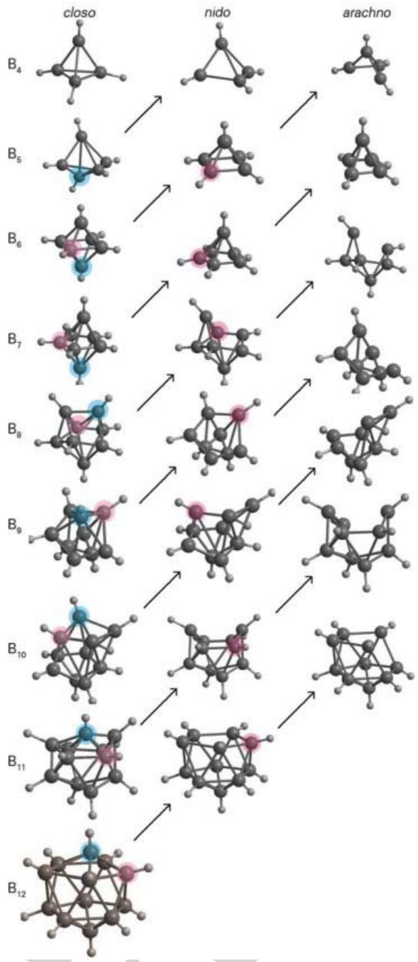

Figure 2: The structural relationships between closo, nido and arachno boranes (elimination from closo boranes of the BH moieties shadowed in light-blue and pink generates in sequence the corresponding nido and arachno borane)

Based on similar considerations, in an arachno-borane we have 2n + 3 bonding MO.

	arachno- B_4H_{10}	arachno-$[B_9H_{14}]^-$	arachno-$[[B_{10}H_{14}]^{2-}$
Valence electrons			
Boron	4 × 3	9 × 3	10 × 3
Hydrogen	10 × 1	14 × 1	14 × 1
Negative charges		1	2
Total	22	42	46
Bonding orbital 2n + 2	11	21	23

Neutral boranes are colorless, diamagnetic, molecular compounds of moderate to low thermal stability. The lower members are gases at room temperature but with increasing molecular weight they become volatile liquids or solids. The thermodynamic instability of boranes results from the exceptionally strong bonds in both elemental boron and H_2, rather than the inherent weakness of the B-H bond. In fact, it has been estimated that typical bond energies in boranes are B-H 380, B-H-B 440, B-B 330 and B-B-B 380 kJ mol^{-1}, compared with a bond energy of 436 kJ mol^{-1} in H_2 and a heat of atomization of crystalline boron of 555 kJ mol^{-1}.

Boranes are extremely reactive and several are spontaneously flammable in air. Arachno-boranes tend to be more reactive (and less stable to thermal decomposition) than nido-boranes and reactivity also diminishes with increasing molecular weight. Closo-borane anions are exceptionally stable, and their general chemical behavior has suggested the term “three-dimensional aromaticity”.

Boron hydrides are extremely versatile chemical reagents but the very diversity of their reactions makes a general classification unduly cumbersome. For reasons of space, the reactivity of boron hydrides will not be discussed here, and the reader can refer to more detailed texts. Nearly all boranes are highly toxic when inhaled or absorbed through the skin though they can be safely and conveniently handled with relatively minor precautions.

The partial or complete replacement of hydrogen atoms in boranes results in the formation of new ligand supported boron clusters, which are structurally and electronically related to boron hydrides.

$$\text{nido-}B_5H_9 + Cl_2 \rightarrow \text{nido-}ClB_5H_8 + HCl$$

$$\text{nido-}B_{10}H_{14} + 2MeCN \rightarrow \text{arachno-}B_{10}H_{12}(MeCN)_2 + H_2$$

$$\text{closo-}[B_{12}H_{12}]^{2-} + 12Cl_2 \rightarrow \text{closo-}[B_{12}Cl_{12}]^{2-} + 12HCl$$

$$\text{closo-}[B_{12}H_{12}]^{2-} + 12H_2O_2 \rightarrow \text{closo-}[B_{12}(OH)_{12}]^{2-} + 12H_2O$$

$$\text{closo-}[B_{12}H_{12}]^{2-} \xrightarrow{+\text{ Mel}} [B_{12}Me_{11}I]^{2-} \xrightarrow{+\text{ AlMe}_3} \text{closo-}[B_{12}Me_{12}]^{2-}$$

Moreover, other substituted neutral polyboranes of the type B_yX_y (X = Cl, Br, I, NR_2, alkyl) are known. All of them have closed deltahedral structures in spite of the fact that the numbers of bonding electrons pairs is only n (2n considering also the ligands). For this reason these homonuclear cluster compounds of boron are called hypercloso boranes.

Three classes of compounds closely related to boron hydrides are the carboranes, the metallacarboranes and the heteroboranes. Carboranes are formally the result of the substitution of one or more B atoms with C atoms in the polyhedron of boranes. Since carbon has one more electron than boron, the C-H moiety is isoelectronic with the $B\text{-}H^-$ or BH_2 moieties, and the replacement of B with C requires the increase of one positive charge in order to maintain constant the number of electrons. The best-studied system,

$C_2B_{10}H_{12}$, is isoelectronic with $[B_{12}H_{12}]^{2-}$ and can be obtained from decaborane and alkynes:

$$B_{10}H_{14} + 2Et_2S \rightarrow B_{10}H_{12}(Et_2S)_2 + H_2$$

$$B_{10}H_{12}(Et_2S)_2 + RC \equiv CR \rightarrow R_2C_2B_{10}H_{10} + 2Et_2S + H_2$$

Three different isomers of $C_2B_{10}H_{12}$ are known, which differ from the relative positions of the two carbon atoms. Several other carboranes are known, all of which conform to the electronic rules given above for boranes and can be classified as closo (*e.g.* $C_2B_3H_5$, $C_2B_5H_7$), nido (*e.g.* CB_5H_9, $C_2B_4H_8$, $C_4B_2H_6$), and arachno (*e.g.* $C_2B_7H_{12}$-, $C_2B_7H_{13}$). (Figure 3)

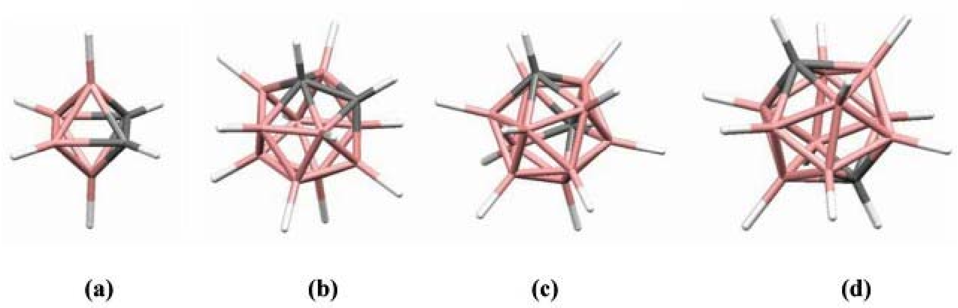
(a) (b) (c) (d)

Figure 3: Some examples of carboranes:
$B_4C_2H_6$ (a), 1,2-$B_{10}C_2H_{12}$ (b), 1,7-$B_{10}C_2H_{12}$ (c) and 1,12-$B_{10}C_2H_{12}$ (d).

The coordination (or, better, inclusion) of metal fragments into carboranes results in the formation of metallacarboranes. A few examples are the following: $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$, $[Mo(CO)_3(\eta^5\text{-}C_2B_9H_{11})]^{2-}$, $[\{Co(C_5H_5)\}_2(C_2B_6H_8)]$, $[\{Co(C_5H_5)\}_2(C_2B_9H_{11})]$. Carboranes and metallacarboranes occupy a strategic position in the chemistry of the elements since they overlap and give coherence to several other large areas including the chemistry of polyhedral boranes, transition-metal complexes, metal-cluster compounds and organometallic chemistry. The field is very vast and nowadays many thousands of compounds are known; therefore, for reason of space these topic can not be adequately covered in this chapter, and we recommend the reader to refer to more dedicated textbooks.

Finally, replacement of B atoms in borane clusters with other group 14, 15 and 16 elements results in the formation of a wide class of compounds known as heteropolyboranes, of which carboranes can be considered a special case.

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Biographical Sketches

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Stefano Zacchini. Born in 1972, he received the Degree in Industrial Chemistry from the University of Bologna in 1996, discussing a Thesis on "New Bimetallic Au-Fe Clusters Stabilised by Phosphines" under the supervision of Prof G. Longoni. In 2001 he received the Ph.D. in Chemistry from the University of Liverpool with a Thesis on "Spectroscopic Studies of Palladium Catalysed Reactions between Carbon Monoxide and Ethene" under the supervision of Prof B. T. Heaton. After a post-doctoral fellowship in Liverpool with Dr A. Steiner (2001-2002), he became research associate at the Dipartminento di Chimica Fisica ed Inorganica of the University of Bologna. His main interests concern the synthesis and characterization of metal carbonyl clusters and their application in nanochemistry.