



New molecular architectures built from metallic nanoclusters

Foreword

The first evidence for the formation of the now so-called a ‘cluster’ was given by Brosset [1] in 1945, during the study of the properties of a saturated solution of molybdenum dichloride. It was proven that the actual species present in solution was a large molecule containing six molybdenum atoms arranged in an octahedron, and linked together by metal–metal bonds as short as about 2.7 Å.

Sixty years after this fundamental discovery, the aim of this special issue is to draw attention to some current trends in this particular aspect of chemistry.

The word ‘cluster’ was first proposed by Cotton [2] in 1964. In his mind, and in the general acceptance of most researchers working in this domain, this word refers to a polynuclear group of metal atoms strongly linked together by metal–metal bonds: this excludes polymeric species based on the arrangement of metal–ligand polyhedra like, for instance, Keggin salts or inorganic polymeric groups. A second criterion is that the cluster has a precise number of metallic nuclei, implying a well-defined point-group symmetry: this excludes the interesting chemistry of metal colloids, even if the boundary is sometimes not very sharp; examples are given by the giant Au and Pd clusters obtained by Schmid [3], which reach the size of gold colloids, but exhibit a precise and predictable number of atoms.

The best documented examples of cluster metallic cores include metal–metal pairs, triangles, tetrahedra and octahedra. More complex architectures can often be described from the condensation of these basic polyhedra.

During the past 30 years the chemistry of clusters extended very quickly in the field of both inorganic and organometallic disciplines and is now at the heart of the extensively developing field of ‘nano-sciences’. Various aspects are covered in the series of books

recently edited by Braunstein et al. [4]; a recent and exhaustive review of rhenium octahedral clusters chemistry by Gabriel et al. [5] completes and updates an earlier work of Perrin and Sergent [6]. In addition, the recent review by Walton [7], focusing on trinuclear rhenium clusters, updates the book of Cotton and Walton [8]. Finally, a short account on $[M_6L_{14}]$ ($M = Mo, W$) and $[M_6L_{18}]$ ($M = Nb, Ta$) cluster-units can be found in [9].

Cluster compounds appear in pure solid-state chemistry mostly for early transition metals, with halogens and chalcogens as typical ligands, while they are encountered in coordination chemistry for heavier transition elements, with ligands such as carbonyls or phosphines, as classical examples. On the other hand, clearly there is a new developing trend towards the synthesis of hybrid inorganic–organic materials. We have chosen to organize this special issue by starting from typical solid-state compounds and going toward coordination ones.

Recent advances in the pure solid-state approach are illustrated by several examples, like the discovery of the first face-capping oxygen ligand in $[Mo_6L_{14}]$ ($L =$ ligand) units and evidence of a Mo_{13} cluster resulting formally from the condensation of three Mo_6 clusters, a compound for which theoretical calculations have been carried out to understand its electronic structure. Some recently obtained octahedral clusters of rhenium are reported, the solubility of which has been investigated. Indeed, as an alternative route, the ‘*chimie douce*’ approach can be applied, as illustrated by the insertion of mercury at quite low temperature into the metastable $[Mo_{15}X_{19}]$.

The molecular chemistry of such clusters, then considered as precursors of a solution chemistry approach, is now extensively developing and is illustrated by numerous and various examples. In the above mentioned account some general strategies are reported:

- exchange of the cationic partner by organic, solvated or complexed counterpart;
- exchange of the (halide) apical ligand;
- exchange of both cations and ligands, giving, for instance, access to a cluster assembling via multidirectional 3d-element complex bridges.

There are numerous other examples. For instance, ionic compounds built from $[\text{Mo}_6\text{Cl}_{12}]$ and guanidinium chloride retain the basic units of the two parent structures with, at least in one example, a stacking reminiscent of the perovskite type. By directly connecting large units, 2-D frameworks have been constructed by association of Mo_6 halide clusters and diruthenium paddlewheel complexes acting as counter cationic spacers; it should be noted that each layer is strongly reminiscent of the parent $\text{Mo}_6\text{Cl}_{12}$ structure, half of the cluster-units being replaced by a diruthenium complex of comparable size. Ta_6 clusters can be coordinated by *n*-BuCN on some apical positions and the resulting compound undergoes a partial oxidation, leading to the coexistence of $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ and $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ units. Replacement of halogens by cyano groups on apical positions is currently under intensive study, and a quantum chemical study highlights the different behaviors of Re_6 and Mo_6 metal cores. Considerably larger ligands can be grafted on the apical positions as illustrated by the synthesis of $[\text{W}_6\text{S}_8 \text{bis}(\text{diphenylphosphino})\text{ethane}]_6$ and $[\text{W}_6\text{S}_8(4,4'\text{-bipyridine})_6]$. A further step is the use of clusters as nuclei for dendrimers, as illustrated by the synthesis of the Mo_6 octadecylferrocenyl dendrimer, a compound able to recognize the $(\text{ATP})^{2-}$ dianion. Indeed, the latter property is related to application of cluster materials in life sciences, a field in strong emergence, illustrated here by both the synthesis and electrochemical studies of tetrameric arrays of Re_6 clusters supported by a porphyrin core, and the use of Ta_6 clusters as phasers in protein crystallography.

The chemistry of tetranuclear clusters is represented by the tetrahedral metal mixed core Mo_3Re , obtained from the triangular Mo_3 cluster. Organizing two triangular clusters affords the unusual prismatic $[\text{W}_6\text{Cl}_{18}]$ hosting a carbon atom inside; this cluster strongly differs from the Tc_6 ones [10] as the ‘pillars’ consist here in very weak W–W bonds bridged by Cl ligands, in contrast to the triple Tc–Tc bonds.

Several papers are related to late transition metal clusters that form classically with carbonyl ligands. Numerous combinations of lanthanides (Ln) with tran-

sition metal carbonyls of groups 7–9 lead to Ln–M direct bonds, ionic associations and carbonyl or cyanide linkages. The chalcogen-capped triiron clusters undergo cluster expansions and transformations, including tetrahedral and di-tetrahedral clusters. A new condensed, mixed cluster is reported, that can be described from the face-sharing condensation of three octahedra, leading to the ordered, multivalent $[\text{Fe}_6\text{Ni}_6\text{N}_2(\text{CO})_{24}]^{n-}$, which can be compared to the Mo_{12} clusters described in the solid-state chemistry of molybdenum chalcogenides. Another example of large clusters is the centered pentagonal prismatic $[\text{Co}_{11}\text{Te}_7(\text{CO})_{10}]$ neutral cluster unit that forms in the complex matrix $[\text{Cp}'_4\text{Nb}_2\text{Te}_2\text{CH}_3]\text{I}$.

Mixed transition metals/main group clusters are also reported. A skeletal isomerism is a priori expected for such cores, and DFT calculations have shown that the relative energies of the different skeletal isomers strongly depend on the nature of the main group element. This topic is also illustrated by new complexes like the trinuclear chain core $\text{Fe}_2\text{Si}_2\text{Sn}$ and the corner plate FeSn_2 characterized by Fe–Sn bonds (with Sn–Fe–Sn angle close to 90°), but no Sn–Sn binding.

Then the last step is pure main group clusters, often called ‘metalloid clusters’. An illustration is given by the synthesis of a chain of dihedral nine-atom germanium cluster, stabilized by alkaline cations sequestered by a cryptate agent that dimerizes during the synthesis. The electronic interactions in bridged bis(cluster) assemblies have been calculated in, for example, the carborane cluster *para*- $\text{CB}_{10}\text{H}_{10}\text{C}$ and compared with *para*- C_6H_4 and C_4 bridges.

On the other end of the periodic classification, alkaline-earth nitrides $(\text{AE})_2\text{N}$ can be viewed as a 2-D, infinite condensation of AE edge-sharing octahedral clusters, hosting the N^{3-} ion in their center. The layers of such so-called ‘void metals’ are separated by a layer of free electrons, leading to anisotropic compressibility and structural changes under pressure.

Finally, a few reports related to oxometallates have been included, although they are not actually clusters based on the restrictive definition given above. First examples are the heterobimetallic bismuth-transition metal coordination complexes, where Bi and the transition metal ion are linked by oxygen bridges without metal–metal bonds; such compounds are interesting as they may act as single-source precursors for the preparation of advanced oxide materials. The second set of

examples refers to polyoxomolybdates, which give complex architectures that could be considered as models of the type of organization that one can encounter when condensing clusters-units either by sharing outer ligands or by bridging them by multidentate spacers. A first illustration is the building of a 2-D framework composed of nanosized $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]$ anions cross-linked by $[\text{Gd}(\text{H}_2\text{O})_5]$ groups. A second illustration of this concept is the diversity of the ring and wheel-shaped discrete cyclic entities that are designed from the building block $[\text{Mo}_2\text{O}_2\text{X}_2]^{2+}$ (X = O, S).

In summary, this thematic issue of *Comptes Rendus Chimie*, launched at the suggestion of Dr P. Braunstein, Editor-in-Chief, and published under the auspices of the French Academy of Sciences, covers a very broad area of up-to-date cluster chemistry. More than 100 researchers, originating from 39 laboratories and institutions that cover 14 countries, have contributed to this work. We wish to express our thanks and gratitude to all these authors who have enthusiastically contributed to this thematic issue. This challenge would not have been successful without the valuable help of many referees; special thanks are addressed to Mrs Marie-Christine Brissot and Fatima Messadi, who have efficiently coordinated the handling of the manuscripts.

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