Coordination Clusters

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INTRODUCTION

Coordination chemistry has come far since Alfred Werner proposed the octahedral configuration for a transition metal complex in 1893 and laid the foundations describing the idea of a ligand and coordination to a metal ion. Perhaps one of the most complex and interesting classes of coordination compounds are polynuclear coordination clusters. These incorporate multiple metal ions into a single molecular entity and are linked by bridging ligands. During the last 20 years, the discovery of coordination cluster compounds has increased exponentially thanks to advances in single crystal X-ray crystallography, which has allowed the unambiguous structural elucidation of molecules with seemingly ever increasing size and complexity. Much of the interest and fascination with coordination clusters lies with the properties of such clusters and possible technological applications arising from their size and molecular characteristics. Some of the most interesting aspects include the discovery of clusters with high-spin ground states, which can afford single-domain magnets and may have applications in storage devices, and the formation of high symmetry and protein-sized clusters built from many hundreds of subunits in a single molecule. Coordination clusters are also essential components of many enzymes and as such are vital for life, for instance playing electron storage and catalytic roles in cofactors employed by nature to activate nitrogen. In this entry, we describe the types of ligands that may define the structure of a given cluster, and we then examine ligand-directed assembly and self-assembly of cluster architectures. We examine polynuclear and polyoxometalate (POM) clusters and outline some of their interesting physical properties. Finally, we discuss nitrogenase as a fundamental example of a co-ordination cluster with an essential biological role.

STRUCTURE OF COORDINATION CLUSTERS

One of the most interesting and exciting aspects of coordination clusters is their extremely variable size, geometry, and nuclearity. However, this also means that one can be faced with a bewildering number of structural types.[1]

The structure of coordination clusters is determined both by the geometrical preferences of the metal ions and the type of bridging and terminal ligands that combine to form the aggregate. In this way, the metal ions and ligands can be seen as ‘‘building blocks,’’ generating an overall structure whose topology is a consequence of the symmetries and connectivities of the constituent parts, rather in the same way that a child might need different Lego® bricks or Meccano® joints to build different models. However, the design of co-ordination clusters is much more complicated since many transition metal ions (e.g., copper II) have a large number of possible coordination geometries. In addition, even the simple bridging ligands such as O^{2-}, OH^{-}, and OAc^{-} can adopt a wide variety of coordination modes. These range from terminal to μ_2, μ_3, and μ_4 bridging modes; even μ_6 has been observed for O^{2-}. It cannot be understated how important the ligand–metal combination is on the overall architecture of the cluster formed; indeed the three contrasting examples shown in Fig. 1 only touch the tip of the iceberg regarding the number of structural types.[1–3]

However, the structure of the cluster does not only depend upon the metal ions (and oxidation states) present and the number of possible binding modes for the ligands. The steric properties of the ligands; presence of templating units and coordinating solvent; factors such as pH, the concentrations and redox potentials of the species present; and the type of counterions can all play decisive and sometimes dramatic roles. Consequently, a particular combination of ligand(s) and metal(s) is often capable of generating a wide range of structures—the favored structure being the result of a subtle balance of many competing factors.

CONSTRUCTION OF COORDINATION CLUSTERS

Ligand Directed

An attractive approach to the synthesis of coordination clusters is ligand-directed rational design, most particularly the ‘‘molecular library’’ approach used by Fujita et al.[4] and Seidel and Stang.[5] Rigid, multibranched

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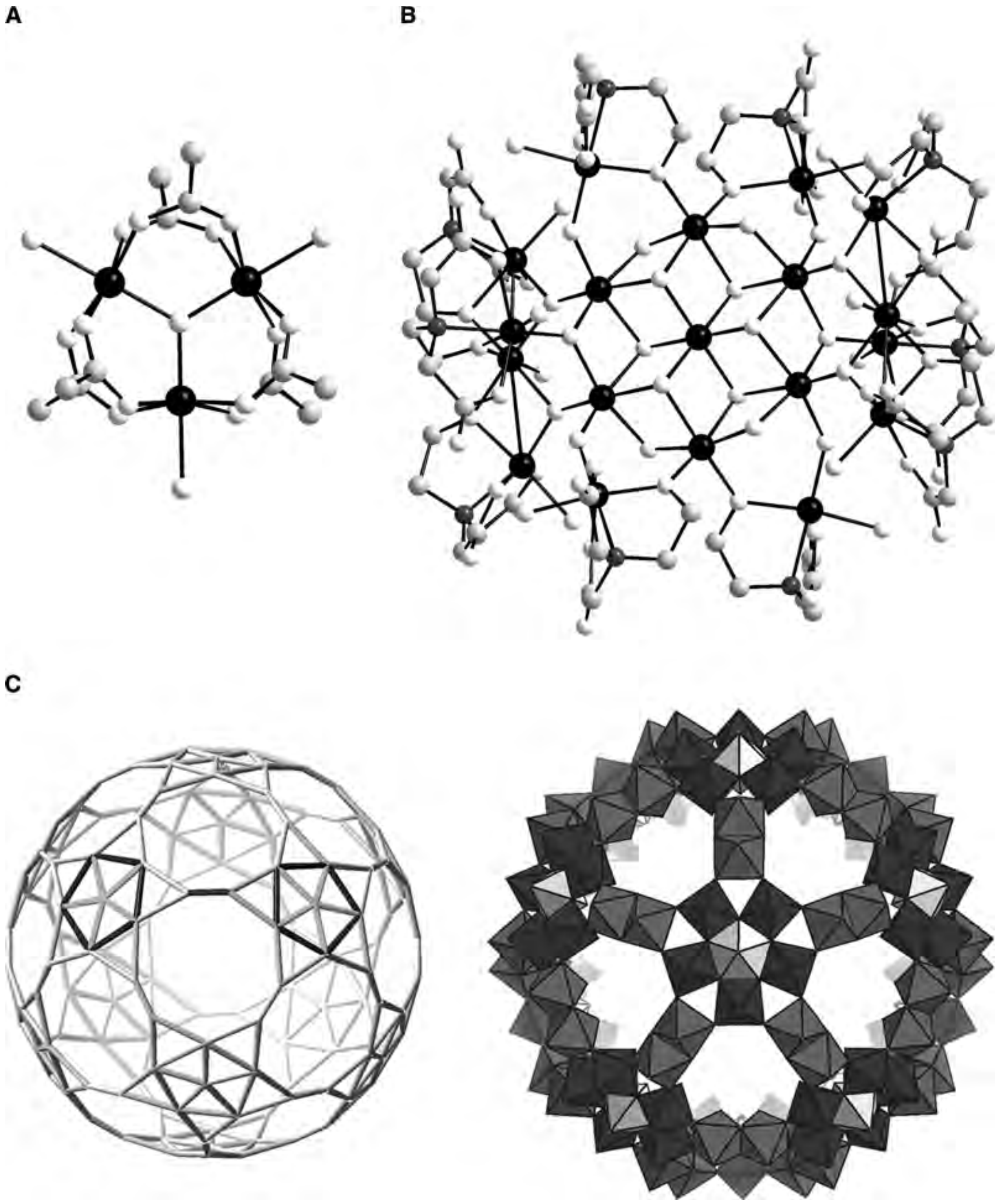

Fig. 1 Representation of the structures of some coordination clusters: (A) A simple oxo-centered iron trimer,[2] $Fe[Fe_3(CH_3COO)_6(O)(H_2O)_3]$. (B) A much more complex $\{Fe_{19}\}$ cluster,[3] $[Fe_{19}(C_6H_8O_5)_{10}(O)_6(OH)_{14}(H_2O)_{12}]^{2+}$ (both clusters are shown in ball and stick with Fe in black, O in white, C in light gray, N in dark gray). (C) The spherical polyoxometalate-based $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ cluster;[1] a stick representation just showing the connected metal framework is given on the left whereas a polyhedral representation is given on the right.

monodentate ligands and partially co-ordinatively saturated, labile metal centers with well-defined coordination preferences are combined in a way that greatly reduces the complexity of the system. By avoiding ligands with multiple binding modes and metals with multiple coordination geometries, it becomes much more practical to view a self-assembling system as ‘‘molecular Meccano’’ (Fig. 2).

The ligand-directed approach frequently employs aromatic amines as ligands, and palladium or platinum(II) ethylenediamine complexes as metal centers. Aromatic amines are rigid, and their bonds to Pd and Pt are labile, allowing correction of defects. Importantly, though, they will not displace the pre-existing ethylenediamine chelators, which occupy two coordination sites and prevent the formation of polymeric products. For instance, a complex three dimensional example is provided by the truncated tetrahedron synthesized by Seidel and Stang.[5] The truncated tetrahedron is the smallest of the 13

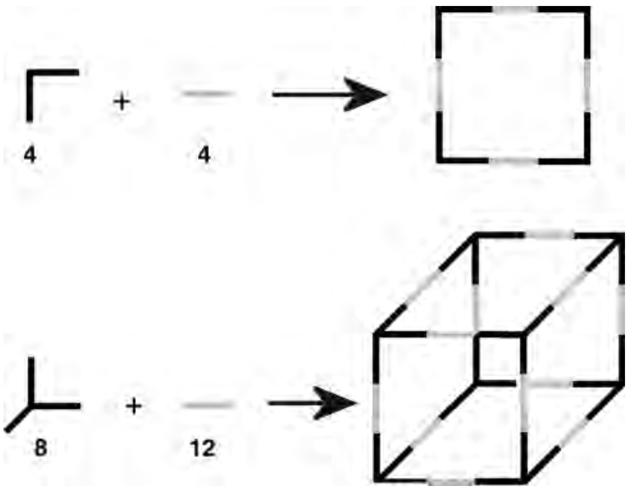

Fig. 2 A schematic showing the assembly of a square and a cube, which require 2D and 3D 90° corner units, respectively, linked by linear spacers.

Archimedean solids, and is created by cutting off the corners of a Platonic tetrahedron to leave a body consisting of four hexagons and four equilateral triangles. Chemically, this was achieved through the use of four tritopic ~120° linkers clipped together by six ditopic ~90° subunits in a number of successful combinations, and this example forms in a yield of 87% (Fig. 3).

A potential application of this approach may develop through the synthesis of supramolecular coordination clusters that can both encapsulate and catalyze the transformation of small molecules. Encapsulation of a chemical reaction in a molecular cage can result in a remarkable acceleration due to the increased concentration and strictly regulated orientation of the substrates in the cavity. One such example is $[Pd_6(L)_4]^{12+}$-based cages [where L is 2,4,6-tri(4-pyridyl)-1,3,5-triazine], which have been shown to facilitate the stereoselective [2 + 2] photodimerization of acenaphthylenes and naphthoquinones (Fig. 4).[6] Working in aqueous media, the bowl shaped coordination cage was able to catalyze the dimerization of naphthoquinone to form the *syn* dimer in >98% yield. By contrast, the same reaction carried out in benzene without the presence of the coordination bowl gave a 21% yield of the *anti* dimer and 2% of the *syn* product, showing that the bowl has a dramatic effect on both the selectivity and yield of the reaction. Fig. 4, in fact, shows the crystal structure of the product trapped in the bowl, which has adopted a box conformation to accommodate the product efficiently.

Self-Assembly of Polynuclear Clusters

The rationally designed clusters shown above offer an enticing suggestion of what future chemists might achieve through design. At present, however, the vast majority of polymetallic complexes with interesting physical properties have been created using ‘‘serendipitous’’ approaches.[1] This is due to the extreme difficulty of accurately predicting the physical properties of a given structure, and the fact that even predicting structures is only possible when working with particularly predictable metal–ligand combinations. Therefore, self-assembly of polynuclear cages is often achieved using a semiempirical approach. Typically, a mismatch is engineered between the number or type

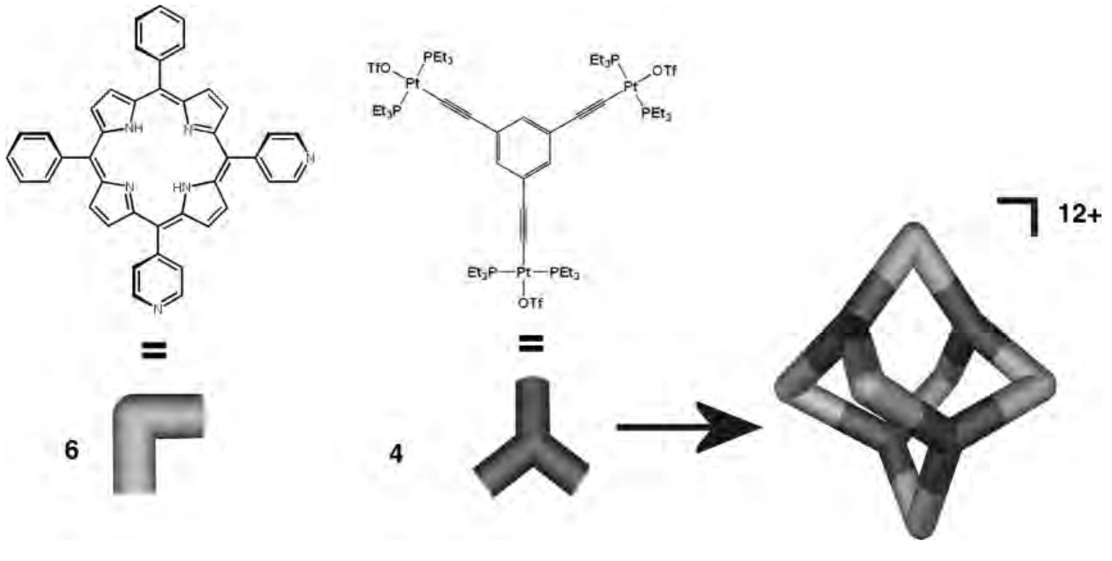

Fig. 3 Self-assembly of a truncated tetrahedron, a $\{Pt_{12}\}$ cluster, constructed using four trigonal planar units (shown in dark gray) along with six 90° units.

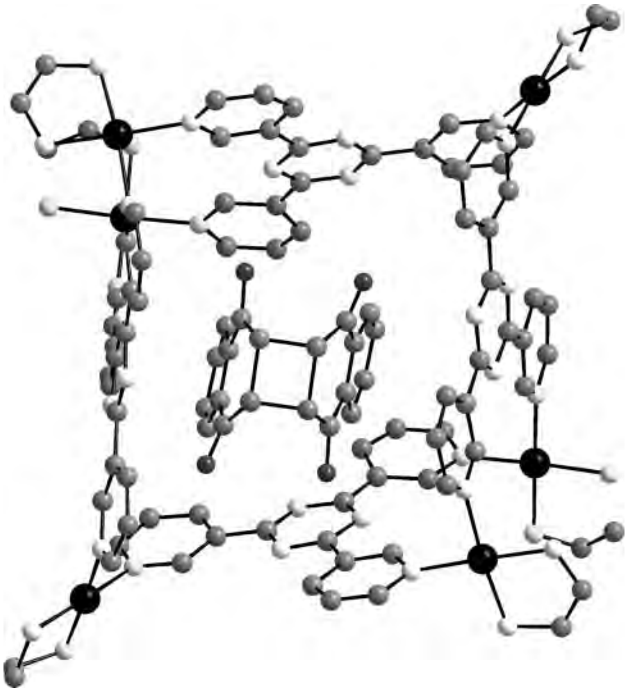

Fig. 4 Structure of the $[Pd_6L_4]^{12+}$ along with the [2 + 2] photodimerized guest is shown. L = 2,4,6-Tri-pyridin-4-yl-[1,3,5]triazine, C = gray, N = white, Pd = large black spheres, O = small black spheres.

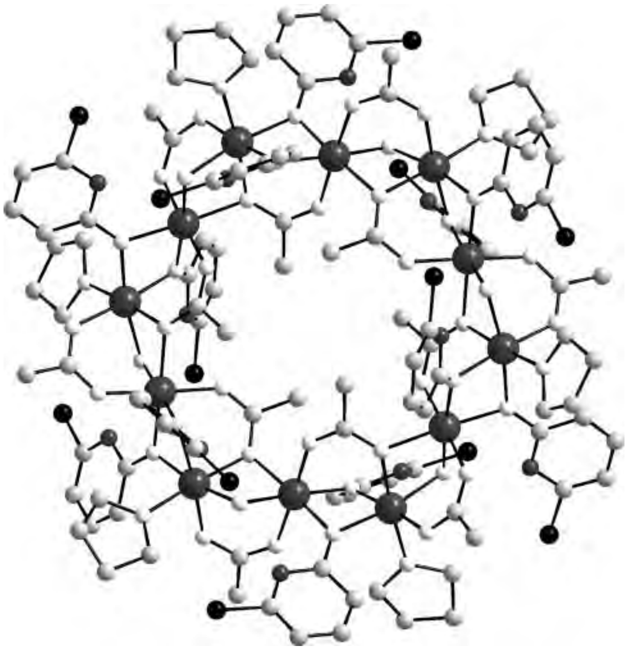

Fig. 5 The structure of the $\{Ni_{12}\}$ wheel complex, $[Ni_{12}(chp)_{12}(OAc)_{12}(H_2O)_6(THF)_6]$. C = light gray, O = white, Ni = black.

of coordination sites available on a single metal site and the donor set provided by the ligand, which forces bridging between metal centers. This may be achieved by choosing a ligand where the positioning of the donor atoms prevents the ligand from binding to a single metal center, or by removing ligands from an existing cluster to generate co-ordinative unsaturation and provoke a rearrangement that links the metal centers.[1]

A sizeable family of wheel complexes has been synthesized following both of these approaches. These are formed from first row transition metals (typically iron, cobalt, or nickel) with carboxylate and oxo bridging ligands, and in some cases other coligands. A good example of the first approach, starting from simple metal salts, is provided by Winpenny and coworkers[1,7] who synthesized isostructural dodecanuclear nickel and cobalt(II) wheels with interesting magnetic properties. This was achieved by heating the metal acetate and 6-chloro-2-hydroxypyridine under reduced pressure, extracting the resulting paste with tetrahydrofuran (THF) and crystallizing the wheel from the THF solution. In each case, the metal centers are linked by a mixture of bridging acetate, 6-chloro-2-pyridonate (chp) and water ligands, with terminal THF ligands also present (Fig. 5). The authors state that discovery of these structures owes a great deal to serendipity. For one thing, only THF will support their formation. Furthermore, acetate is the only carboxylate that fits the central cavity to template the wheel and the bonding mode adopted by the pyridonate is only found for chp.

The second approach, reacting pre-existing clusters to generate new, larger structures, has been used in the synthesis of both iron[8] and chromium[9] wheel complexes. An interesting example with chromium is provided by Sessoli and coworkers[9] who employed a solvothermal technique permitting the use of extremely high temperatures (200°C) with low boiling solvents (MeOH or EtOH). In this way, the trinuclear starting cluster basic chromium acetate, $[Cr_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]Cl \cdot 6H_2O$, was rearranged to form the decanuclear wheels $[Cr_{10}(\mu\text{-}OAc)_{10}(\mu\text{-}OR)_{20}]$, where R = Me or Et depending on the solvent used. In the structure (Fig. 6), it can be seen once again that acetate ligands bridge the metal centers, this time assisted by alkoxides providing an oxo bridge. Notably, while the ethoxide bridges resulted in antiferromagnetic interactions between Cr(III) centers, ferromagnetic coupling was seen when methoxide was present. This is precisely the type of difference in physical properties that, at present, tends to be discovered rather than predicted or designed.

The interest in the magnetic properties of polynuclear coordination clusters stems from the discovery of the first single molecule magnets (SMMs) in 1993 in the form of an Mn_{12}-based cluster.[10] Single molecule magnets may eventually offer substantial

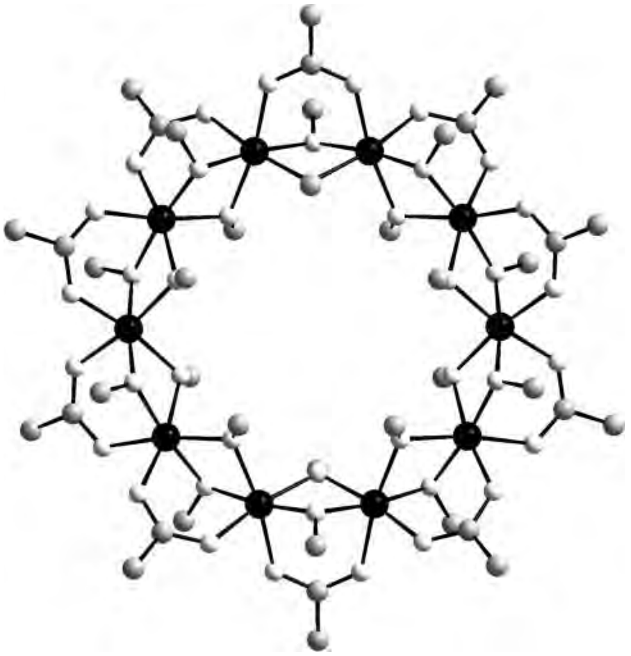

Fig. 6 Crystal structure of $[Cr_{10}(\mu\text{-}OAc)_{10}(\mu\text{-}OMe)_{20}]$. C = light gray, O = white, Ni = black.

advantages in the miniaturization of computer hard disk drives, although at present no such molecules have been discovered displaying the requisite properties close to room temperature. Recently, a new family of manganese clusters with the general formula $[Mn_{12}O_8X_4(O_2CPh)_8L_6]$ was synthesized by Christou and coworkers[11] by reacting the octanuclear manganese complex (NBu_4) $[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$ with the chelating ligands 2-(hydroxymethyl) pyridine (hmpH) and 2-(hydroxyethyl) pyridine (hepH). Single molecule magnet properties were displayed by a cluster with X = Cl and L = hmp. Furthermore, the largest ever SMM, an $\{Mn_{84}\}$ cluster wheel of composition $[Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6]$ has recently been discovered (Fig. 7).[12] This represents the largest ever wheel cluster comprising 1st row transition metal ions, with an inner diameter of 1.9 nm, an outer diameter of 4.2 nm, and a thickness of 1.2 nm. This was synthesized using $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ as a precursor. The wheels line up in the solid state to reveal a nanoporous supramolecular nanotube, and magnetic studies of this cluster reveal SMM-type behavior at 1.5 K.

Interesting magnetic properties are not limited to manganese complexes. The nickel and cobalt wheels discussed earlier[7] show that a change of high-spin ion can alter the magnetic properties of high-spin clusters. While both the nickel ($S = 12$) and cobalt ($S = 6$) clusters possess high spins and magnetic anisotropy, only the nickel version displays SMM properties below 0.4 K and, in fact, represented the first ever nickel-based SMM.

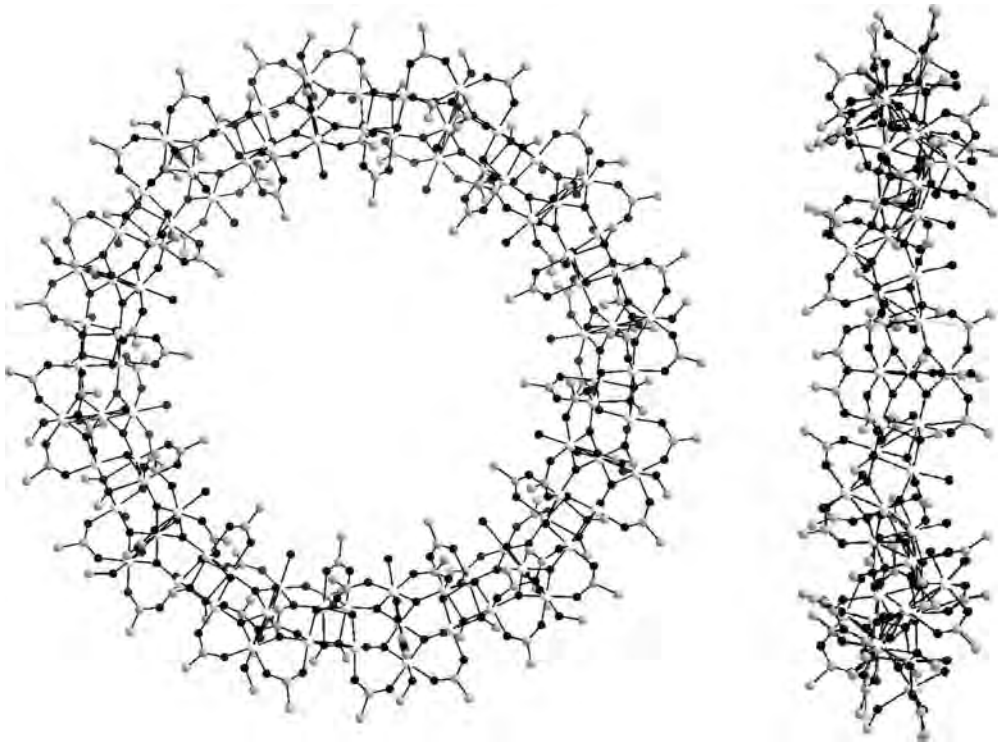

Fig. 7 A representation of the structure of $\{Mn_{84}\} = [Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6]$ wheel cluster (top view LHS, side view RHS). C = gray, Mn = large black spheres, O = small black spheres.

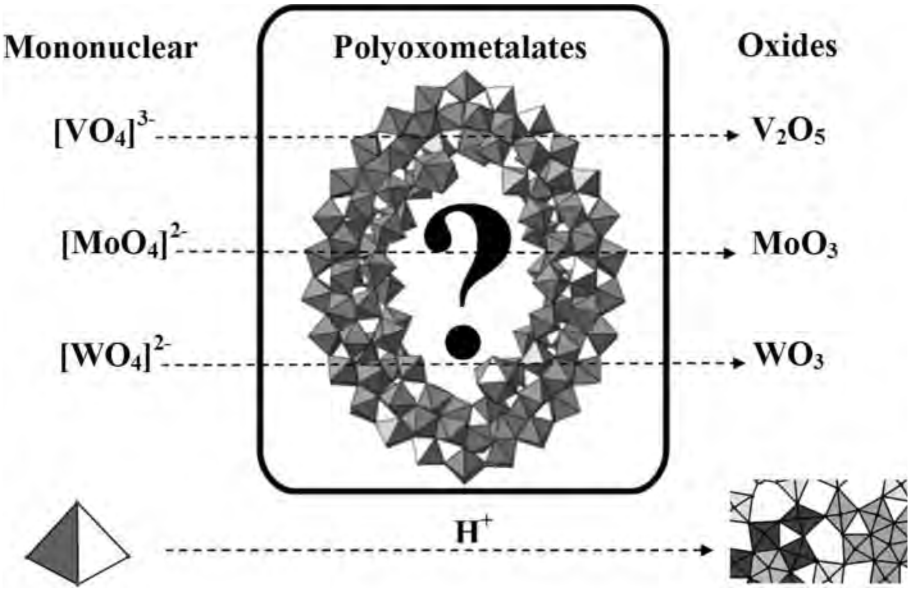

Fig. 8 Polyoxometalates are formed in experimental conditions that allow linking of polyhedra. Discrete structures are formed as long as the system is not driven all the way to the oxide. One such example, in this case a part of an $\{Mo_{256}Eu_8\}$ cluster unit, is depicted in the square.

Polyoxometalate Clusters

Polyoxometalates represent an extremely diverse range of clusters. Their potential for extremely high nuclearities allows them to stretch from the subnano to the nanoscale, and an interesting range of physical properties lead to applications in areas as diverse as catalysis, electronic materials, dyes, and even medicine as antiviral and antibacterial agents. In general, POMs can be synthesized *via* the acidification of aqueous alkaline solutions, which contain mononuclear oxoanions of the early transition metals (such as V, Mo, or W). This can be followed by addition of heteroanions (e.g., SO_4^{2-}), reducing agents, electrophiles, and other ligands leading to the isolation of a large range of POMs, often with complex structures formed through conservative self-organization processes (Fig. 8). However, it is extremely useful, at least conceptually, to regard these metal–oxo units as metal-centered polyhedra and their aggregates as structural building blocks that can be used to both help understand, and perhaps manipulate the synthesis of clusters. The structures can even be considered to form via a self-assembly process involving the linking or aggregation of these polyhedra.[1]

Even the simplest synthetic system, the acidification of an aqueous solution of molybdate under ambient conditions, has been shown to yield an $\{Mo_{36}\}$ cluster,[13] $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, with two $\{Mo_{17}\}$ groups linked by two MoO_2 units. The cluster crystallizes readily from the solution, in which it appears to be the dominant species (Fig. 9). The overall structure is best understood by realizing that the $\{Mo_{17}\}$ unit can be further divided into two $\{Mo_8\}$ units and one linking $\{Mo_1\}$ unit. If the synthesis is adapted slightly by the incorporation of heteroanions such as PO_4^{3-} or SO_4^{2-}, then it is possible to synthesize more compact anion templated clusters including those with the well-known Keggin structure,[14] e.g., $\{Mo_{12}(PO_4)O_{36}\}^{3-}$ and those with the Dawson structure,[15] e.g., $\{Mo_{18}(SO_4)_2O_{54}\}^{4-}$ (Fig. 10). Both cluster types can be constructed with Mo and W ions, and the Dawson Keggin in particular has a rich electrochemistry.

The synthesis of POM clusters (based on Mo) under reducing conditions is particularly important since this

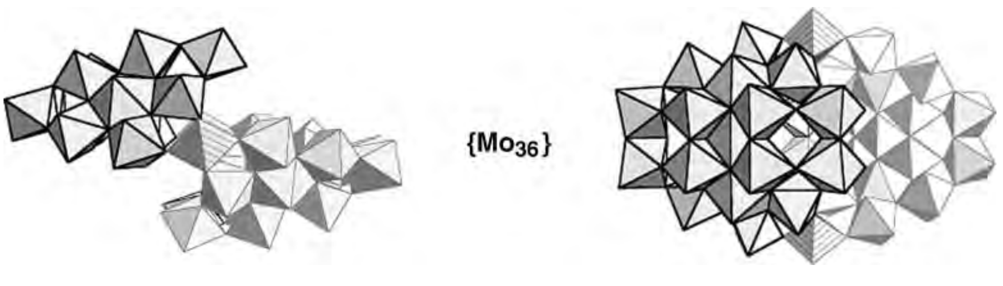

Fig. 9 Polyhedral representations of the structure of the $\{Mo_{36}\}$ cluster (top view shown on the left and side view shown on the right). The representations show two $\{Mo_{17}\}$ units (shown outlined and in light gray) connected via two $\{Mo_1\}$ groups shown as shaded polyhedra.

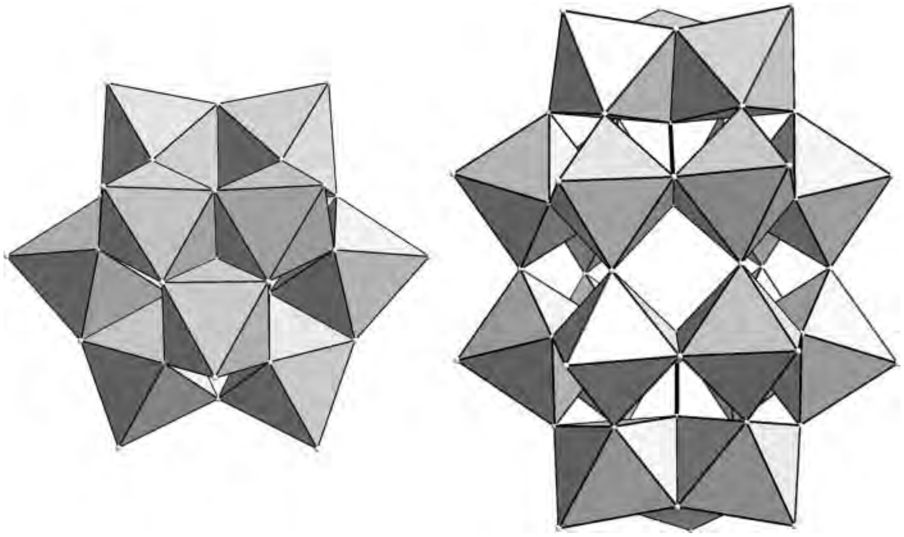

Fig. 10 Polyhedral representations of the structures of the tetrahedral Keggin ion $\{Mo_{12}(PO_4)O_{36}\}^{3-}$ and the D_{3h} Dawson cluster $\{Mo_{18}(SO_4)_2O_{54}\}^{4-}$ are shown on the left and right, respectively.

has produced some ultralarge clusters. For instance, reduction of ca. 20% of the molybdate to Mo(V) at pH 1–2 leads to a giant wheel shaped $\{Mo_{154}\}$ cluster,[16] $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$, ca. 3 nm in diameter with a 1.5 nm cavity. Furthermore, increasing the amount of reducing agent present [ca. 40% of the molybdate reduced to Mo(V)] and including ligands capable of bridging two adjacent Mo centers allows the formation of a giant spherical cluster,[1] $\{Mo_{132}\} = [Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, ca. 3 nm in diameter. Changing the ligand to sulfate and employing reducing conditions intermediate between the other examples [30% of molybdate reduced to Mo(V)] produces a massive $\{Mo_{368}\}$[17] "lemon" shaped cluster with the approximate formula $[H_{16}Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$. This cluster incorporates both positively and negatively curved surfaces, has a maximum diameter of ca. 5 nm and characteristics that resemble a hybrid between the wheel and sphere clusters; a comparison of these clusters is shown in Fig. 11.

BIOLOGICAL COORDINATION CLUSTERS

Co-ordination clusters are common in biology. Among the most frequently observed are iron–sulfur clusters, which are reasonably robust, cofactor-like species with functions that include electron transfer, catalysis, gene

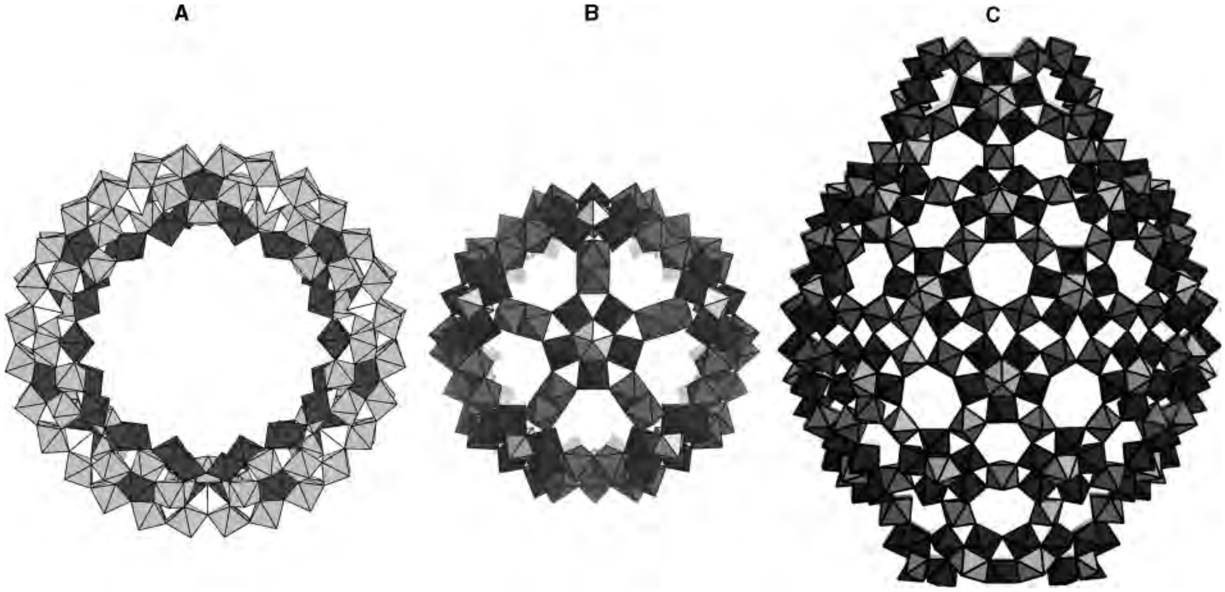

Fig. 11 Polyhedral representations of the structures of the $\{Mo_{154}\}$ (A), $\{Mo_{132}\}$ (B), and the $\{Mo_{368}\}$ clusters.

regulation, and the sensing of iron and oxygen.[18] They range in size from 1 to 8 iron atoms, the crystallographically demonstrated types being shown in Fig. 11. Interconversion of these different cluster types is remarkably facile both in free and protein bound conditions, and they also display significant redox chemistry—this versatility being vital to their wide range of functions. Synthetic analogs for nuclearities of up to four iron atoms have been created, showing that protein structure is not essential for their existence (Fig. 12).[18,19]

Nitrogenase

One of the most important roles of iron–sulfur clusters is in the nitrogenase enzymes of certain bacteria that "fix" atmospheric nitrogen as ammonia. Nitrogenase is a complex enzyme, consisting of an iron protein and an iron–molybdenum protein (known as the iron–molybdenum cofactor), which contains the actual catalytic site.[20,21] This combination allows dinitrogen to be converted to ammonia by the overall reaction:

$$\begin{aligned}&N_2 + 8H^+ + 16MgATP + 8e^-\\&\quad\rightarrow 2NH_3 + H_2 + 16MgADP\\&\qquad + 16P_i \text{ } (P_i \text{ is inorganic phosphate}).\end{aligned}$$

The purpose of the iron protein is to provide the iron–molybdenum cofactor with the electrons required for the reduction of N_2, and to this end it contains an $[Fe_4S_4(S\text{-}Cys)_4]$ cubane cluster (Fig. 11) in an exposed position (S-Cys = the amino acid cysteine, donating to iron via a thiol moiety).[20] This cluster can exist in two oxidation states, $[Fe_4S_4]^+$ and $[Fe_4S_4]^{2+}$, which are separated by a redox potential of roughly –300 mV. However, when MgATP binds to the reduced protein, a conformational change occurs in the protein structure, lowering this redox potential by around 100 mV and facilitating transfer of an electron to the Fe–Mo protein catalytic site.[21] At the same time, two MgATPs are

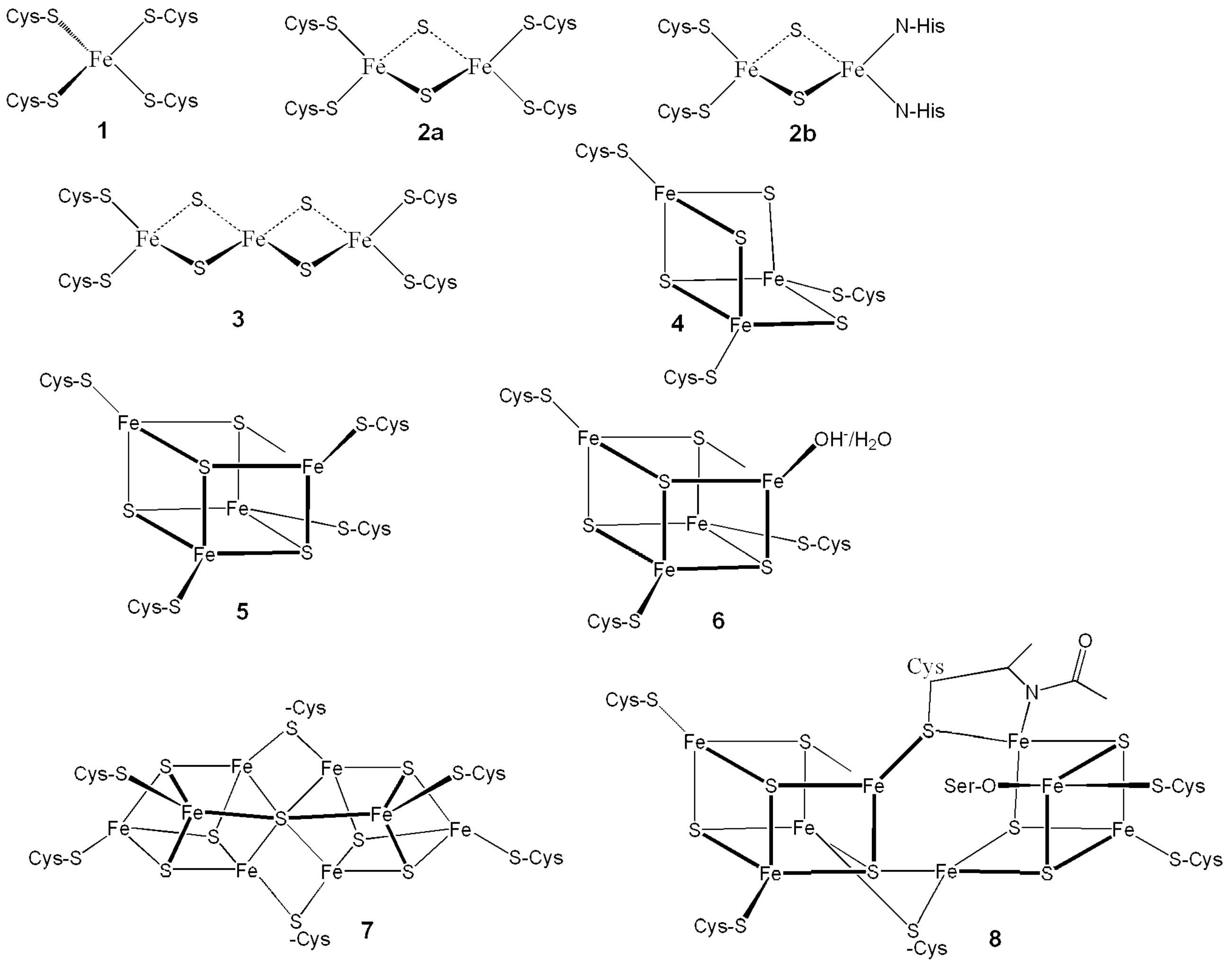

Fig. 12 Schematic of sites from iron–sulfur proteins containing one (1), two (2), three (3, 4), four (5, 6), and eight (7, 8) sulfur atoms.

hydrolyzed. So far, the Fe protein is the only chemical entity known to reduce the Fe–Mo cofactor.

The Mo–Fe protein contains four clusters, two are iron–sulfur clusters referred to as P clusters, the other two being cofactor or M clusters that also contain molybdenum. Both types were previously unknown in proteins or by synthesis. The P clusters are the μ_6-S bridged species shown as 7 in Fig. 11, where the μ_6-S simultaneously occupies the vertices of two FeS cubanes. In cluster 8, representing the two electron oxidized state,[19] the μ_6 bridge becomes μ_4, with the vacant iron coordination sites being filled by amino acid N and O donors. It is believed that the P clusters receive electrons from the FeS cluster of the iron protein before passing them onto the M cluster.[20,21]

The structure of the M cluster, believed to be the catalytic site, is shown in Fig. 13.

Cuboidal Fe_4S_3 and $MoFe_3S_3$ units are connected by three μ_2-S atoms to form an $MoFe_7S_9$ core with C_{3v} symmetry, best described as an Fe_6 trigonal prism capped on the C_3 axis by an Fe atom at one end and an Mo atom at the other.[20] Peripheral ligation by a Cys-S ligand at the capping iron atom and a His-N at the molybdenum site connects the cluster to the protein, while 6-coordination at the molybdenum is completed by the hydroxyl and carboxylate atoms of homocitrate. Notably, the iron atoms of the trigonal prism are all three-co-ordinated; this co-ordinative unsaturation may allow capture of the substrate, N_2. However, the mechanism of dinitrogen activation is at present unclear, since: 1) theoretical studies show that capture by molybdenum cannot be ruled out; and 2) either Fe–S bond breakage or cavity enlargement would be necessary for N_2 to fit inside the cluster.

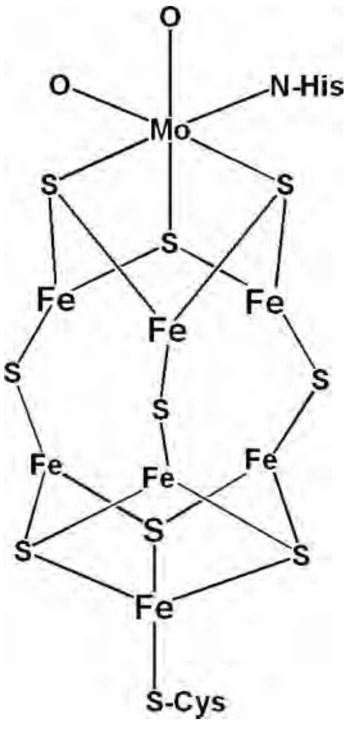

Fig. 13 A representation of the Mo–Fe (M) metal cluster found in the nitrogenase enzyme.

CONCLUSIONS

There is no doubt that polynuclear coordination clusters represent a diverse and fascinating class of materials with extraordinary physical properties. The investigation of such properties has even revealed new phenomena in the case of SMMs, which could potentially be used to store data and therefore produce storage media with very high capacity. Consequently, a long-term goal of coordination cluster chemistry is the exploitation of cluster properties such as SMM behavior in efficient, man-made devices comparable to the natural example in ‘‘Biological Coordination Clusters.’’ Advances toward this goal are driven both by pressures for miniaturization of electronic devices and developments in supramolecular chemistry, scanning probe microscopies, and surface spectroscopic techniques, which allow increasing sophistication in the design, characterization, and manipulation of new molecular devices.[22] Understanding and mastering the design and discovery of cluster architectures is pivotal in the further development of this area, both in terms of cluster properties and assembly of clusters into devices, and remains a fantastic challenge.

ARTICLES OF FURTHER INTEREST

Chemical Topology, p. 229–235.
DNA Nanotechnology, p. 475–483.
Molecular Squares, Boxes, and Cubes, p. 909–916.
Molecular-Level Machines, p. 931–938.
Soft and Smart Materials, p. 1302–1306.
The Template Effect, p. 1493–1500.

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