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Coordination Chemistry Without Frontiers: A Short Analysis and Applications of a New Method for the Description of Closed Coordination Clusters

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With the deposition of a crystal structure at the end of 2009, which can be recorded as the half million mark for Cambridge Crystallographic Data Centre (CCDC) database, it is now clear that synthetic chemistry is in an extremely productive period that is aided and abetted by the exquisite detail available at the atomic level from crystal structure determinations on "small" molecules or molecular units. Currently about 150 crystal structures are deposited daily in the CCDC.[1] In the light of this, it is becoming increasingly clear that certain classes of compounds, especially coordination clusters in which collections of metal ions are linked together through auxiliary ligands that generally allow the metal ions to interact in some way, require a further level of classification to enable the use of physicochemical structure correlations.[2] The main problem here is the need to use complex nomenclature, which is necessary to describe and classify such a molecule but gives no direct clue as to the composition, topology and therefore the structure of the molecular entity of interest. An example of the lengthy description of the formula alone of a coordination cluster is given in the Supporting Information, and the nomenclature of the molecule by using IUPAC guidelines would be correspondingly lengthy and hard to follow. This means that, generally, coordination clusters tend to be described relatively vaguely apart from the cases in which the authors have recognised a certain structural description of the metal core in terms of a trapped mineral,[3] or have found analogies with motifs found in main group chemistry such as Zintl and Chevrel phases and bronzes.[4] These facts suggested to us that it should be useful to find a way to describe open-shell coordination clusters in a fusion of the ways proposed by researchers such as Wade for electron-precise clusters and the topological approach used to describe connected nets (actually largely based on ideas by Wells, initially adopted by Batten and Robson et al.[5a,b] and formalised by O'Keeffe and Yaghi), and in terms of the Reticular Chemistry Structure Resource (RCSR).[5c] Here two- and three-dimensional coordination polymers, the latter known also as metal-organic frameworks (MOFs), have been deposited according to their topology in a similar way to the Database of Zeolite Structures.[6]

Two fields that have burgeoned over the past two decades are bioinorganic chemistry and the chemistry of molecular nanomagnets. These have led to the synthesis and structural characterisation of a large number of interesting polymetallic compounds, built up by using coordination chemistry principles, which we term coordination clusters. Taking the concept of using a topological representation of coordination polymers as our inspiration, we mapped this concept on to describing the topology of polynuclear clusters of zero-dimensional systems.[7] We start from the idea that each metal centre is perceived as a node and each monoatomic bridge of O, N or any other atom that can mediate magnetic exchange as a rod or linker. The end result is that this simplified metallic core can be described in terms of numbers corresponding to the number of the nodes and their connectivities, whereas subscripts are used to indicate, in an additive way, the nuclearity of the cluster.

The approach is most easily illustrated through worked examples as we have shown in previous articles.[2,7] Thus, if we take a coordination cluster relevant to this article, the compound $[Co^{II}_4(OH)_2(H_2O)_6(ntp)_2]\cdot 2H_2O$ (**1**; $ntpH_3$ = nitrilotripropionic acid), this would normally be described in terms of a defect dicubane or butterfly structure (Figure 1, left). However, by using our approach, Co(1) and Co(1') are two-connected nodes (c.n.) and participate in a three-membered ring, Co(2) and Co(2') are three-c.n. and participate in two three-membered rings and one four-membered ring

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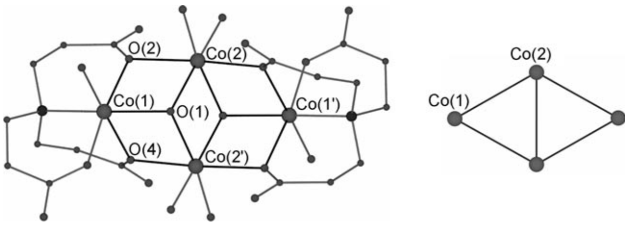

Figure 1. Crystal structure of **1** (left; hydrogen atoms have been omitted for clarity) and the decorated core of **1** (right).

to give the vertex symbol $(3^2.4)$ (Figure 1, right). Therefore, the cluster can be described as a binodal (2,3) and the vertex symbol (v.s.) is $(3)_2(3^2.4)_2$.

By applying this method to high-nuclearity coordination clusters, it becomes easier to describe the "decorated" core by nodes and their connectivity, rather than to find or devise a suitable polyhedron to describe the overall cluster core geometry. Furthermore, the method can be extended to describe the geometry of 3d/4f coordination cluster cores and, given the growing interest in these, this should be a useful way to compare structural and physical properties in these often isostructural compounds. Amongst the 3d/4f coordination clusters reported to date are the high-nuclearity examples, abbreviated as $Pr_{20}Ni_{21}$ (**2**),[8a] $La_{20}Ni_{30}$ (**3**)[8b] or $La_{60}Ni_{76}$ (**4**),[8c] and without doubt many other clusters with higher nuclearities will be reported in the future. Thus, taking the description of the decorated core of compound **3** as an example, this can be simply represented as a binodal cluster (2,6) with total v.s. $(3)_{30}(3^3.5^3.6^6.7^3)_{20}$ (Figure 2).

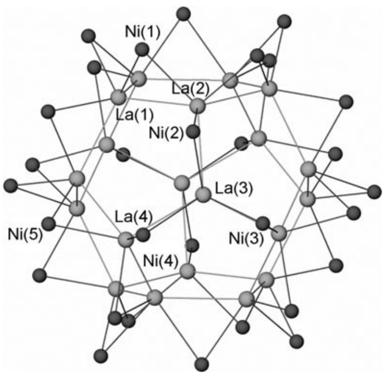

Figure 2. The decorated core of compound **3**.

Manganese chemistry has been the driving force for an explosion of interest in molecular magnetism and the quest to find new examples of molecules displaying single-molecule magnet (SMM) behaviour, arising largely as a result of the anisotropy of high-spin Mn^{III}. Thus, much effort has been directed towards synthesising new coordination clusters, which we recently reviewed in terms of our topological approach.[9a] The decorated cores of some related Mn compounds are depicted in Figure 3. For example, a Mn^{III}_6 (**5**) cluster in which the metal ions are arranged in an octahedral topology is a core feature of the "supertetrahedron", which is inscribed within a tetrahedral arrangement of Mn^{II} ions such that each Mn^{III} bisects an edge of the tetrahedron. This motif can be found, for example, in the cluster $[Mn^{II}_4Mn^{III}_6O_4(N_3)_4(hmp)_{12}](X)_2$ abbreviated as $\{Mn_{10}\}$ (**6**; hmpH = 2-(hydroxymethyl)pyridine; Figure 3, upper right). Up to now, we have found compounds in which two supertetrahedral $\{Mn_{10}\}$ units can be further fused in two of the three possible ways. These are, firstly, corner-sharing as in $[Mn^{II}_7Mn^{III}_{12}O_8(N_3)_8(HL)_{12}(MeCN)_6]Cl_2{\cdot}$(solvent) $\{Mn_{19}\}$ (**7**; LH_3 = 2,6-bis(hydroxymethyl)-4-methylphenol) Figure 3, middle right), which equates to the fusion of two supertetrahedra sharing one vertex and, therefore, node. Secondly, edge-sharing is seen in $[Mn^{II}_6Mn^{III}_{11}O_8Cl_4(OAc)_2(dpd)_{10}Cl_{2.34}(OAc)_{0.66}(py)_3^-(MeCN)_2]{\cdot}$(solvent) $\{Mn_{17}\}$ (**8**; $dpdH_2$ = 2,2-dimethyl-1,3-propanediol; Figure 3, middle left), in which the two supertetrahedra share an edge and thus two nodes. This latter motif has been described elsewhere in terms of a large (but rather squashed) octahedron of Mn^{II} ions with the 11 Mn^{III} ions captured within it in the form of a squashed cubic array with one Mn^{III} bisecting each edge of the octahedron and the remaining three arranged along a central axis of the cube (Figure 3).[9b] Although such a description is perfectly valid, it rather ignores the higher-symmetry polyhedra present in this motif. Up to now, no example in which two supertetrahedra share a face, and thus three nodes, has been reported. In the coordination cluster $[Mn^{II}_3Mn^{III}_{15}(N_3)_{12}O_{12}(tea)_2(teaH)_4(OMe)\text{-}(MeOH)]{\cdot}$-(solvent) $\{Mn_{18}\}$ (**9**; $teaH_3$ = triethanolamine) Murray et al. noted the presence of a supertetrahedral unit and used the description for the coordination cluster. This can alternatively be thought of as a supertetrahedron (with one vertex as a Mn^{III}) in which a seven-membered ring and a extra Mn node have been attached to the main core (Figure 3, lower left).[9c] This underlines the ambiguity that can arise when attempting to describe core structures in words, whereas the topological description we have put forward can be used in both directions. A symbolic representation can be translated directly to the topology of a core because it describes the connectivity of each node. In Table S1 in the Supporting Information the numerical representations of all these compounds are summarised, thereby underlining their relationship to one another.

As a consequence, adopting this topological approach simplifies the understanding of how polynuclear clusters derive from reactions or formal fusions that involve lower-nuclearity clusters. For example, the synthesis and structure of a decanuclear cluster formulated as $[Er_3Fe_7(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(mdea)_7(PhCO_2)_4(N_3)_6]{\cdot}2H_2O{\cdot}7CH_3OH$ (**10**; mdea = *N*-methyldiethanolamine) was reported recently.[10a] Varying the reaction procedure results in a pentanuclear cluster formulated as $[ErFe_4(\mu_4\text{-}O)(mdea)_3(mdeaH)(PhCO_2)_2(N_3)_4]$ (**11**), and changing the reaction solvent led to the isolation of the decanuclear cluster $[Er_4Fe_6(\mu_3\text{-}OH)_4(mdea)_6(mdeaH)_2(N_3)_8(PhCO_2)_4(H_2O)_2]{\cdot}4MeCN$ (**12**).[10b] The decorated core of compound **10** can be described as four nodal (2,3,5,7) with v.s. $(3)_2(3^2.4)_2(3^3)_2(3^5.4^3.5^2)_2(3^6.4^4)(3^8.4^8.5^4.6)$,

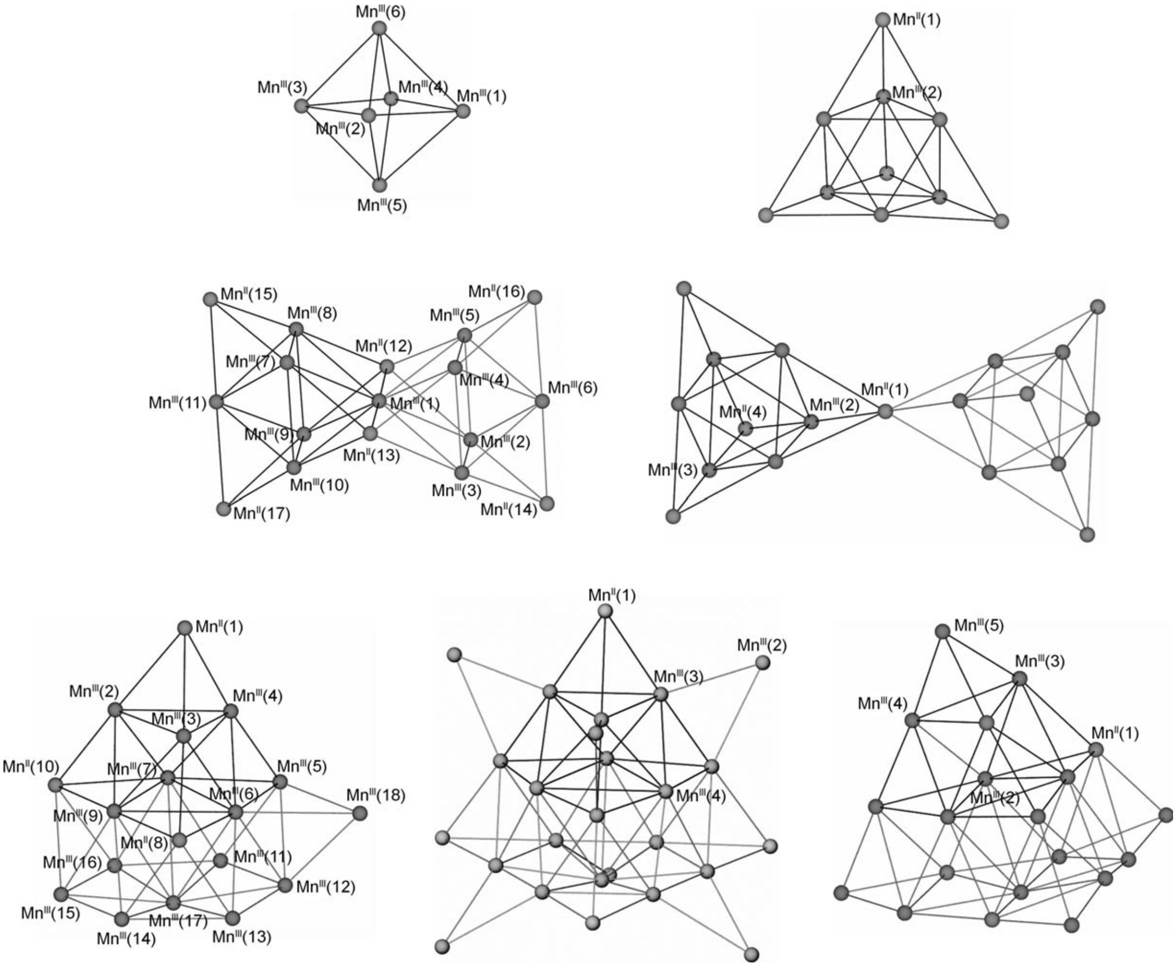

Figure 3. The decorated cores of Mn_6 (upper left) and Mn_{10} super tetrahedron (upper right); Mn_{17} (middle left) and Mn_{19} (middle right); Mn_{18} (lower left), Mn_{26} (lower middle) and Mn_{20} (lower right), emphasising the supertetrahedron motif.

for **11** as three nodal (2,3,4) with v.s. $(3)(3^3)_2(3^4.4^2)_2$ and finally for **12** as four nodal (2,3,5,6) with v.s. $(3)_2(3^2.4)_2(3^3)_2$-$(3^5.4^3.5^2)_2(3^7.4^6.5^2)_2$. A comparison of the molecular formulae of **10** and **11** shows that the two clusters are closely related because **10** can be considered as arising through bringing together a molecule of **11** and its mirror image **11'** (Figure S1 in the Supporting Information) accompanied by the "breaking" of two bonds and simultaneous replacement of one Fe with an Er atom. In other words, a hypothetical decanuclear intermediate "Er_2Fe_8" cluster is formed, which is transformed to **10** by the replacement of one Fe in the centre with an Er centre. The same hypothesis can also be considered for compound **12**. The addition of pentanuclear cluster of **11** along with its two-fold rotoinversion analogue **11''** forms a hypothetical decanuclear cluster intermediate Er_2Fe_8, which is transformed to **12** with the replacement of the two central Fe atoms by Er (Figure S2 in the Supporting Information). By taking into account the difference in the molecular formulae of the two decanuclear compounds and the fact that different synthetic pathways are followed for the construction of **10** and **12**, we might conclude that these two reactions are in competition with the formation of the pentanuclear cluster **11**, with the hypothetical Er_2Fe_8 being the "intermediate" step for the synthesis of **10** and **12**.

The construction of the $\{Fe^{III}_{11}O_{74}(L)_3(O_2CCMe_3)_{12}]Cl\}$·(solvent) $\{Fe_{11}\}$ (**13**)[11a] cluster from $[Fe^{III}_8O_3(tea)(teaH)_3$-$(O_2CCMe_3)_6(N_3)_3]$·(solvent) $\{Fe_8\}$ (**14**) and $[Fe^{III}_7O_3(L)_3$-$(O_2CCMe_3)_6(O_2CCMe_3)_3(H_2O)_3]$ $\{Fe_7\}$ (**15**) clusters,[11b] gives another example in which the significance of this method in modern synthetic inorganic chemistry is clear. In Figure 4 the decorated cores of these three compounds are depicted and the relationship between these structures become clear. The octanuclear core of **14** derives from the addition of a further central Fe centre to the heptanuclear core of **15**, and the undecanuclear core of **13** arises from the addition of a capping triangle of Fe centres to the octanuclear core of **14**. The numerical representations of these are a four-nodal (4,5,7,10) cluster with v.s. $(3^4.4^2)_3(3^5.4)_3(3^6.4^4)_3(3^{12}.4^9)$-$(3^{18}.4^{24}.5^3)$ for **13**, a binodal (4,7) with v.s. $(3^5.4)_6(3^{12}.4^9)_2$ for **14** and a binodal (3,6) with v.s. $(3^2.4)_6(3^6.4^6.5^3)$ for **15**. Note that by replacing acetates with formates, Wang and Gao were able to isolate $\{[Fe_8O_3(tea)(teaH)_3(HCOO)_6]_8$-

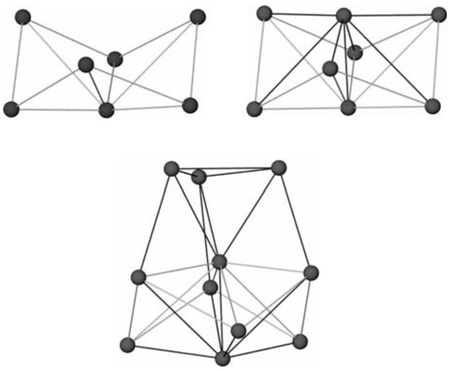

Figure 4. The decorated cores of Fe_7 (**15**) (top left), Fe_8 (**14**) (top right) and Fe_{11} (**13**) (lower).

$(HCOO)_{12}\}(ClO_4)_{12}\cdot$(solvent) $\{Fe_{64}\}$ (**16**), which consists of eight metallic cores of **14** that are linked through the formates.[11c]

Another useful application of this approach is in dealing with the comparison of compounds with the same nuclearity but that crystallise in different space groups. For example, a search in the CCDC for Mn_{26} clusters shows that $[Mn^{II}_4Mn^{III}_{22}O_{16}(OMe)_{12}(pdol)_{12}(N_3)_6]$ (**17**; $pdol^{2-}$ = di-2-pyridylmethanediol)[12a] and $[Mn^{II}_4Mn^{III}_{22}O_{16}(OMe)_{12}(pdol)_{12}(MeOH)_6](OH)_6$ (**18**),[12b] which were solved in the *Fd*3 space group, possess the same decorated metallic core as the compound $[Mn^{II}_4Mn^{III}_{22}O_{16}(OMe)_{18}(pdol)_{12}(OH)_2(H_2O)]ClO_4$ (**19**),[12c] which was solved in the *P*31*c* space group. This motif can be described as a "super supertetrahedron" (Figure 3 lower middle) with the addition of six Mn nodes. Numerically, this cluster is very close to Mn_{10}, Mn_{17} and Mn_{19} clusters (Table S1 in the Supporting Information) because it is a four-nodal (2,3,7,8) cluster with total v.s. $(3)_6(3^3)_4(3^9.4^8.5^3.6)_{12}(3^{15}.4^{18}.5^3)_4$. In the meantime a Mn_{20} cluster (Figure 3, lower right) with a molecular formula of $[Mn^{II}_4Mn^{III}_{16}O_{12}(OH)_4(tea)_8(chp)_4]\cdot$(solvent) (**20**; chpH = 6-chloro-2-hydroxypyridine) was reported by Murray et al.,[12d] which can be numerically represented as three-nodal (3,6,9) with v.s. $(3^3)_4(3^8.4^6.5)_{12}(3^{15}.4^{18}.5^3)_4$. A comparison of the numerical representation of **19** and **20** shows that those two decorated motifs are closely related.

Note that at present a number of compounds cannot be classified by using this approach, such as metallocrowns and cyanide-bridged compounds, although we are developing the structural analysis of such compounds. However, the importance of this effort is perceived when we take into account the increasingly large number of high-nuclearity paramagnetic aggregates that are being reported. The impact of this phenomenon can be gauged if we look at the manganese and iron clusters with the highest nuclearities reported. For example, in 1998 these were 18[13a] and 19,[3a] respectively, whereas in 2009 they were 84[13b] and 168, respectively.[13c] We decided to explore the development of this numerical representation of coordination clusters because of the difficulties that chemists have in finding structural elements within such molecules that can be universally appreciated. For example, although some chemists readily identify trapped portions of certain mineral structures within some clusters, others might not. In addition, a description in words requires a numerical quantification of the number of metal centres corresponding to the trapped mineral and gives no real idea of how the other metal ions that are present in the cluster are arranged. Similarly, as we have shown for the manganese systems derived from the superterahedral $\{Mn_{10}\}$ motif, different ways have been used to describe the same overall core structure (e.g., in $\{Mn_{17}\}$), and it is possible for the reader to overlook the underlying similarities in such systems. By adopting a numerical approach it is possible to overcome these problems and a glance at the numbers instantly gives an impression of any analogies. Our motivation for developing the approach came from our appreciation of the usefulness of the numerical analysis of nets and coordination polymers, developed by O'Keeffe and Yaghi. We realised that it should be possible to use a similar method on a closed zero-dimensional system and that the long-hand form of the symbol acts as a set of instructions that makes it possible to construct the core structure without seeing a picture of it. This is the point we have reached at present, but we hope to develop a shorthand notation that embodies all of the necessary information in the same way as can be applied to Schläfli symbols in terms of simple **xyz**-type codes.

This approach could also influence the way future researchers will think about coordination clusters and their chemistry. Our aims are manifold: 1) to establish a new method to simplify and rationalise the description of high-nuclearity coordination clusters to make the comparison of related compounds more clear than when schematic representations are used; 2) to categorise all of these coordination clusters according to the number of nodes, connectivity and v.s.; 3) to gain insights into the crystal growth and evolution of coordination clusters, because it is easier to compare and "link" lower-nuclearity to higher-nuclearity clusters; 4) to facilitate the comparison of the magnetic properties of compounds that possess similar or only slightly different cores, which will assist in finding any magnetostructural relationships. A successful example of this in extended nets is provided by the topological analysis of two 2D coordination polymers with almost similar molecular formulae[14] $[Cu(L)(N_3)(H_2O)_{0.5}]_n$ (**21**) in which L = nicotinate N-oxide and $[Cu(L)(N_3)]_n$ (**22**) in which L = *p*-cyanophenoxyacetic acid. These were found to possess the same **gek1** topology and exhibit very similar spin-orientation magnetic behaviour.[2] Similar successful analyses on coordination cluster systems would simplify the aim to direct synthetic procedures towards molecules with tailored properties.

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Keywords: cluster compounds • coordination modes • coordination clusters • nuclear growth • topology

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