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Azide as a Bridging Ligand and Magnetic Coupler in Transition Metal Clusters

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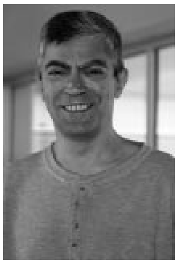
The synthesis of transition metal spin-clusters has become an important sub-discipline of coordination chemistry, especially since the discovery of single-molecule magnets (SMMs) in the early nineties. In this context, complexes with high spin-numbers and large anisotropy are particularly desired. The use of the azide ligand to act as a bridge and magnetic coupler within cages of paramagnetic ions has become increasingly common in this field, especially during the last five years, mainly because of the coordination versatility of this ligand, which is capable of bridging several metals in a variety of coordination modes, and its ability to induce ferromagnetic interactions. Several high-spin 3d metal aggregates have been prepared in this manner, a significant number of which behave as SMMs. This review covers the rapid progress made with this relatively recent synthetic approach by describing the structures and summarising the magnetic properties of the systems prepared in this manner. Some of the trends identified could serve as a privileged starting point for the further development of this promising area.

Introduction

The synthesis of coordination polynuclear complexes has been stimulated to a large extent by the field of molecular magnetism.[1,2] Most of these species contain paramagnetic 3d ions and are thus susceptible to exhibiting large spin-numbers as a result of intramolecular magnetic exchange. Such high-spin molecules have been perceived as potential building blocks in the construction of molecule-based magnets. In this context, magnetic studies on the cluster $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$, hereafter referred to as $[Mn_{12}OAc]$ (**1**),[3] led to the discovery of single-molecule magnet (SMM) behaviour.[4,5] SMMs are molecular species capable of maintaining the orientation of their magnetisation fixed below a certain *blocking temperature*, T_b. This molecular property is caused by an energy barrier to the equilibration of the various spin angular momentum orientations, which is calculated as $S_T^2|D|$ (integer spin) or $(S_T^2 - 1/4)|D|$ (half-integer spin),[6] where S_T is the total spin of the molecule at the ground state and D is the zero-field splitting parameter gauging the axial anisotropy, which has



Albert Escuer was born in Lleida, Spain, in 1956. He completed both his BSc (1978) and PhD (1984) degrees at the Universitat de Barcelona, the latter under the supervision of Prof. J. Ribas. In 1986 he was a postdoc with Prof. Dante Gatteschi at the Universita degli Studi di Firenze (Italy). He became full professor of Inorganic Chemistry in 2003 and he is the current director of the Inorganic Chemistry Department of the Universitat de Barcelona. His research interests concern the study of coordination compounds with small bridging ligands, mainly pseudohalides, with particular interest in magnetochemistry. He is the author of more than 150 papers in international chemistry journals.

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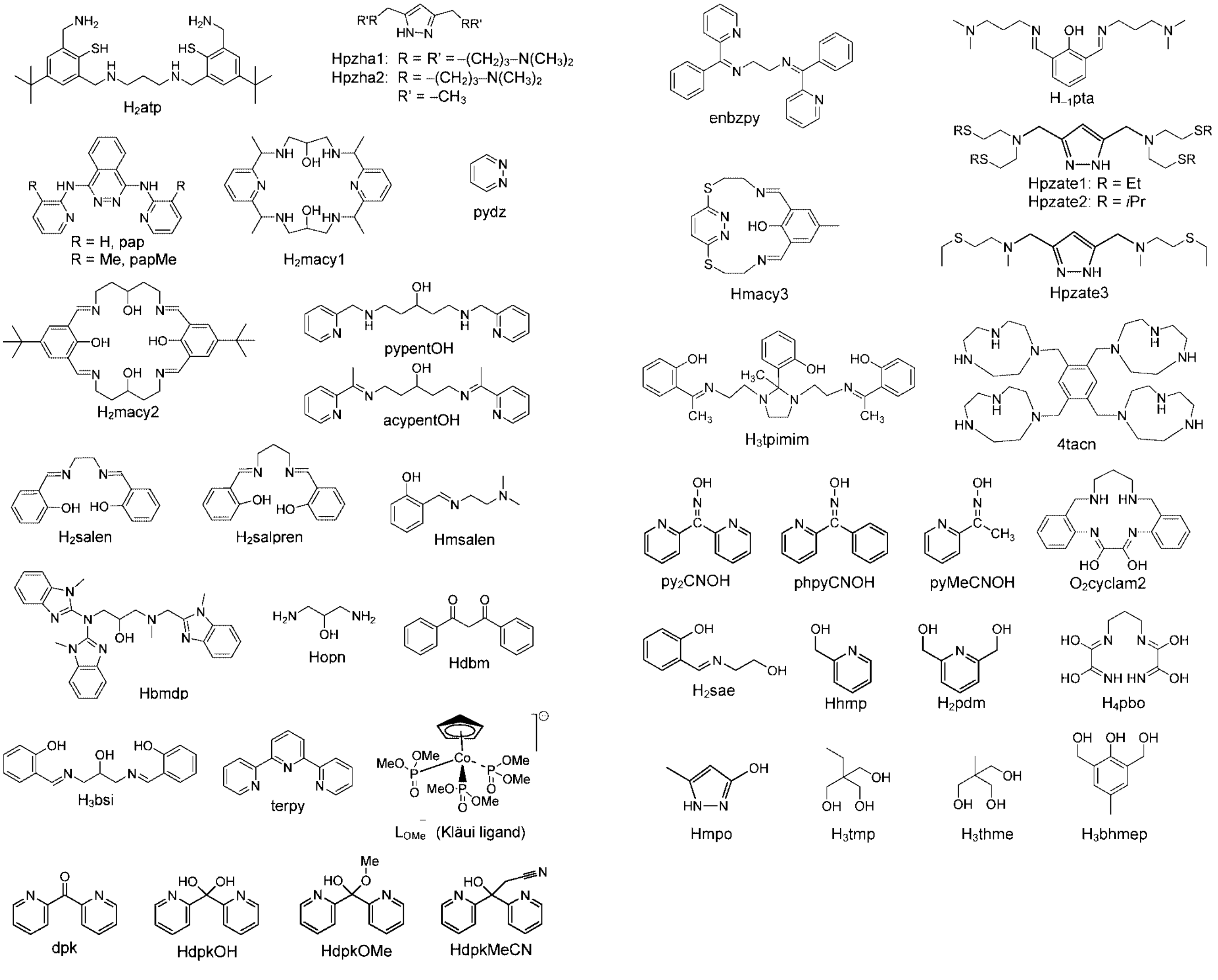
to be of the Ising type ($D < 0$). The search for new examples of SMMs has undoubtedly intensified efforts aimed at the preparation of more and different cluster coordination complexes,[7] possibly with high spin numbers and enhanced magnetoanisotropy.

The vast majority of these compounds have been prepared by the so-called method of “serendipitous self-assembly“.[2] In this methodology, transition metal ions react with small bridging ligands (e.g. O^{2-}, OH^-, OMe^-, Cl^-, N_3^-) to form stable polynuclear arrays. Growth into infinite networks is blocked by terminal ligands that can either be monodentate (e.g. pyridine, alcohols, MeCN, carboxylic acids) or polydentate (e.g. bipyridine, 1,3-diketonates, picolinic acid). Additional bridging ligands are commonly included in the reaction system, and these, because of their versatility and varied coordination modes, have led to the formation of very diverse and large families of clusters. Among these categories of compounds are those containing carboxylates,[1] pyridones,[8] polyalcohols,[9] amino alcohols,[10] dipyridyl ketones,[11] etc. Of this important number of compounds, a relatively low percentage display spin ground-states larger than 5/2 (the maximum spin that can be achieved with a mononuclear d metal complex). This is, in part, true because antiferromagnetic interactions are more common than ferromagnetic ones.

Azide ligands have been widely employed in coordination chemistry, most of the time as part of 1-, 2- or 3D extended arrays or dinuclear complexes.[12] This research has allowed the discovery of magnetostructural correlations,[13,14] which have established, for example, that end-on N_3^- ligands usually mediate ferromagnetic interactions, except in some recognized situations.[15] Moreover, this ligand has been shown to exhibit a wide variety of coordination modes (see below). For these reasons, the azide ligand constitutes a suitable entry into novel high-spin clusters, although this has been recognized only recently. Indeed, many members of the growing family of azide-bridged discrete polynuclear complexes display ferromagnetic interactions and large spin-numbers, of which an exceptionally large portion behave as SMMs. Interestingly, more than 80% of examples (containing four or more metal centres) have been reported during the last five years. It is thus clear that this category of com-



Scheme 1. Ligands discussed in this review.

pounds constitutes a large and promising field of open investigation in the search for magnetic clusters and SMMs. The area, however, is developing quite rapidly, and thus constitutes an excellent topic for a microreview, where the achievements made up to now are summarised while possible trends for future developments may be suggested. All the azide-bridged clusters containing four or more metal centres reported to date are gathered together in this account and organized, where possible, by structural types. The structures of the co-ligands of all the compounds reviewed are shown in Scheme 1. Structural descriptions are presented along with summaries and short discussions of their magnetic properties, where possible. A few compounds that are yet to be published have also been included in this compendium with the permission of the authors of their discovery.

Structural Overview

A survey of the literature reveals that the metals most frequently observed as part of azide-bridged clusters are Ni and Cu, followed at a distance by Mn, Co and Fe. All nuclearities from four to ten have been observed, and there is then a large gap until the next observed metal count of nineteen. This number is then followed by twenty five and the highest nuclearity of thirty two. Of these topologies, the tetranuclear arrangement clearly dominates, making up about 70% of examples. Thus, most examples in the latter category can be analysed according to certain structural patterns, namely cyclic types (metallacrowns), linear arrays, cubanes and defective cubanes. Among all the complexes structurally characterised, about 10% behave as SMMs. Of the compounds reviewed, Cu derivatives are the most numerous, although most of their azide bridges are of the axial–equatorial type and consequently the intramolecular magnetic exchange is severely diminished. These compounds have, nevertheless, been included in this review for completeness. The clusters discussed in this review are listed in Table 1.

Cyclic M_4 Clusters

The seven documented tetranuclear compounds with a cyclic topology (Figures 1 and 2) are $[Ni_4(atp)_2(pydz)_2(N_3)_2](BPh_4)_2$ (**1**),[16] $[Ni_4(pzha1)_2(N_3)_4](BPh_4)_2$ (**2**),[17,18] $[Ni_4(pzha2)_2(N_3)_4](X)_2$ (**3**; X = ClO_4^-, BF_4^-),[18] $[Cu_4(pap)_2(N_3)_8(MeOH)_2]$ (**4**),[19,20] $[Cu_4(papMe)_2(N_3)_4(H_2O)_2(NO_3)_2](NO_3)_2$ (**5**),[19] $[Mn_2(Hmacy1)(N_3)_2]_2(ClO_4)_2$ (**6**),[21] $[Cu_4(macy2)(N_3)_4]$ (**7**)[22] and $[Ni_4(N_3)_4(opn)_2(Hopn)_2](ClO_4)_2$ (**8**).[23] Of these, complexes **1**–**6** can be described as dimers of dinuclear units linked to each other by azide ligands where the co-ligand is playing the role of a dinucleating scaffold. The N_3^- bridges linking the dimers are all of the end-to-end (EE) type (see Scheme 2), with the exception of **6**, where the end-on (EO) mode is observed. Presumably, EE coordination only occurs when the steric encumbrance prevents the EO mode from occurring, and this can be argued for complexes **1**–**6**. Complexes **7** and **8** are closer to true cycles rather than dimers-of-dimers.

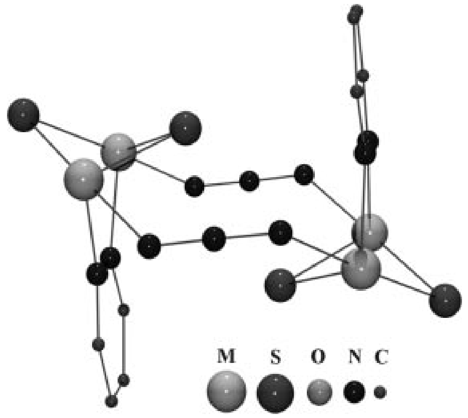
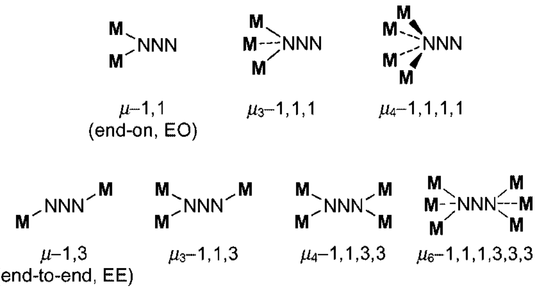


Figure 1. The core of $[Ni_4(atp)_2(pydz)_2(N_3)_2](BPh_4)_2$ (**1**) and the grey scale and size code of atoms used throughout the whole paper.



Scheme 2. Coordination modes observed for the azide ligand.

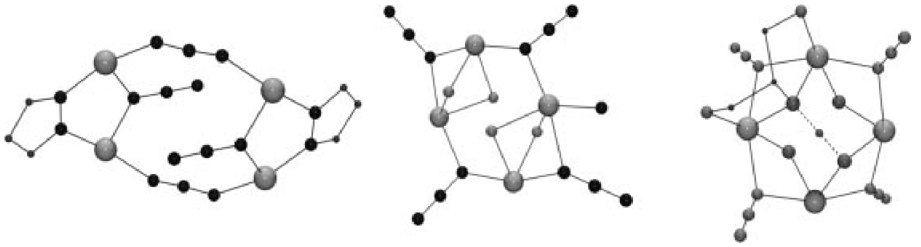


Figure 2. Several representative cores for cyclic M_4 azido clusters. Left: the $\mu_{1,3}$-azido-bridged dimer-of-dimers core of $[Ni_4(pzha1)_2(N_3)_4](BPh_4)_2$ (**2**), which is very similar to **3**, **4** and **5**. Centre: $\mu_{1,1}$-azido-bridged dimer-of-dimers core of $[Mn_2(Hmacy1)(N_3)_2]_2(ClO_4)_2$ (**6**). Right: true cyclic core of $[Ni_4(N_3)_4(opn)_2(Hopn)_2](ClO_4)_2$ (**8**) showing one of the H-bonds that helps to stabilize the structure (dashed bonds).

Table 1. List of all the clusters discussed in this review, including, in this order, formula, reference, ground spin state S (where known) and compound number used in the text.

Complex	Lit.	S	
$[Ni_4(atp)_2(pydz)_2(N_3)_2](BPh_4)_2$	[16]	4	**1**
$[Ni_4(pzha1)_2(N_3)_4](BPh_4)_2$	[17,18]	0	**2**
$[Ni_4(pzha2)_2(N_3)_4](ClO_4)_2$	[18]	4	**3a**
$[Ni_4(pzha2)_2(N_3)_4](BF_4)_2$	[18]	0	**3b**
$[Cu_4(pap)_2(N_3)_8(MeOH)_2]$	[19,20]	0	**4**
$[Cu_4(papMe)_2(N_3)_4(H_2O)_2(NO_3)_2](NO_3)_2$	[19]	0	**5**
$[Mn_2(Hmacy1)(N_3)_2]_2(ClO_4)_2$	[21]	0	**6**
$[Cu_4(macy2)(N_3)_4]$	[22]	0	**7**
$[Ni_4(N_3)_4(opn)_2(Hopn)_2](ClO_4)_2$	[23]	4	**8**
$[Fe_4(N_3)_6(pypentO)_2]$	[27]	0	**9**
$[Fe_4(N_3)_4(acpypentO)_2]$	[28]	0	**10**
$[Ni_4(pzha2)_2(N_3)_6]$	[17]	0	**11**
$[Cu_4(msalen)_2(N_3)_2(H_2O)(MeOH)]$	[33]	–	**12**
$[Cu_4(salen)_2(N_3)_4]$	[29]	0	**13**
$[Cu_4(salpren)_2(N_3)_4(DMSO)_2]$	[34]	–	**14**
$[Cu_4(bmdp)_2(OAc)_2(N_3)](ClO_4)_3$	[35]	0	**15**
$[Cu_4(O_2cyclam1)_2(tmen)_2(N_3)](ClO_4)_3$	[36]	–	**16**
$[Cu_4(acac)_2(phen)_4(N_3)_4(ClO_4)_2]$	[37]	2	**17**
$[Ni_4(N_3)_4(dbm)_4(EtOH)_4]$	[38,39]	4	**18**
$[Mn_4O_3(N_3)(OAc)_3(dbm)_3]$	[40]	9/2	**19**
$[Ni_4(L_{OMe})_4(N_3)_4]$	[43]	–	**20**
$[Co_4(L_{OMe})_4(N_3)_4]$	[43]	–	**21**
$[Cu_4(bsi)_2(N_3)_2]$	[44]	0	**22**
$[Ni_4(dpkOH)_2(dpkOCH_3)_2(N_3)_2(H_2O)_2](ClO_4)_4$	[45]	4	**23**
$[Ni_4(dpkOH)_4(N_3)_4]$	[46]	4	**24**
$[Ni_4(N_3)_8(enbzpy)_2]$	[47]	4	**25**
$[Co_4(dpkOH)_4(N_3)_2(OBz)_2]$	[48]	“2“[a]	**26**
$[Co_4(dpkOH)_4(N_3)_2(AcO)_2]$	[49]	“2“[a]	**27**
$[Co_4(dpkOH)_2(dpkOCH_3)_2(N_3)_2(H_2O)_2](BF_4)_2$	[50]	“2“[a]	**28**
$[Co_4(dpkOH)_2(dpkOMe)_2(N_3)_4]$	[51]	“2“[a]	**29**
$[Mn_4(dpkOH)_2(dpkOMe)_2(N_3)_4]$	[51]	0	**30**
$[Cu_4(macy3)_2(OEt)_2(N_3)_4]$	[52]	0	**31**
$[Cu_4(pta)_2(N_3)_6](ClO_4)_4$	[53]	0	**32**
$[Ni_4(pzate1)_2(N_3)_3(O_2CMe)](ClO_4)_2$	[54]	0	**33**
$[Ni_4(pzate1)_2(N_3)_3(O_2CPh)](ClO_4)_2$	[55]	0	**34**
$[Ni_4(pzate2)_2(N_3)_3(O_2CPh)](ClO_4)_2$	[55]	0	**35**
$[Ni_4(pzate1)_2(N_3)_3(O_2CMe)_2](ClO_4)$	[54]	0	**36**
$[Ni_4(pzate2)_2(N_3)_3(O_2CPh)_2](ClO_4)$	[57]	0	**37**
$[Ni_4(pzate2)_2(N_3)_3(O_2CAda)_2](ClO_4)$	[57]	0	**38**
$[Ni_4(pzate3)_2(N_3)(O_2CAda)_4](ClO_4)$	[57]	0	**39**
$[Cu_4(tpimim)_2(N_3)]Cl$	[58]	0	**40**
$[Mn_4O(N_3)(O_2Bz)_3(phpyCNO)_4]$	[59]	6	**41**
$[Ni_4(SO_4)_2(N_3)_2(SH)_2(pyMeCNOH)_4]$	[60]	–	**42**
$[Cu_4(4tacn)(N_3)_4](PF_6)$	[61]	–	**43**
$[Ni_5(N_3)_4(phpyCNO)_4(O_2CH)_2(MeOH)_4]$	[62]	5	**44a**
$[Ni_5(N_3)_4(phpyCNO)_4(O_2CCH_3)_2(MeOH)_4]$	[62]	5	**44b**
$[Ni_5(N_3)_4(phpyCNO)_4(phpyCNOH)_4](ClO_4)_2$	[63]	–	**45**
$[Cu_5(terpy)_2(N_3)_{10}]$	[64]	$3 + 2 \times 1/2$[b]	**46**
$[KNi_6(CO_3)(N_3)_6(OAc)_3(dpkMeCN)_3]_2[K_2(H_2O)_2]$	[65]	6	**47**
$Na_2[Ni_4Cu_2(dpa)_4(pbo)_2(H_2O)_2](ClO_4)_4$	[68]	0	**48**
$[Cu_6(tmen)_6(N_3)_2(C_2O_4)_3(H_2O)_2](ClO_4)_4$	[68]	0	**49**
$[Ni_7(AcO)_6(py_2CNO)_6(N_3)_2(H_2O)_2]$	[70]	3	**50**
$[Ni_8Na_2(N_3)_{12}(OBz)_2(mpo)_4(Hmpo)_6(EtOAc)_6]$	[71]	8	**51**
$[\{Mn_4O(sae)_4(N_3)(MeOH)\}_2(N_3)](N_3)$	[72]	0	**52**
$[Ni_9(N_3)_2(AcO)_8(dpkO)_4]$	[73]	9	**53**
$[Co_9(N_3)_2(AcO)_8(dpkO)_4]$	[74]	“9/2“[a]	**54**
$[Fe_9(N_3)_2(AcO)_8(dpkO)_4]$	[75]	14	**55**
$[Ni_{10}(tmp)_2(N_3)_8(acac)_6(MeOH)_6]$	[76]	10	**56**
$[Mn_{10}O_4(N_3)_4(hmp)_{12}](N_3)_2$	[77]	22	**57**
$[Mn_{10}O_4(N_3)_4(hmp)_{12}](ClO_4)_2$	[77]	22	**58**
$[Mn_{19}O_8(N_3)_8(Hbhmep)_{12}(MeCN)_6]Cl_2$	[78]	83/2	**59**
$[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6](Cl)_2$	[79]	$51/2 \pm 1$[c]	**60**
$[Mn(bpy)_3]_{1.5}[Mn_{32}(thme)_{16}(bpy)_{24}(N_3)_{12}(OAc)_{12}](ClO_4)_{11}$	[80]	9	**61**
$[Cu_4(O_2cyclam2)_4Mn_2(N_3)_4]$	[86]	0	**62**
$[(\gamma\text{-}SiW_{10}O_{36})_2Mn_4(OH)_4(N_3)_2(H_2O)]^{10-}$	[89]	0	**63**
$[(\gamma\text{-}SiW_{10}O_{36})_2Cu_4(N_3)_4]^{12-}$	[89]	2	**64**
$[(\gamma\text{-}SiW_{10}O_{36})_2Cu_4(H_2O)_2(N_3)_4]^{12-}$	[88]	1 + 1[b]	**65**
$[(SiW_8O_{31})_3Cu_9(OH)_3(H_2O)_6(N_3)_4]^{10-}$	[88]	0	**66**

[a] Resulting from considering a effective spin of $S = 1/2$ for Co^{II}. [b] Resulting from uncoupled spins within the molecule. [c] Value subject to uncertainty of ±1.

$[Ni_4(atp)_2(pydz)_2(N_3)_2](BPh_4)_2$ (1)

The core of complex **1** is shown in Figure 1.[16] It is a rectangular array resulting from the bridging by two $\mu_{1,3}$-N_3^- ligands of two dinuclear $[Ni^{II}_2]$ units, held together by a hexadentate aminothiophenolate ligand (atp), with the additional support of a pyridazine (pydz) group. This molecule forms from independent $[Ni_2(atp)_2]^+$ dinuclear complexes as a precursor of the higher nuclearity species upon reaction with N_3^-. It displays an $S = 4$ spin ground-state, which can be modelled as the result of ferromagnetic interactions through both type of bridges — the thiophenolato-pyridazine and the EE-azido. In the first case, it can be argued that the ferromagnetic coupling occurs because the Ni–S–Ni angle is close to 90°, whereas for the N_3^- bridge, the observed Ni–N–N–N–Ni torsion angle of 76.4° (i.e. larger than 55°) is the cause of the ferromagnetism.[24–26]

$[Ni_4(pzha1)_2(N_3)_4](BPh_4)_2$ (2) and $[Ni_4(pzha2)_2(N_3)_4](X)_2$ ($X = ClO_4^-$, 3a; BF_4^-, 3b)

Complexes **2** and **3** are similar to **1**, with each $[Ni^{II}_2]$ moiety now supported by one polyaminopyrazolyl group (pzha, Scheme 1) and one $\mu_{1,1}$-N_3^- ligand. Both dinuclear entities are connected by EE azide groups to complete the cyclic structure (Figure 2, left).[17,18] The spin ground-state, however, was found to be either $S = 0$ or $S = 4$. Fits of bulk magnetisation data were conducted by considering constants for the intra- and interdimer couplings. The first one was always found to be ferromagnetic, as expected from the influence of the EO azide bridge. The interactions through the EE azides, however, were found to be of either sign, depending on the value of the Ni–N_3–Ni torsion angle. Thus, torsion angles sufficiently close to 180° (as commonly encountered) facilitate antiferromagnetic coupling (as observed for **2** and **3b**, $S = 0$), whereas values close to 90° lead to ferromagnetic interactions (as seen for **3a**, $S = 4$).[24–26]

$[Cu_4(pap)_2(N_3)_8(MeOH)_2]$ (4) and $[Cu_4(papMe)_2(N_3)_4(H_2O)_2(NO_3)_2](NO_3)_2$ (5)

Complexes **4** and **5** are related[19,20] and their structure is analogous to those of **1**, **2** and **3**. The dinucleating ligand of both is a phthalazine aminopyridyl ligand (pap or papMe) with the Cu pairs also linked by EO N_3^- ligands. The $[Cu^{II}_2]$ dimers in **4** and **5** are linked to each other by EE N_3^- groups and the difference between both complexes lies in the terminal ligands, which affect the charge of the complex, and the fact that **4** possesses two additional μ-MeOH molecules. The coupling in both complexes is antiferromagnetic, presumably because of the dominant influence of the phthalazine ligand. However, the magnetic data do not fit the Bleaney–Bowers equation satisfactorily and give unrealistic Weiss terms θ. This was ascribed to the presence of a temperature-dependent J value as a result of the possible variation of the Cu–N–Cu angle with temperature within the $[Cu^{II}_2]$ groups. Possible exchange through the EE N_3^- groups was not considered.

$[Mn_2(Hmacy1)(N_3)_2]_2(ClO_4)_2$ (6)

Complex **6** is an $[Mn^{II}_2]_2$ species with each pair of metals assembled by one octadentate macrocycle (Scheme 1) containing amino, pyridyl and alcohol groups.[21] An EO N_3^- bridge serves as an additional support of the intradimer connection (Figure 2, centre). Interestingly, both dimers are bridged here by N_3^- ligands in the end-on form, instead of end-to-end. All Mn^{II} ions in **6** are seven-coordinate, with a pentagonal bipyramidal geometry. Magnetic measurements show the overall coupling within **6** to be antiferromagnetic, thus indicating an $S = 0$ ground state. Although these results were not discussed in terms of the bridging ligands, it is conceivable that the alkoxide bridges cause a strong antiferromagnetic interaction within the dimers, which masks any possible (weaker) ferromagnetic pathway mediated by the $\mu_{1,1}$-N_3^- links.

$[Cu_4(macy2)(N_3)_4]$ (7)

The large macrocyclic ligand in complex **7** (Scheme 1) keeps the tetranuclear cycle together by means of four alkoxide bridges, whereas two EE N_3^- bridges support the link between two pairs of Cu^{II} ions.[22] The coupling is antiferromagnetic due to the alkoxide bridges of the macrocycle.

$[Ni_4(N_3)_4(opn)_2(Hopn)_2](ClO_4)_2$ (8)

Of the series of tetranuclear compounds with a cyclic arrangement, complex **8** is the only one that is square rather than rectangular (Figure 2, right).[23] All Ni^{II} ions in this complex are equivalent and bridged by one EO azide group and the O atom of 1,3-diaminopropan-2-ol (Hopn). In fact, four diamino alcohol molecules share two of the hydroxy protons, which connect the four oxygen atoms pairwise through hydrogen bonds above and below the plane of the molecule. The $\chi_M T$ vs. T curve of **8** (χ_M is the molar paramagnetic susceptibility) clearly indicates that the Ni···Ni interactions here are ferromagnetic and suggests an $S = 4$ ground state. When first published, complex **8** was the first azide-bridged, ferromagnetically coupled tetranuclear Ni^{II} cluster ever synthesised. More than ten years after its discovery, ultra-low-temperature studies are underway to determine whether this complex behaves as an SMM.

Linear M_4 Clusters

Of the nine reported clusters of this type, all but one can be described as two $[M^{II}_2]$ dimers linked together by N_3^- ligands in either an EO or an EE fashion. In all these cases, the dimers are kept together by polydentate ligands and the azide ligands complete the coordination and/or act as bridges between them.

$[Fe_4(N_3)_6(pypentO)_2]$ (9) and $[Fe_4(N_3)_4(acpypentO)_2]$ (10)

Complexes **9**[27] and **10**[28] are analogous. Both consist of two $[Fe^{II}_2]$ units mutually linked by two $\mu_{1,1}$-N_3^- ligands. Each dimeric unit is held together by one pentadentate hydroxy/amine (**9**) or imine (**10**)/pyridyl ligand, supplemented by another EO azide (Figure 3). Their magnetic behaviour is also very similar; in both cases the intradimer coupling is antiferromagnetic and the interdimer interaction ferromagnetic.

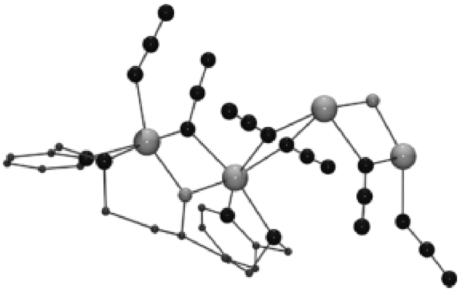


Figure 3. Plot of $[Fe_4(N_3)_6(pypentO)_2]$ (**9**). For clarity, only one of the pypentO ligands is represented.

[Ni$_4$(pzha2)$_2$(N$_3$)$_6$] (11)

Compound **11** is very similar to complexes **2** and **3**, where the pyrazolyl $[Ni^{II}_2]$ units are now shifted so that the azide groups linking the dimers are in the very rare $\mu_{1,1,3}$ coordination mode.[17] As for **2** and **3**, the intradimer interactions are ferromagnetic due to the presence of EO azide ligands, whereas in this case the EE N_3^- groups mediate antiferromagnetic coupling.

[Cu$_4$(msalen)$_2$(N$_3$)$_2$(H$_2$O)(MeOH)] (12), [Cu$_4$(salen)$_2$(N$_3$)$_4$] (13) and [Cu$_4$(salpren)$_2$(N$_3$)$_4$(DMSO)$_2$] (14)

These three complexes are related. They all consist of two dimers of Cu^{II} formed by polydentate Schiff-base ligands (see Scheme 1) that are connected linearly through a pair of $\mu_{1,1}$-N_3^- groups. Fitting of the magnetic susceptibility data from **13** yielded antiferromagnetic coupling constants for both Cu···Cu bridges.[29] This compound was claimed to be the first to exhibit antiferromagnetic coupling for the Cu–$(\mu_{1,1}$-$N_3)_2$–Cu bridging mode. It needs to be pointed out, however, that such an interaction has been found several times before for this moiety, where some of the Cu–N bonds do not lie in equatorial positions.[30,31] In such cases the interaction is always very weak since the asymmetric bridge causes very little overlap between the magnetic orbitals of Cu^{II} ($d_{x^2-y^2}$), contrary to the case where the bridge takes place through all basal positions.[32] The antiferromagnetic coupling in this complex was modelled theoretically on an experimental structure by means of density functional calculations,[15] although no explanation for this behaviour was offered. The magnetic analysis of complexes **12**[33] and **14**[34] was not provided.

[Cu$_4$(bmdp)$_2$(OAc)$_2$(N$_3$)](ClO$_4$)$_3$ (15) and [Cu$_4$(O$_2$cyclam1)$_2$(tmen)$_2$(N$_3$)](ClO$_4$)$_3$ (16)

Complexes **15** and **16** are formed by two dimers of asymmetric dinucleating ligands, each featuring a coordinatively unsaturated Cu^{II} that reacts selectively with one azido ligand to form $\mu_{1,3}$-N_3^--linked tetranuclear complexes. In **15**,[35] the large ligand is based on 1,3-diaminopropan-2-ol and three *N*-methylbenzimidazole groups and this system shows weak ferromagnetic coupling, which could not be unambiguously assigned as either intra- or interdimeric coupling. In complex **16** (tmen = *N*,*N*,*N*′*N*′-tetramethylethylenediamine), the dinucleating ligand is a cyclic oxamide ligand. No magnetic properties were reported.[36]

[Cu$_4$(acac)$_2$(phen)$_4$(N$_3$)$_4$(ClO$_4$)$_2$] (17)

This complex is a genuine linear tetranuclear array exclusively bridged by (single or double) μ-N_3^- ligands, with the remaining coordination sites saturated by chelating ligands [acetylacetonate (acac) and phenanthroline (phen)] or perchlorate.[37] Despite occurring through bridges of the axial–equatorial type, the coupling within this molecule is ferromagnetic and the ground state $S = 2$.

M$_4$ Cubanes

The cubic arrangement is one of the most common structural motifs of tetranuclear coordination clusters {236 hits in the CCDC (version 5.27, August 2006) for the cubic $[M_4O_4]$ feature; M = first row transition metal}. Some of these have been found to act as SMMs (M = Ni, Mn, Fe, Co).[7] In most cases the cube is formed by four symmetrically equivalent metals and four monoatomic donors in a μ_3-bridging mode, which are usually alkoxides, hydroxides or oxides. Because of its coordination versatility (Scheme 2), the N_3^- group has also been found to act as a core ligand within cubane structures on a few occasions.

[Ni$_4$(N$_3$)$_4$(dbm)$_4$(EtOH)$_4$] (18)

Complex **18** features four metals that are equivalent by idealised symmetry (Figure 4, top).[38,39] This compound was the first reported paramagnetic cluster containing N_3^- ligands in the triply bridging mode, although many more examples have been reported since then (see below). These ligands are responsible for the weak ferromagnetic coupling that yields a spin ground state of $S = 4$. The peripheral ligation around the cubic core is completed by one chelating dibenzoylmethine (dbm$^-$) and one monodentate ethanol ligand on each Ni^{II} ion.

[Mn$_4$O$_3$(N$_3$)(OAc)$_3$(dbm)$_3$] (19)

Complex **19**[40] belongs to a group of cubane clusters with general formula $[Mn_4O_3X(OAc)_3(dbm)_3]$ that contain a distorted $[Mn^{III}_3Mn^{IV}XO_3]$ cubane core with a variable ligand X (X = OH$^-$, OMe$^-$, F$^-$, Cl$^-$, Br$^-$, N_3^-, NCO$^-$, AcO$^-$, NO_3^-, etc.)[40–42] along with a bridging AcO$^-$ that links each Mn^{III} to a Mn^{IV} ion and chelating ligands (dbm$^-$, on each Mn^{III}; Figure 4, bottom). Several features of these compounds make them good models of the [Mn$_4$] complex of Photosystem II. Ferromagnetic coupling between the Mn^{III} centres, together with the antiferromagnetic interaction within the Mn^{IV}···Mn^{III} pairs, invariably confer the $S = 9/2$ spin ground state to all these clusters, which make up the second most important family of structurally related SMMs (after the [Mn$_{12}$] complexes); complex **19** is the member of this family in which X = N_3^-. In this series of compounds, the X ligand consistently mediates ferromag-

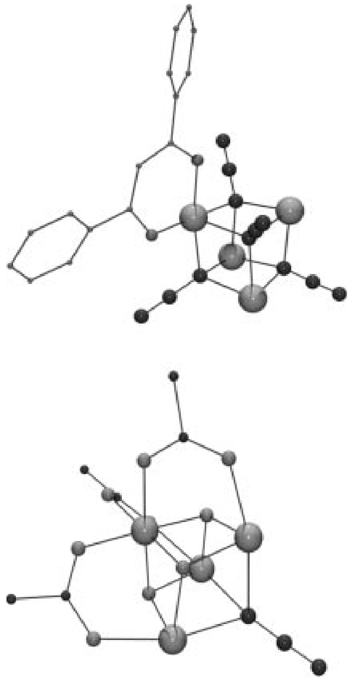


Figure 4. Top: core of $[Ni_4(N_3)_4(dbm)_4(EtOH)_4]$ (**18**), representative of the cubane systems with exclusively end-on azido bridges in the corners. One of the four dbm ligands is also shown. Bottom: core of $[Mn_4O_3(N_3)(OAc)_3(dbm)_3]$ (**19**), an unusual asymmetric cubane with only one azido bridge in one of the corners.

netic coupling between the metals it bridges, therefore replacement of any μ_3-X ligand by azide does not imply the change to ferromagnetism observed for other families of complexes (see below).

$[Ni_4(L_{OMe})_4(N_3)_4]$ (20) and $[Co_4(L_{OMe})_4(N_3)_4]$ (21)

Complexes **20** and **21** were obtained while studying the reactivity of the Kläui tripodal ligand L_{OMe} (Scheme 1) with 3d transition metals[43] in an attempt to isolate adducts different from full-sandwich compounds $[M(L_{OMe})_2]$. Both clusters were obtained in the same manner, namely from the reaction of the labile mononuclear precursor $[M(L_{OMe})(NO_3)(acetone)]$ with NaN_3. The molecular structure of both complexes consists of a cubane with four M^{II} metals and four μ_3-N_3^- ligands in the core, the hexacoordination around each metal being completed by a tripodal L_{OMe} ligand. The magnetic properties of these compounds were not studied.

$[Cu_4(bsi)_2(N_3)_2]$ (22)

This complex displays a very unconventional cubane structure with a $[Cu_4N_2O_2]$ core[44] where the N atoms belong to azide groups and the O donors are from alkoxides provided by a pentadentate Schiff-base ligand, which also serves to complete the peripheral ligation around Cu^{II}. The particularity of **22** within the category of cubanes is that it has two missing edges since these would be too long to consider them as bonds, which means that the cubane is open and the bridging N and O core atoms are μ and μ_3, respectively. Magnetic measurements revealed that the coupling within the cubane core is dominated by antiferromagnetic interactions, which leads to a spin ground state of $S = 0$. This was modelled by considering three coupling constants describing single alkoxido, bis-alkoxido, and alkoxido/azide-bridged Cu···Cu pairs. The first two were found to be negative, as expected, whereas the mixed bridge was described as mediating ferromagnetic exchange, consistent with most instances involving EO azide.

Defective Dicubane M_4 Arrangements

This topology has been described for ten complexes; three of Ni^{II}, four of Co^{II}, one of Mn^{II} and two of Cu^{II}. Their formulae are $[Ni_4(dpkOH)_2(dpkOCH_3)_2(N_3)_2(H_2O)_2](ClO_4)_4$ (**23**),[45] $[Ni_4(dpkOH)_4(N_3)_4]$ (**24**),[46] $[Ni_4(N_3)_8(enbzpy)_2]$ (**25**),[47] $[Co_4(dpkOH)_4(N_3)_2(OBz)_2]$ (**26**),[48] $[Co_4(dpkOH)_4(N_3)_2(AcO)_2]$ (**27**),[49] $[Co_4(dpkOH)_2(dpkOCH_3)_2(N_3)_2(H_2O)_2](BF_4)_2$ (**28**),[50] $[Co_4(dpkOH)_2(dpkOMe)_2(N_3)_4]$ (**29**),[51] $[Mn_4(dpkOH)_2(dpkOMe)_2(N_3)_4]$ (**30**),[51] $[Cu_4(macy3)_2(OEt)_2(N_3)_4]$ (**31**)[52] and $[Cu_4(pta)_2(N_3)_6](ClO_4)_4$ (**32**).[53] The two latter complexes are best described as two dimers linked through very long axial bonds. In these, the magnetic behaviour is dominated by the coupling within the dimers, as imposed by the phenolate-based dinucleating ligands (very strongly antiferromagnetic). Seven of the remaining clusters (**23**, **24** and **26**–**30**) have been prepared using dipyridyl ketone (dpk) as reagent and exhibit a common skeleton in which the four metallic atoms are bridged by two end-on μ-azide groups, two μ-oxido and two μ_3-oxido centres (Figure 5, top). The remaining coordination sites are occupied by four dpkOH or dpkOMe ligands and two monodentate terminal groups such as aquo, azido, acetato or benzoato. In contrast, although with the same metal topology, the skeleton of **25** contains only N_3^- bridges (Figure 5, bottom) and is one of the rare examples of clusters with a mainly azide based core. Of the non-copper clusters, only **30** (Mn^{II}) shows an overall antiferromag-

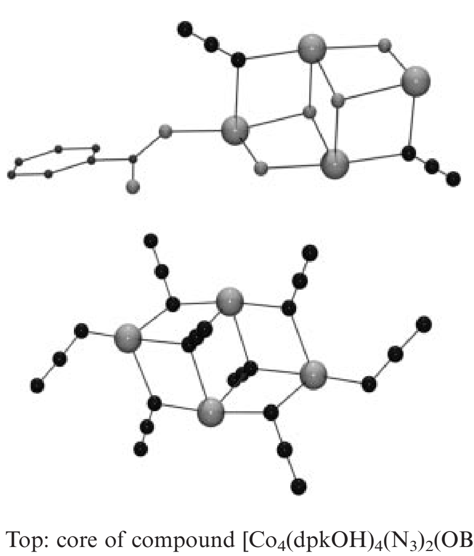


Figure 5. Top: core of compound $[Co_4(dpkOH)_4(N_3)_2(OBz)_2]$ (**26**). This core is common to compounds **23**, **24** and **26**–**30**, which differ in the counteranion or in the monodentate ligand. Bottom: end-on azido core of compound $[Ni_4(N_3)_8(enbzpy)_2]$ (**25**).

netic coupling with $S = 0$. The Ni^{II} clusters all display ferromagnetic interactions due the EO-N_3^- bridges and/or Ni–O–Ni angles close to 90°, which leads to an $S = 4$ ground state. This situation is analogous to the case of the Co^{II} compounds. In these clusters, however, the analysis of the magnetic behaviour is complicated by the effect of spin-orbit coupling within the metals. Since at low temperature the Co^{II} ions are better described as local $S_i = 1/2$ centres, the ground state of the $[Co_4]$ clusters can be considered as displaying a total $S = 2$ spin ground state with fairly large g_{eff}.

Genuine $\mu_{1,1,3}$-N_3^- Coordination in an M_4 Cluster

The group of complexes with general formula $[Ni_4(pzate\mathit{n})_2(N_3)_3(O_2CR)](ClO_4)_2$ (R = Me, pzate1 **33**; R = Ph, pzate1 **34**; R = Ph, pzate2; **35**) were the first examples with azide in the $\mu_{1,1,3}$-bridging mode (Scheme 2).[54,55] They are described as two $[Ni_2]$ dimers of a pyrazole/amine-based ligand that are bridged asymmetrically by azide (seen in three different coordination modes) and carboxylate (Figure 6). Dominant antiferromagnetic interactions were observed for the three complexes, resulting in a diamagnetic ground state. Modelling of the bulk magnetisation data unveiled the presence of a combination of antiferromagnetic and ferromagnetic coupling (two J constants of each type). The Ni···Ni pair bridged by two $\mu_{1,1}$-N_3^- groups was assigned a moderate ferromagnetic constant in the three complexes, whereas weak ferromagnetic coupling was attributed to the pathway formed by a single $\mu_{1,3}$-N_3^- ligand. The strongest antiferromagnetic coupling was ascribed to the link built by one $\mu_{1,1,3}$-azide and one pyrazolate, whereas the remaining single $\mu_{1,1,3}$-azide bridge was associated with the weakly antiferromagnetic constant. The last three assignments were made on the basis of the Ni–NNN–Ni torsion angles and the Ni–N–N angles. Indeed, observation of ferromagnetism within Ni^{II} pairs as mediated by only one EE azide is very uncommon and requires these two angles to be close to 90° and larger than 155°, respectively.[16,56]

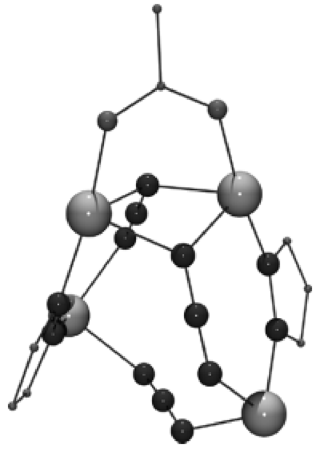


Figure 6. Core of compound $[Ni_4(pzate1)_2(N_3)_3(AcO)](ClO_4)_2$ (**33**), common to compounds **33**–**35**.

Rare $\mu_{1,1,3,3}$-N_3^- Coordination in an M_4 Cluster

The $\mu_{1,1,3,3}$ coordination mode (Scheme 2) was first observed in a group of compounds with formulae $[Ni_4(pzate\mathit{n})_2(N_3)_3(O_2CR)_2](ClO_4)$ (pzate1: R = Me **36**, R = Ph **37**; pzate2: R = adamantyl **38**) and $[Ni_4(pzate3)_2(N_3)(O_2CR)_4](ClO_4)$ (R = adamantyl **39**). These complexes are $[Ni^{II}_4]$ rectangles with a central μ_4-N_3^- ligand, a pair of opposite sides occupied by bridging "pzate" ligands (Scheme 1) and the other pair of edges formed by either one μ-N_3^- and one μ-O_2CR^- (**36**, **37** and **38**; Figure 7), or by two bridging carboxylates (**39**).[54,57] Interestingly, the structural differences imposed by the bridging of these edges determine the disposition of the central azide ligand. Thus, in complexes of the former type the central azide caps the Ni_4 plane on one of its faces to form a sort of roof with C_{2v} symmetry, whereas in complex **39** the metals form a flattened tetrahedron with the μ_4-N_3^- azide ligand inserted inside; this fragment displays D_2 symmetry. The magnetic properties of both types of complexes are marked by the coupling through the central azide, which is strongly antiferromagnetic along the edge spanned by the pyrazolate bridge (because of the EE azide) and ferromagnetic along the other edge (because of the EO mode of the μ_4-N_3^- ligand and reinforced by an additional EO azide in complexes **36**, **37** and **38**). The diagonal exchange is weakly ferromagnetic because of the large Ni–NNN–Ni torsion angle involved. The overall result is an $S = 0$ ground state for all complexes.

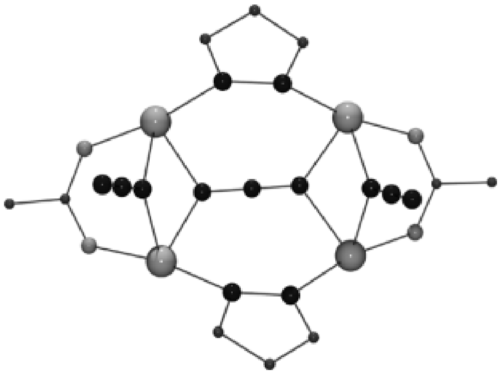


Figure 7. Core of compound $[Ni_4(pzate3)_2(N_3)_3(AcO)_2](ClO_4)$ (**36**), common to compounds **36**–**38**. Compound **39** shows a very similar core with coordination of a second carboxylate instead of the end-on azido ligands.

$[Cu_4(tpimim)_2(N_3)]Cl$ (40)

Complex **40** is the only Cu^{II} species that contains azide in the $\mu_{1,1,3,3}$ mode.[58] As in complexes **36**–**39**, the central μ_4-N_3^- in **40** bridges a rectangle of four metals that now exhibits C_{2h} symmetry. The metals spanned by two of the opposite edges are not supported by any additional ligand, while the other two sides are also spanned by two heptadentate tpimim ligands. Contrary to the Ni compounds with a central μ_4-N_3^- ligand, complex **40** exhibits very weak magnetic coupling. The likely reason for this is that the ligand is bound to Cu^{II} at the apical positions and is thus far from the magnetic orbitals. The interaction between the ions bridged by the tpimim ligand is weakly ferromagnetic, most probably because of the imidazolidine bridge, rather than the azide. The coupling mediated by EE azide pathways is, as usual, antiferromagnetic.

A Tetrahedral and a Rectangular M_4 Cluster

The cluster $[Mn_4O(N_3)(O_2Bz)_3(phpyCNO)_4]$ (**41**)[59] shows a tetrahedral $[Mn^{IV}Mn^{II}_3O]^{8+}$ core (Figure 8) and is a rare example of a mixed-valent tetranuclear manganese complex exhibiting a $2e^-$ difference between oxidation states. There are four types of bridging ligands, including one N_3^- group, which contributes to the ferromagnetic interaction between Mn^{II} centres. The Mn^{IV} ion is, in turn, coupled antiferromagnetically to the other three metals and this leads to a total spin ground state of $S = 6$, as shown by bulk magnetic measurements as well as EPR spectroscopy. The cluster $[Ni_4(SO_4)_2(N_3)_2(SH)_2(pyMeCNOH)_4]$ (**42**)[60] is a rectangle with two edges spanned by EO μ-N_3^- and the other two by μ-SH^- groups. The latter presumably originate from reduction of sulfate ligands. Two such ligands cap each face of the rectangle in an η^2:μ_4-SO_4^{2-} coordination mode and four pyridyl oxime ligands chelate the four metals to complete their octahedral coordination environment. No magnetic data are yet available for this compound.

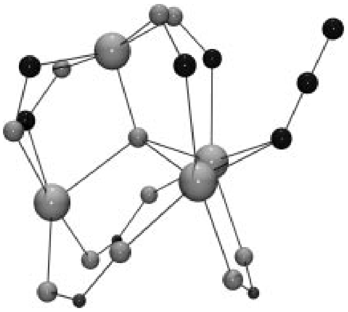


Figure 8. Core of compound $[Mn_4O(N_3)(O_2Bz)_3(phpyCNO)_4]$ (**41**).

An Mn_4 Dimer of Separate Dimers

The compound $[Cu_4(4tacn)(N_3)_4](PF_6)$ (**43**)[61] is formed by a large ligand containing four tacn macrocycles (Scheme 1) that bind four Cu^{II} ions, which are linked as two separate pairs through double μ-N_3^- bridges. As expected, ferromagnetic coupling operates within these pairs, whereas the presence of zero-field splitting and/or inter-pair interactions was modelled with a Curie–Weiss constant.

Three Azido Bowties in M_5 Clusters

Azido-bridged clusters of five metals are much less common than tetranuclear complexes. Three Ni derivatives exhibit this nuclearity, namely $[Ni_5(N_3)_4(phpyCNO)_4(O_2CR)_2(MeOH)_4]$ (R = H **44a**, Me **44b**)[62] and $[Ni_5(N_3)_4(phpyCNO)_4(phpyCNOH)_4](ClO_4)_2$ (**45**).[63] These three compounds can be described as two Ni^{II} triangles with a common vertex (a bowtie) linked by means of oximato and azido bridges in two different arrangements (Figure 9): **44a** and **44b** contain oximato bridges between the central and the peripheral Ni^{II} atoms with $\mu_{1,1}$-azido and carboxylate bridges between the external cations and $\mu_{1,1,1}$ bridges at the centre of each triangle, whereas **45** has four $\mu_{1,1}$ bridges between the central and external Ni^{II} atoms and the centres of the triangles are occupied by oximate μ_3-(NO) bridges. The main difference in the preparation of these compounds is the presence in the reaction mixture of either a coordinating anion (carboxylate) or a non-coordinating one (perchlorate). Preliminary magnetic measurements indicate an $S = 5$ ground state for **44b** and **44b**. Moreover, the frequency dependence of the magnetisation has been observed for **44a**, which constitutes initial evidence that this compound behaves as an SMM. No magnetic data have been collected yet for complex **45**.

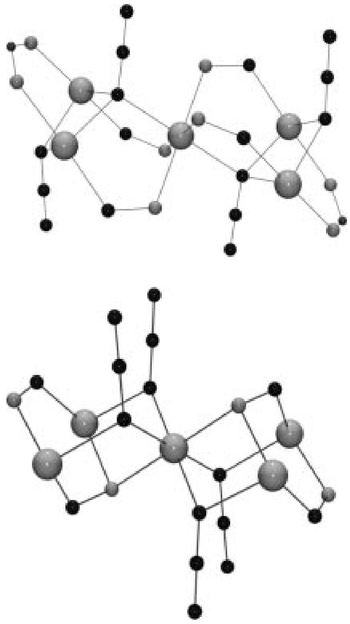


Figure 9. Core of compounds $[Ni_5(N_3)_4(phpyCNO)_4(O_2CH)_2(MeOH)_4]$ (**44**) (top) and $[Ni_5(N_3)_4(phpyCNO)_4(phpyCNO)_4](ClO_4)_2$ (**45**; bottom). It is noticeable that N_3^- and oximate exchange their roles from one compound to the other.

A Linear Cu^{II}_5 Arrangement

The compound $[Cu_5(terpy)_2(N_3)_{10}]$ (**46**; terpy = terpyridine) comprises a linear central trinuclear unit held together by two double μ-N_3^- bridges, with each external copper ion of this unit linked by a single EO azido ligand to a $[Cu(terpy)(N_3)]^+$ moiety.[64] Bulk magnetisation studies reveal that the peripheral Cu^{II} centres essentially do not interact with the central unit, and the latter exhibits weak ferromagnetic coupling.

M_6: The Largest Cycle

The only example of an azide-bridged cyclic cluster with six metals (Figure 10) is the complex $[KNi_6(CO_3)(N_3)_6(OAc)_3(dpkMeCN)_3]_2[K_2(H_2O)_2]$ (**47**).[65] It crystallises in the form of dimers of hexanuclear wheels that are connected through weak interactions to K^+ ions. Complex **47** is the only known metallacycle that is symmetrically bridged by N_3^-, besides complex **8** (see above). In addition to azide, the bridges within the cycle are completed by three *syn*,*syn*-OAc groups, which alternate with the μ-O atoms from three $dpkMeCN^-$ ligands, and by a central μ_6-CO_3^{2-} group. This compound exhibits intramolecular ferromagnetic coupling, as expected, which confers it the spin ground state $S = 6$. Fitting of the experimental data yielded the values $J_1 = 2.9$ and $J_2 = 25.4\ cm^{-1}$, respectively, for the two types of bridge present (using the convention $H = \Sigma\text{–}J_{ij}S_iS_j$ for the exchange coupling). In both cases, the μ-N_3^- bridge determines the ferromagnetic nature of the coupling. The strongest coupling is ascribed to the countercomplementarity effect[66] caused by the simultaneous presence of a μ-OAc^- ligand. The other path involves an alkoxide bridge, which does not have the symmetry to cause this effect. D was found to be positive ($10.3\ cm^{-1}$) in this complex, which explains the lack of SMM behaviour.

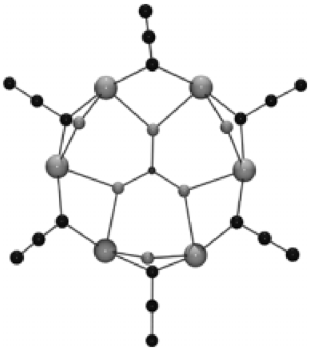
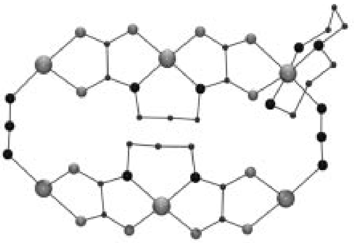


Figure 10. Core of one of the hexanuclear subunits of $[KNi_6(CO_3)(N_3)_6(OAc)_3(dpkMeCN)_3]_2[K_2(H_2O)_2]$ (**47**) showing the unusual μ_6-carbonato anion in the centre of the complex.

M_6: A Dimer of Trinuclear Units and a Trimer of Dinuclear Motifs

The complex $Na_2[Ni_4Cu_2(dpa)_4(pbo)_2(H_2O)_2](ClO_4)_4$ (**48**; dpa = 3,3′-diaminodipropylamine) consists of a hexanuclear cyclic structure in which the azido ligands bind two [NiCuNi] subunits (Figure 11, top). In spite of the heterometallic nature of the cycle, the azido bridges only link nickel atoms. Inside each trinuclear unit there is strong antiferromagnetic coupling via the oxamato ligands ($J_1 = –101\ cm^{-1}$). The large Ni–N_3–Ni torsion angle justifies the low value for the interaction provided by the azido bridge ($J_2 = –3.2\ cm^{-1}$ in the $H = \Sigma\text{–}J_{ij}S_iS_j$ convention), which results in an $S = 0$ ground state.[67]



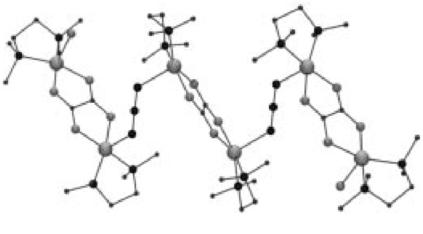


Figure 11. Top: plot of the dimer of trimers $Na_2[Ni_4Cu_2(dpa)_4(pbo)_2(H_2O)_2](ClO_4)_4$ (**48**). The copper atoms show a square-planar coordination whereas the Ni atoms in the corners exhibit an octahedral environment. For clarity, only one complete coordination sphere of the Ni atoms is shown. Bottom: plot of the trimer of dimers $[Cu_6(tmen)_6(N_3)_2(C_2O_4)_3(H_2O)_2](ClO_4)_4$ (**49**).

The hexanuclear complex $[Cu_6(tmen)_6(N_3)_2(C_2O_4)_3(H_2O)_2](ClO_4)_4$ (**49**; tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[68] is a rare combination of $[Cu_2(tmen)_2(C_2O_4)]^{2-}$ units connected by two EE N_3^- groups, with both external metallic ions capped by H_2O molecules (Figure 11, bottom). The magnetic behaviour of this linear cluster is governed by the strong antiferromagnetic coupling within the oxalate-bridged pairs, with the coupling through azide remaining negligible. Another hexanuclear cluster results from dimerisation of $[Cu_3]$ units bound to a trinucleating ligand, each of which features one pair of Cu^{II} ions supported by μ-N_3^-.[69]

M_7: An Unusual Nuclearity

There is only one compound with a nuclearity of seven containing azido bridges and it has the formula $[Ni_7(AcO)_6(py_2CNO)_6(N_3)_2(H_2O)_2]$ (**50**).[70] The compound consists of two pairs of Ni^{II} triangular arrays fused through one edge and sharing the central cation (Figure 12). The four triangles are supported by four μ_3-(NO) oximate bridges, and additional bridging is provided by two deprotonated oximate groups, six *syn*,*syn* acetate ligands and two EO azides, whereas peripheral coordination is completed by

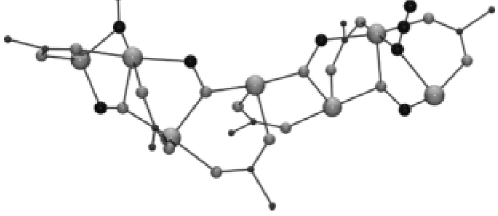


Figure 12. Core of $[Ni_7(AcO)_6(py_2CNO)_6(N_3)_2(H_2O)_2]$ (**50**).

two water molecules. Preliminary susceptibility measurements indicate an $S = 3$ ground state, which is greater than the expected value ($S = 1$) for a purely antiferromagnetic cluster and suggests the presence of ferromagnetic interactions between the nickel atoms bridged by the azido bridge; the remaining interactions remain antiferromagnetic.

M_8: A Nickel-Based SMM

The SMM $[Ni_8Na_2(N_3)_{12}(OBz)_2(mpo)_4(Hmpo)_6(EtOAc)_6]$ (**51**; Figure 13)[71] was prepared in light of the benefits of using N_3^- to dramatically increase the spin of metal clusters in a family of $[M_9]$ complexes (see below). Complex **51** features an $[Ni_8(N_3)_{12}]^{4+}$ core in the form of four "defective cubanes" bound to two additional peripheral Ni^{II} ions. In addition, the complex contains two Na^+ ions. The bridging within this cluster is completed by two μ-OBz^- groups and four pyrazolinolate ligands (mpo^-); terminal ligands saturate the remaining positions of the metals (six Hmpo and six EtOAc molecules). The presence of EO N_3^- groups connecting all Ni^{II} centres confers ferromagnetic character on this cluster and leads to an $S = 8$ spin ground state. Many high-spin clusters do not behave as SMMs because they do not possess magnetic anisotropy ($D \approx 0$) or because they are not of the Ising type ($D > 0$). In this case, however, $D = -0.07\ cm^{-1}$, and the cluster exhibits slow relaxation of the magnetisation, as manifested by the presence of hysteresis loops at very low temperatures.

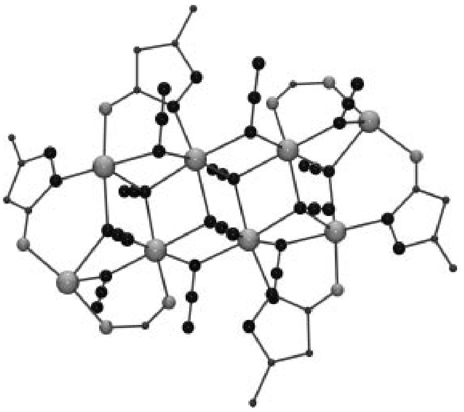


Figure 13. Plot of $[Ni_8Na_2(N_3)_{12}(OBz)_2(mpo)_4(Hmpo)_6(EtOAc)_6]$ (**51**). For clarity, only the bridging ligands are shown. Compound **51** is one of the few complexes in which the inner core contains exclusively end-on azido bridges.

$[\{Mn_4O(sae)_4(N_3)(MeOH)\}_2(N_3)](N_3)$ (52)

Complex **52** is the other only example of an azide-bridged cluster with a nuclearity of eight. The structure consists of two tetranuclear units linked to one other by a single $\mu_{1,3}$-N_3^- ligand and held together by Schiff-base ligands (sae) and one EO azide.[72] The overall coupling within the cluster was found to be antiferromagnetic and no further discussion was offered.

M_9: Activation of High Spin Numbers by Azide

The nuclearity of nine has been found for three analogous azide-containing complexes obtained with three different metals. These are $[Ni_9(N_3)_2(AcO)_8(dpkO)_4]$ (**53**),[73] $[Co_9(N_3)_2(AcO)_8(dpkO)_4]$ (**54**)[74] and $[Fe_9(N_3)_2(AcO)_8(dpkO)_4]$ (**55**).[75] The core of these compounds can be described as two square pyramids of metals with a common apex, the latter exhibiting (Figure 14) an unusual eight coordination environment (MO_8). Each doubly deprotonated $dpkO^{2-}$ ligand links up to five cations. The basal edges of each pyramid are spanned by a crown of four *syn,syn* acetate ligands and its square face is capped by one μ_4-N_3^- ligand. Azido ligands acting as a bridge between four cations are very unusual and these three compounds are currently the only examples of the monoatomic $\mu_{1,1,1,1}$ coordination mode for this ligand. The nickel and cobalt compounds are highly symmetric due to the presence of a crystallographic C_4 axis, whereas for the iron compound (**55**) the structure is the same but the symmetry is only idealised. In the three compounds, introduction of EO N_3^- signifies the establishment of ferromagnetic interactions within both groups of four basal metals, thereby dramatically increasing

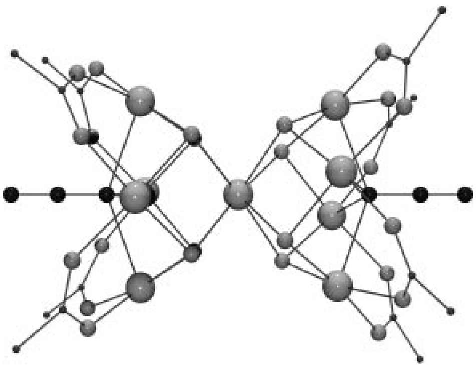


Figure 14. Core of compound $[Ni_9(N_3)_2(AcO)_8(dpkO)_4]$ (**53**). With minor differences besides the metals, this core is the same for **54** and **55**.

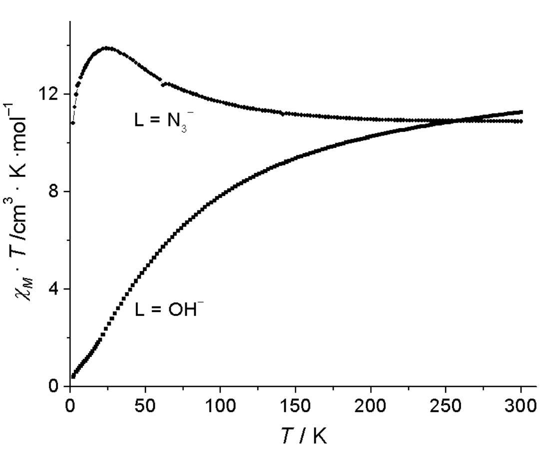


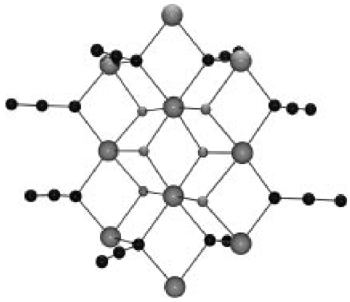
Figure 15. Plots of $\chi_M T$ vs. T for complexes $[Ni_9(L)_2(AcO)_8(dpkO)_4]$ [$L = N_3^-$ (**53**) and the related compound with $L = OH^-$]. These compounds provide a good example of how end-on azido coordination can drastically modify the magnetic properties of clusters with the same skeleton.

the spin ground states (S = 9 for **53**, S = 14 for **55** and undetermined for **54** because of the spin-orbit coupling). These values are in sharp contrast to those observed for analogous clusters containing OH^- bridges instead of N_3^-, where the coupling is systematically antiferromagnetic and the ground state is the equivalent to that of only the central metal (Figure 15). When studied under an ac magnetic field, complex **55** showed an SMM response, with frequency-dependent χ_M'' signals (out-of-phase magnetic susceptibility) peaking between 2.34 and 2.00 K for frequencies varying between 1000 and 50 Hz. The energy barrier, ΔE, calculated from these signals is 29 cm^{-1}.

High-Spin Decanuclear Clusters

[$Ni_{10}(tmp)_2(N_3)_8(acac)_6(MeOH)_6$] (56)

This complex is an elegant example of one of the main messages of this review, which is that incorporation of azide within reaction schemes leading to coordination clusters is not only beneficial from a structural point of view but is potentially very convenient for changing the magnetic properties. Compound **56** originates from the reaction between $Ni(acac)_2$, the tripodal ligand H_3tmp and NaN_3 in methanol.[76] The structure (Figure 16, top) comprises a planar [$Ni_{10}O_{10}(N_3)_8$] core where the oxygens originate from two μ_6-tmp^{3-} ligands and $acac^-$ groups. The latter appear in two coordination modes (terminal and bridging), whereas the N_3^- ligands are all bridging (μ or μ_3). Magnetic measurements show this compound to possess an S = 10 spin ground state and large, Ising-type magnetoanisotropy, which converts it into the slowest relaxing Ni SMM known to date. This property is corroborated by the presence of temperature-dependent hysteresis loops of the magnetisation (Figure 17).



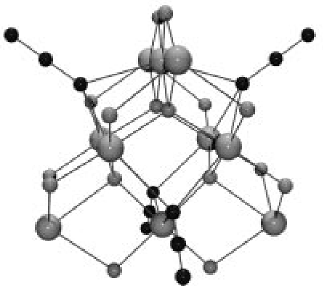


Figure 16. Top: core of [$Ni_{10}(tmp)_2(N_3)_8(acac)_6(MeOH)_6$] (**56**). In a similar way to **51**, the core is formed by defective cubanes linked by end-on azido bridges. Bottom: core of [$Mn_{10}O_4(N_3)_4(hmp)_{12}$]-$(X)_2$ (**57**, **58**) in which the peripheral end-on azido bridges link the sub-sheets of Mn atoms.

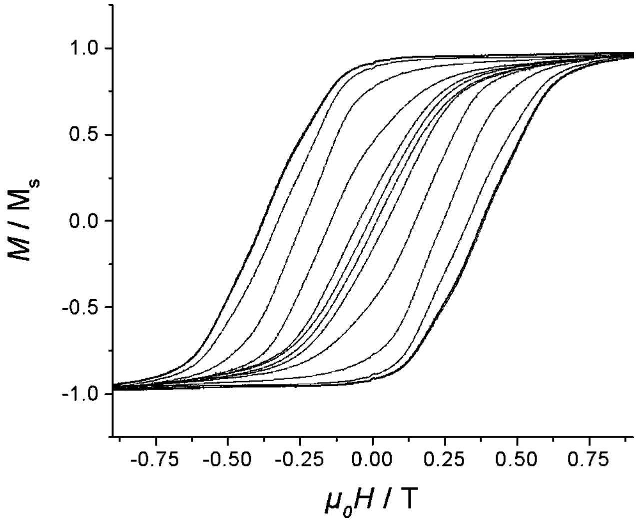


Figure 17. Single crystal magnetisation (M) vs. field (H) hysteresis loops for complex **56** at a field sweep rate of 0.002 $T s^{-1}$ and temperatures of 0.7, 0.6, 0.5, 0.4, 0.3, 0.2 and 0.04 K (the loops become wider with increasing temperature); the magnetisation is normalised to its saturation value.

[$Mn_{10}O_4(N_3)_4(hmp)_{12}$]$(X)_2$ (X = N_3^- 57, ClO_4^- 58)

The very recently reported complexes **57** and **58**[77] display high symmetry (crystallographically imposed T) and each is formed by a central [Mn^{III}] octahedron bridged by four μ_3-N_3^- ligands and four μ_4-O^{2-} atoms that also bind to four external Mn^{II} ions (Figure 16, bottom). There are twelve hmp^- ligands that ensure the bridging between the Mn^{III} and Mn^{II} centres as well as the peripheral ligation. The spin ground state in both clusters is S = 22, the maximum possible, thanks to the ferromagnetic interaction induced by the azide ligands and by the Mn^{III}–O–Mn^{II} connections with very acute angles. Given the high symmetry of the cluster, the total D value is practically zero and therefore these compounds do not show SMM behaviour despite displaying one of the highest spin values ever observed for a molecular system.

M_{19}: The Highest Ground Spin State (S = 83/2)

The use of azide in combination with an oxide source and the polyalcohol H_3bhmep (Scheme 1) in a reaction with $MnCl_2$ led to the formation of the nonadecanuclear cluster [$Mn_{19}O_8(N_3)_8(Hbhmep)_{12}(MeCN)_6$]$Cl_2$ (**59**, Figure 18).[78] The presence of azide leads again to the maximum possible spin multiplicity for the cluster, leading to the highest molecular spin ground state ever observed (S = 83/2). The small overall magnetic anisotropy, however, is the reason why hysteresis of the magnetisation is only observed below 0.5 K. Whether this behaviour at low temperature is ascribed to the SMM nature of **59** or is due to other reasons remains an open question.

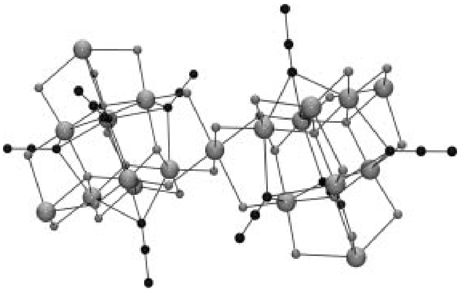


Figure 18. Core of $[Mn_{19}O_8(N_3)_8(Hbhmep)_{12}(MeCN)_6]Cl_2$ (**59**).

The M_{25} Cluster $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6](Cl)_2$ (60)

Complex **60** is the second highest nuclearity cluster constructed to date with the help of azide ligands (Figure 19).[79] The composition of the metal ions is 6 Mn^{II}, 18 Mn^{III} and Mn^{IV}. Of the twelve N_3^- ligands, six are terminal and six bridge two metals each. The structure is held together by μ_4-O^{2-}, μ_3-O^{2-} and μ_3-OH^- ions, with the help of Hpdm or pdm^- ligands. The total spin of the cluster is postulated to be $51/2 \pm 1$, presumably as a result of a combination of ferro- and antiferromagnetic interactions. The SMM behaviour of **60** was proven through micro-squid measurements, which revealed the presence of low-temperature hysteresis loops of the magnetisation.

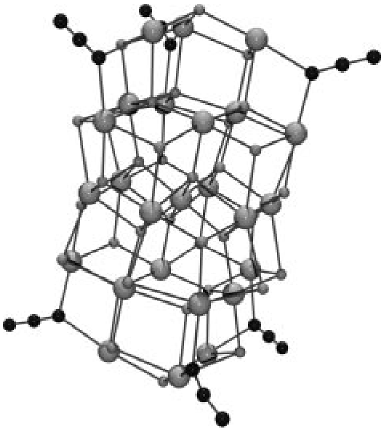


Figure 19. Core of $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6](Cl)_2$ (**60**).

Mn_{32}: A Truncated Cube

The largest manganese cluster containing bridging azides is $[Mn(bpy)_3]_{1.5}[Mn_{32}(thme)_{16}(bpy)_{24}(N_3)_{12}(OAc)_{12}](ClO_4)_{11}$ (**61**).[80] This spectacular cluster is made up of eight tetranuclear moieties, each cemented by the oxygen atoms of six tripodal $thme^{3-}$ ligands (Figure 20). These $[Mn_4]$ "stars" are located at the vertices of a cube and connected to each other through acetate and EO azide bridges. Chelating bpy helps to complete the coordination. A combination of weak ferro- and antiferromagnetic interactions leads to a spin ground state of close to 9 (or 10) with many low lying excited states, which precludes an accurate determination and characterisation of the spin ground state.

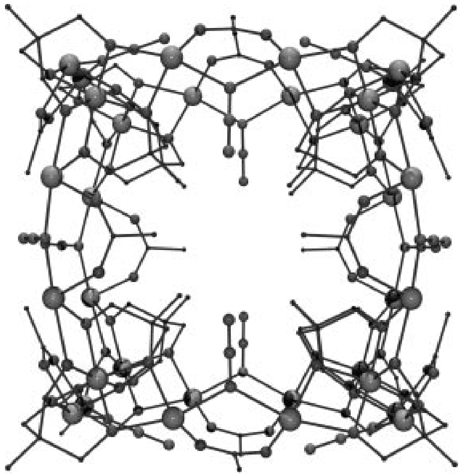


Figure 20. Core of $[Mn(bpy)_3]_{1.5}[Mn_{32}(thme)_{16}(bpy)_{24}(N_3)_{12}(OAc)_{12}](ClO_4)_{11}$ (**61**).

Clusters with Heterometallic Azide Bridges

Compared with the plethora of homometallic azido systems reported to date, compounds in which the azido ligand acts as a bridge between two different paramagnetic centres (excluding different oxidation states of the same metallic atom) are extremely rare. The first such compound reported was an $[Ni_2Mn]$ triangular system containing $\mu_{1,1}$-azido bridges.[81] A few more examples of low nuclearity systems of this type have been reported recently, such as one [CuNi] dinuclear complex with $\mu_{1,1}$-azido bridges,[82] two trinuclear clusters, [FeCuFe] and [FeNiFe], linked by means of $\mu_{1,3}$-azido bridges[83,84] and two $\mu_{1,3}$ chain-like [NiMn] or [CoMn] alternating compounds.[85]

To the best of our knowledge, there is only one system with a nuclearity higher than four that contains heterometallic azido bridges, namely $[Cu_4(O_2cyclam2)_4Mn_2(N_3)_4]$ (**62**).[86] The asymmetric unit of this compound consists of a [CuMnCu] trinuclear unit in which the manganese atom is bridged to both copper atoms by means of oxamide bridges (Figure 21). Each Cu^{II} ion is embedded within a macrocycle that is part of the oxamide moiety. The remaining coordination sites of the octahedral coordination sphere around manganese are occupied by two azido ligands. One of them acts as a terminal ligand whereas the second azido binds to the axial position of the square-pyramidal copper atom of

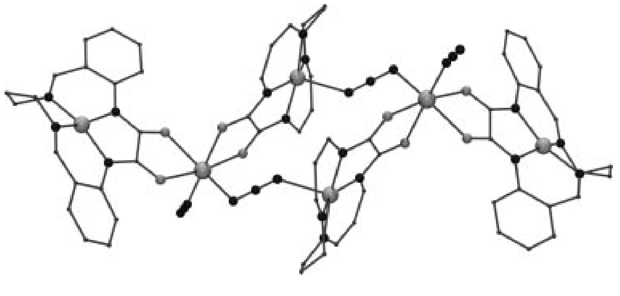


Figure 21. Plot of the structure of compound $[Cu_4(O_2cyclam2)_4Mn_2(N_3)_4]$ (**62**). Mn atoms exhibit hexacoordination whereas Cu atoms are coordinated only to the macrocyclic ligand.

a second trinuclear unit. The role of the azido bridges in the magnetism of **62** is marginal since these are coordinated to the axial sites of the copper atoms.

Azido Clusters of Transition Metals and Polyoxometallates

A relatively new class of molecular magnetic materials is that whose members are prepared by using lacunary polyoxometallates (POMs) in combination with paramagnetic transition metal ions.[87] Recently, very interesting examples have been reported where the azide ligand has been employed as both bridge and magnetic coupler. Thus, the new cluster anions $[(\gamma\text{-SiW}_{10}O_{36})_2Mn_4(OH)_4(N_3)_2(H_2O)]^{10-}$ (**63**), $[(\gamma\text{-SiW}_{10}O_{36})_2Cu_4(N_3)_4]^{12-}$ (**64**), $[(\gamma\text{-SiW}_{10}O_{36})_2Cu_4(H_2O)_2(N_3)_4]^{12-}$ (**65**) and $[(SiW_8O_{31})_3Cu_9(OH)_3(H_2O)_6(N_3)_4]^{10-}$ (**66**) have been prepared,[88,89] and their magnetic properties analysed. The latter is especially remarkable because it features an unprecedented coordination mode for azide, namely $\mu_{1,1,1,3,3,3}$ (Scheme 2).[88]

General Remarks about the Coordination by Azide

The above sections of this review have shown that the azido ligand is able to act as a bridge within high nuclearity clusters and can do so in a large variety of coordination modes. These are summarised in Scheme 2, and can be divided into two main groups: (i) modes in which the two ends of the ligand act as donors ($\mu_{1,3}$, $\mu_{1,1,3}$, $\mu_{1,1,3,3}$ or $\mu_{1,1,1,3,3,3}$), which need at least two metallic ions placed at more than 5 Å, and (ii) modes where the azido ligand acts as a monoatomic bridge ($\mu_{1,1}$, $\mu_{1,1,1}$ or $\mu_{1,1,1,1}$ modes) linking two or more metallic centres separated by about 3 Å.

EE N_3^- bridges typically lie within the core of the cluster and are usually surrounded by other organic ligands, as can be seen in Figure 22, left. In contrast, EO azido bridges are attached to the metallic centres and point outwards approximately perpendicular to the surface of the cluster (Figure 22, right). In the latter case, the space requirement is minimal.

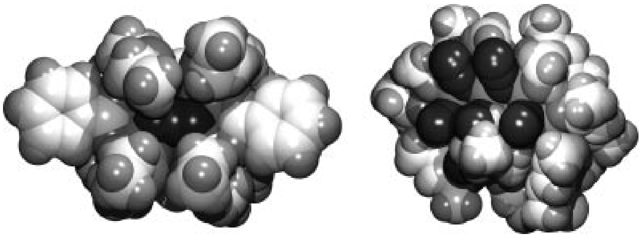


Figure 22. Left: space-filling diagram of complex **37**, emphasising the insertion of the EE N_3^- ligand within the cluster. Right: space-filling diagram of complex **56**, showing the efficiency of EO N_3^- in bridging metals with minimal space requirements.

EE is the most common coordination mode in extended systems such as chains, planes or 3D azido derivatives, whereas alternating $\mu_{1,3}/\mu_{1,1}$ compounds are not rare. However, coordination polymers with exclusively EO azido bridges are very scarce. In contrast, cluster azido chemistry is clearly dominated by EO coordination modes. Because of the similar stability of both coordination modes, the steric hindrance becomes one of the most determining factors favouring monoatomic coordination over EE modes.

Analysis of the structures reviewed above allows other trends regarding coordination by azide to be identified. It has been observed that single EO azido bridges are extremely rare, something that was known already from extended azido-based systems. Therefore, additional bridges always support the presence of μ-N_3^- groups. These are often the usual bridges found in cluster coordination chemistry, such as oxido, hydroxido, alkoxido, oximato or carboxylate groups (in addition to N_3^- itself), which accommodate pairs of metals at M···M distances in the neighbourhood of 3 Å (Figure 23). Therefore, the core of most azido clusters reported to date is made up of such combinations of ligands. It must be pointed out, however, that a few prominent examples exist where the metallic core is held together almost exclusively by N_3^- ligands, such as complexes **18** (cubane), **25** (double defective cubane), **46** (linear pentanuclear) and **51** (Ni_8).

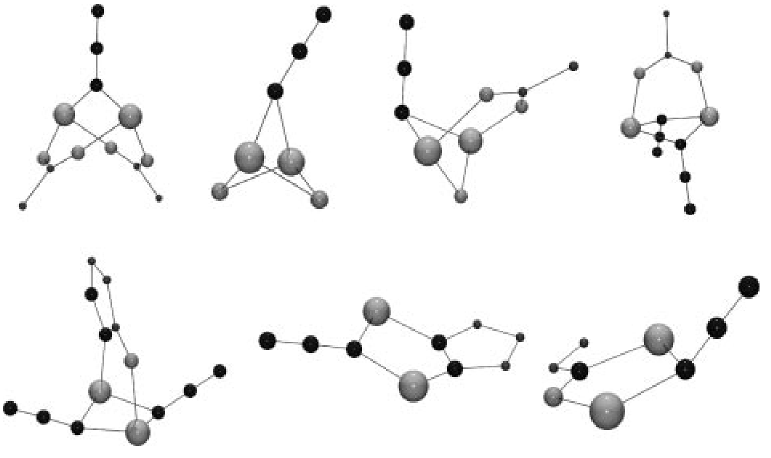


Figure 23. Several of the bridges encountered within the clusters of this review, involving the end-on azido ligand and at least a second bridge. Among the latter, the most common are oxido, hydroxido or carboxylato, but other bridges such as pyrazolato, pyrazolinolato or oximato are also not rare.

Conclusions and Perspectives

The azide ligand has characteristics that render it very attractive for the synthesis of magnetic clusters. From a structural point of view it can participate in multiple bridges, very often in combination with other conventional ligands of cluster coordination chemistry (such as oxides or carboxylates). Magnetically, it usually induces ferromagnetic interactions that have yielded clusters with ground states ranging between $S = 4$ and 83/2. The unusually high number of compounds in this family that show SMM responses is also notable.

If we consider that the vast majority of these compounds have been synthesised in the last five years, we can suppose that the exploitation of this ligand for the synthesis of novel clusters with new and interesting properties relevant to SMM research is only in its infancy and that a very eventful and promising future lies ahead. We hope that this review will constitute an adequate reference for scientists eager to know about the state of this sub-discipline of magnetic cluster synthesis in its early stages. Given the speed at which this sub-area is developing, we are acutely aware that this account will soon become outdated.

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