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Rational Assembly of High-Spin Polynuclear Magnetic Complexes into Coordination Networks: the Case of a [Mn_4] Single-Molecule Magnet Building Block

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Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday

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The synthesis of transition-metal high-spin complexes and of infinite coordination networks of these high-spin carriers now represents a recognized subdiscipline of coordination chemistry. This new research trend has been particularly encouraged by the discoveries that molecular and one-dimensional coordination aggregates may behave as nanomagnets, as illustrated by the so-called single-molecule magnets (SMMs) and single-chain magnets (SCMs). While the synthesis of isolated polynuclear high-spin complexes still rely mostly on serendipitous assembly with appropriate ligands, the synthesis of SCMs or extended networks of high-spin complexes demands a more designed and controlled bottom-up assembly of precursor complexes and bridging species selected for their coordination abilities. In this context, the case of a [Mn_4] SMM is unique in the literature, as one-, two-, and three-dimensional networks have been rationally designed by using this SMM unit as a building block, giving rise to original magnetic properties. This review gathers all reported systems that we know of, having the corresponding [Mn_4O_6] core, either in isolated complexes or in frameworks. Their structures and, when relevant, the synthetic strategy and magnetic properties are described. The demonstrated and potential outcomes, in terms of physical properties, of such coordination assemblies of high-spin complexes are then discussed. These are highlighted through examples with other building blocks, to broaden the scope of possible strategies and building blocks, and thus provide a basis for the further development of this promising area.

Introduction

The synthesis of paramagnetic metal complexes of high nuclearity and/or spin ground state (*S*) is currently an active field of research, stimulated to a large extent by the field of molecular magnetism,[1,2] and in particular since the discovery of single-molecule magnets (SMMs) in the early 1990s.[3] SMMs are coordination complexes that behave as single-domain magnetic particles exhibiting, at the molecular scale, slow thermal and quantum relaxation of magnetization and in some cases quantum phase interference below a so-called blocking temperature.[4] Intensified efforts towards the isolation of polynuclear coordination complexes also arose from the interest in biomimetics of natural polynuclear enzymes,[5] such as the water oxidation complex (WOC) of the photosynthetic system PSII, a Mn mixed-valent species with a [$CaMn_4$] core.[6] Nevertheless, and especially in the case of SMMs, these synthetic efforts largely rely on serendipitous assembly[7] of transition-metal ions in the presence of sources of small bridging ligands such as O^{2-}, N_3^-, Cl^-, or OH^-, in combination with chelating-bridging polydentate ligands. Obviously, these latter ligands are chosen for their ability to bridge metal ions in a closely packed manner, but also to form chelates preventing the formation of infinite networks. As a consequence of using mixtures of ligands with versatile coordination modes, this synthetic strategy has led to very diverse and large families of complexes,[8] but without a real control over the topology of the polynuclear metallic cores. Nevertheless, a number of examples are known, in which the ligands or precursor complexes have been designed to force a certain arrangement of the metal ion in the final polynuclear complexes.[9–13]

As shown by the pioneering work of W. Wernsdorfer et al. on dimers of SMMs,[14] the introduction of magnetic interactions between SMMs may allow the control of their quantum properties. Therefore, organizing SMMs or high-spin complexes into controlled coordination or supramolecular architectures became an appealing new goal for chemists, in particular because new magnetic properties may

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arise from such assemblies. Indeed, by using a step-by-step assembly of building blocks with selected magnetic properties such as SMMs, one-dimensional (1D) systems have been recently shown to potentially present slow relaxation of the magnetization, i.e. to exhibit magnet behavior.[15] In these materials, called by analogy single-chain magnets (SCMs),[16] the slow relaxation of magnetization depends on magnetic 1D correlations (J), although the high-spin ground state (S_T) and uniaxial anisotropy (D) of each unit along the chain remain of importance. More generally, these compounds are 1D assemblies of spins (metal ions, organic radicals, or metal–ion complexes) that can be coupled ferro- or antiferromagnetically. The latter case corresponds to systems with a noncompensation of spins along the chain (ferrimagnetic or canted-antiferromagnetic arrangements).

More generally, isolation of extended coordination networks based on paramagnetic ions or polynuclear complexes is sought for traditional magnetic properties. In order to obtain high-temperature magnets, chemists working in this field have tried to stabilize three-dimensional (3D) structures, although most of the time low-dimensional assemblies (1D, 2D) are obtained. To gain some molecular control in this so-called bottom-up approach, important synthetic parameters must be considered such as (i) the ligands used as coordination and magnetic links, (ii) the metal ions used and their coordination preferences, and (iii) the complexes used as building blocks and their coordination abilities. In this respect, the complex-as-ligand approach and the use of cyanide bridging represent two widely used strategies, which have resulted in numerous interesting systems.[17,18] In this context, the use (and selection) of stable preformed complexes possessing coordination properties allowing their assembly into extended networks is particularly attractive. The richness of possibilities is tremendous. The choice of the complex building-block allows access to different types of nodes (control over dimensionality through the number and position of potential coordination sites) and properties (spin state, magnetic anisotropy, optical or electrical properties, etc.). Furthermore, variation of the linker will also affect the organization of the nodes within the solid and thus influence the dimensionality of the system. In the case of magnetic materials, the linker is of paramount importance for the control of the magnetic interactions among the building blocks. Obviously, the way these building blocks are assembled in the solid (orientation, isolation) is fundamental for its physical properties, and therefore the rational assembly of the building blocks represents a major issue for chemists of this field.

There are still only a limited number of examples in which extended coordination compounds presenting interesting and original magnetic properties were obtained *rationally* from preformed polynuclear complexes. Nevertheless, the field is very active and constitutes an ideal topic for a microreview. A particular focus on a specific [Mn_4] SMM building block will be given here, as it allows the description of various synthetic approaches, dimensionalities, and potential outcomes of such assemblies. As far as we know, all coordination compounds containing the corresponding [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core[19] are included in this review and are listed in Table 1. Isolated complexes are first described, highlighting those that could be used as building blocks. Compounds presenting significant intermolecular interactions between the [Mn_4] building blocks resulting in infinite supramolecular arrays are given separately, and the effect of these weak interactions on the magnetic properties are described when relevant. Then the systems presenting infinite coordination networks of the [Mn_4] building blocks are reviewed, with a short description of their magnetic properties. The compounds in which the [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core was found only as part of a larger (oxido, hydroxido, carboxylato) core[20] will not be discussed here. In

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Rodolphe Clérac, born in 1971 in Versailles (France), received his education at the University of Bordeaux 1, France. His Ph.D. work was devoted to the physical properties of molecular antiferromagnetic materials under the supervision of Prof. C. Coulon (in 1997). After a short post-doctoral stay in the group of Prof. O. Kahn (ICMCB, Bordeaux), he joined Prof. K. R. Dunbar's group at Michigan State University (East Lansing, Michigan, USA) in 1998 and worked on the magnetic properties of coordination-chemistry-based materials. In 1999, he moved with Prof. K. R. Dunbar's group to Texas A&M university (College Station, Texas, USA), where he collaborated with Prof. F. A. Cotton on the magnetic properties of metal–metal-bonded complexes. He joined the University of Bordeaux 1 in 2000 as associate professor and then in 2008 became a full CNRS researcher. Since 2000, Dr. R. Clérac has developed at the Centre de Recherche Paul Pascal (CNRS) a new research group interested in the synthesis and physical studies of "molecular magnetic materials". In this research field, he has published ca. 170 articles. The main subjects currently developed in his group deal with hybrid magnetic materials (liquid crystals, gels, nanocomposites) and molecule-based magnets (including single-molecule magnets and single-chain magnets).

Table 1. List of all the compounds containing the butterfly $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ core discussed in this review, including in this order, formula, reference, dimensionality of the $[Mn_4]$ assembly, ground spin state S of the $[Mn_4]$ unit, uniaxial magnetic anisotropy D of the ground spin state, intra-$[Mn_4]$ magnetic interaction constants (where known), other relevant magnetic property data and compound number used in the text.

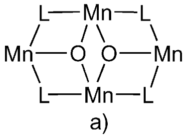
Compound[a]	Ref.	Dim.	S_T	D/k_B (K)[b]	J_{bb}/J_{wb} ($/k_B$ in K)[c]	Δ_{eff} or $\Delta_\tau/J'/k_B/T_C$ (K)[d]	Compound number
$[Mn_4(hmp)_6(NO_3)_2(MeCN)_2](ClO_4)_2\cdot 2MeCN$	[33]	0D	9	–0.31	9.1/6.0	SMM	**1**
$[Mn_4(hmp)_6(NO_3)_2(NO_3)_2]\cdot MeCN$	[33]	0D	9	–0.27	14.2/1.4	SMM	**2**
$[Mn_4(hmp)_6(NO_3)_2(H_2O)_2](NO_3)_2\cdot 2.5H_2O$	[34]	0D	9	–0.35	7.1/0.8	12.3	**3**
$[Mn_4(hmp)_6(H_2O)_2(NO_3)_2](ClO_4)_2\cdot 4H_2O$	[35]	0D	9	–0.34	13.3/1.23	19.6	**4**
$[Mn_4(hmp)_6(NO_3)_2(dcn)_2]\cdot 2MeCN$	[36]	0D	9	–0.34	9.80/1.61	20.9	**5**
$[Mn_4(hmp)_6(MeCO_2)_2(H_2O)_2](ClO_4)_2\cdot 4H_2O$	[37]	0D	9	–0.32	8.0/0.77	11.9	**6**
$[Mn_4(hmp)_6(PhCO_2)_2(H_2O)_2](ClO_4)_2\cdot 4MeCN\cdot 2H_2O$	[37]	0D	9	–0.37	7.5/1.3	13.8	**7**
$[Mn_4(hmp)_6(acac)_2(MeOH)_4](ClO_4)_2$	[33]	0D	9	–0.31	7.6/1.1	SMM	**8**
$[Mn_4(hmp)_6(H_2O)_4](ClO_4)_4\cdot 2H_2O$	[34]	0D	9	–	5.0/0.55	23.3	**9**
$[Mn_4(hmp)_6(Hhmp)_2](ClO_4)_4\cdot 2MeCN$	[34]	0D	1	–	0.25/–0.92	–	**10**
$[Mn_4(hmp)_6(Cl_3CCO_2)_2(H_2O)_2](ClO_4)_2$	[37]	0D	9	–	5.3/0.9	SMM	**11**
$[Mn_4(hmp)_6(MeCN)_2(H_2O)_2](ClO_4)_4\cdot 2MeCN$	[38]	0D	9	–0.33	8.56/0.66	23.3	**12**
$[Mn_4(Hpdm)_6(MeCO_2)_2](ClO_4)_2\cdot 2MeCN\cdot 2Et_2O$	[40]	0D	8	–0.35	11.6/0.6	17.3	**13**
$[Mn_4(Hpdm)_6(MeCO_2)_2](ClO_4)_2\cdot 2.5H_2O$	[40]	0D	9	–0.37	12.5/1.6	17.3	**13b**
$[Mn_4(mda_2)_2(mdaH)_2(PhCO_2)_4]\cdot CH_2Cl_2\cdot Et_2O$	[42]	0D	9	–0.22	–	15.3	**14**
$[Mn_4(bdea)_2(bdeaH)_2(tBuCO_2)_4]$	[43]	0D	9	–0.27	6.7/0.4	SMM	**15**
$[Mn_4(bdea)_2(bdeaH)_2(PhCO_2)_4]$	[43]	0D	9	–0.34	11.0/1.3	26.7	**16**
$[Mn_4(HL^1)_2(OH)_2(MeO)_2(bpy)_2]$	[44]	0D	1	–	–20.3/–5.0	–	**17**
$[Mn_4(tBu_2cat)_4(py)_6]$	[45]	0D	–	–	–	–	**18**
$[Mn_4(L^2)_2(O)_2](PF_6)_2\cdot 4MeCN$	[46]	0D	0	–	–	–	**19**
$[Mn_4(L^2)_2(O)_2](MnCl_4)\cdot MeCN$	[47]	0D	0	–	–	–	**20**
$[Mn_4(L^3)_2(O)_2(MeCO_2)_2]\ 4H_2O\cdot 2MeOH$	[48]	0D	0	–	–14.4/–5.3	–	**21**
$[Mn_4(L^4)_2(O)_2(MeCO_2)_2]\cdot 2MeCN$	[49]	0D	0	–	–3.6/–3.1	–	**22**
$[Mn_4(hmp)_6Br_2(H_2O)_2]Br_2\cdot 4H_2O$	[50]	1D/3D	9	–0.50	18.2/1.9	15.8/< 0/1.33	**23**
$[Mn_4(teaH_2)_2(teaH)_2(PhCO_2)_2](PhCO_2)_2\cdot MeCN$	[52]	1D H	9	–	9.5/0.6	20.3	**24**
$[Mn_4(teaH_2)_2(teaH)_2(PhCO_2)_2](PhCO_2)_2\cdot 0.7MeCN\cdot 0.3EtOH$	[43]	1D H	9	–0.33	12.3/2.6	22.6	**24b**
$[Mn_4(teaH_2)_2(teaH)_2(tBuCO_2)_2](tBuCO_2)_2$	[53]	1D H	9	–	10.1/0.1	SMM/< 0	**25**
$[Mn_4(teaH_2)_2(teaH)_2(MeCO_2)_2](MeCO_2)_2\cdot 2H_2O$	[52]	2D H	9	–	9.3/2.4	22.4	**26**
$[Mn_4(teaH_2)_2(teaH)_2(EtCO_2)_2](ClO_4)_2$	[52]	2D H	9	–	15.7/0.3	SMM/< 0	**27**
$[Mn_4(L^5)_2(MeO)_2(MeOH)_2]$	[54]	1D H		–	–		**28**
$[Mn_4(HL^6)_4Cl_2(MeOH)_4]\cdot 2Et_2O$	[56]	2D H	9	–	11.1/4.9	SMM	**29**
$[Mn_4(HL^6)_4Br_2(MeOH)_4]\cdot 2Et_2O$	[56]	2D H	9	–	17.9/4.7	SMM	**30**
$[\{Mn_4(hmp)_6(MeCN)_2\}\{Pt(mnt)_2\}_4][Pt(mnt)_2]_2$	[57]	2D, π	9	–0.30	14.4/0.8	18.7	**31**
$[Mn_4(hmp)_6(MeCO_2)_2](ClO_4)_2\cdot H_2O$	[37]	1D	9	–	6.5/1.9	37.3/–0.10	**32**
$[Mn_4(hmp)_6(ClCH_2CO_2)_2](ClO_4)_2\cdot 2H_2O$	[37]	1D	9	–	7.0/1.6	41.6/–0.12	**33**
$[Mn_4(hmp)_6(N_3)_2](ClO_4)_2$	[35]	1D	9	–	8.6/0.7	47/–0.15	**34**
$[Mn_4(hmp)_6Cl_2](ClO_4)_2$	[59]	1D	9	–0.62	–	SMM/–0.077	**35**
$[\{Mn_4(hmp)_6(MeCN)_2\}\{Pt(mnt)_2\}_2][Pt(mnt)_2]_2\cdot 2MeCN$	[57]	1D	9	–0.25	6.2/0.9	SMM	**36**
$[Mn_4(hmp)_6(dcn)_2](ClO_4)_2$	[36]	2D	9	–	9.12/1.02	–/–/4.6	**37**
$[Mn_4(hmp)_4(Hpdm)_2(dcn)_2](ClO_4)_2\cdot 2H_2O\cdot 2MeCN$	[36]	2D	9	–0.41	12.66/1.15	12.8/–/< 0.6	**38**
$[Mn_4(hmp)_4Br_2(MeO)_2(dcn)_2]\cdot 0.5H_2O\cdot 2thf$	[36]	2D	9	–	10.89/1.30	SMM/–/2.1	**39**
$[Mn_4(hmp)_4(OH)_2Mn(dcn)_6]\cdot 2MeOH\cdot 2thf$	[62]	3D	9	–0.41	7.1/1.5	–/–/4.1	**40**

[a] H_4L^1 = 1,2-bis(2-hydroxybenzamido)benzene; H_3L^2 = saltren; H_3L^3 = 1,5-bis(salicylidenamino)pentan-3-ol; H_3L^4 = 2,6-bis(salicylidenaminomethyl)-4-methylphenol; H_3L^5 = 1,5-bis(3-chlorido-5-nitro-salicylidenamino)pentan-3-ol; H_3L^6 = 2,6-bis(hydroxymethyl)-4-methylphenol. [b] Of the high-spin ground state. [c] Data reported in cm^{-1} have been converted to K for comparison; J_{bb} describes the interaction among the inner Mn ions, while J_{wb} describes that between an external and an inner Mn ion, whatever their oxidation states. [d] Magnetic properties: energy gap Δ_{eff} or Δ_τ associated with slow relaxation of magnetization in SMM or SCM, respectively; "SMM" indicates the observation of slow relaxation of magnetization without the evaluation of Δ_{eff}/inter-$[Mn_4]$ interaction constant J'/when relevant, critical temperature of the ordered antiferromagnetic phase.

the second part of this review, we intend to summarize the potential outcomes in terms of physical properties of such rational assembly of high-spin complexes, giving some relevant examples with other building blocks and various types of links. The reader will be systematically oriented to the original publications for detailed description of the magnetic properties, which are beyond the scope of this microreview.

Isolated $[Mn_4]$ Complexes: a Versatile Building Block

Tetranuclearity in oxido-based manganese complexes is quite common. Several families have been described in the literature in which the $[Mn_4]$ core presents a linear,[21] square,[22] basket,[23] cubane,[24] adamantane,[25] or so-called butterfly[26,27] topology. The butterfly $[Mn_4(\mu_3\text{-}O)_2]$ core is normally completed with additional bridges between external (or "wing") Mn ions and internal (or "body") ones. These additional bridges are either polynuclear (mostly carboxylates) or monatomic μ-oxido or μ-alkoxido groups resulting in a rhombic $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ core similar to the butterfly one (see Scheme 1).[28]

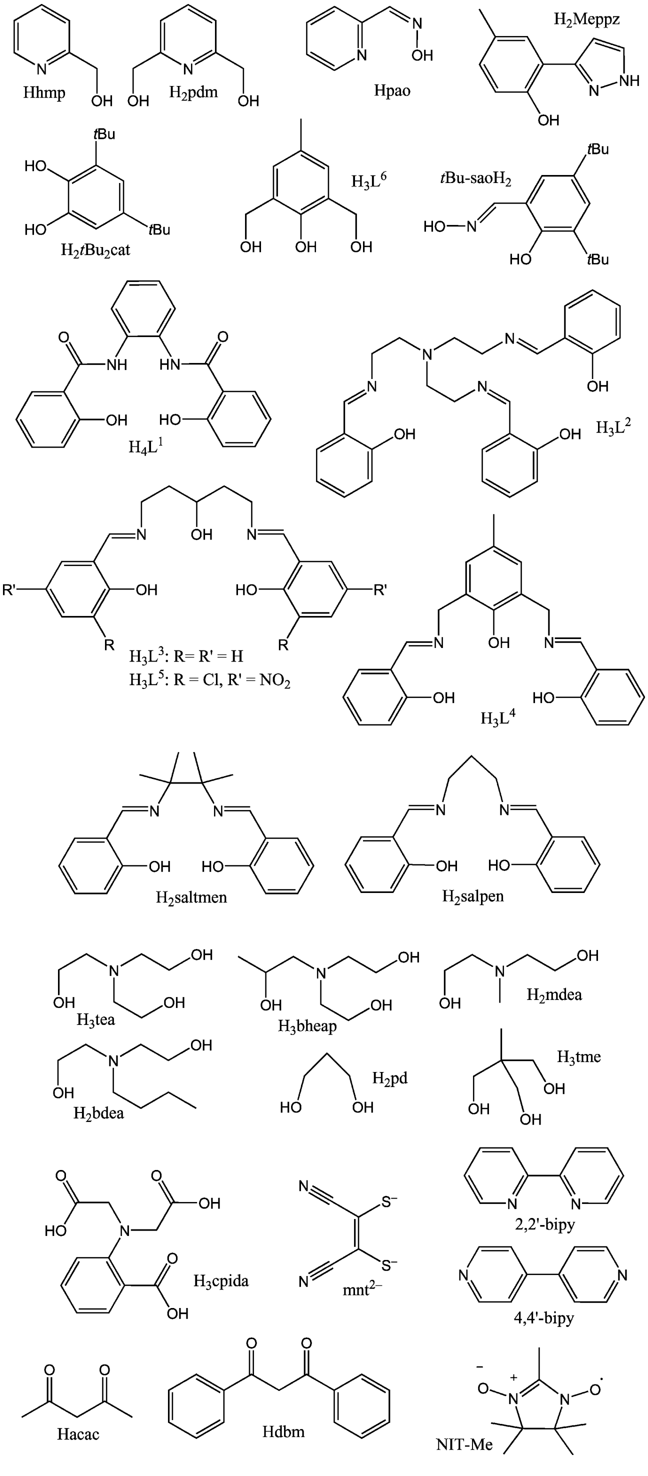


Scheme 1. (a) The so-called butterfly $[Mn_4(\mu_3\text{-}O)_2]$ core completed by additional polynuclear bridging ligands L (usually carboxylates) and (b) the rhombic $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ core, which is the subject of this microreview.

While in the former case mostly $[Mn^{III}_4]$ systems dominated by antiferromagnetic interactions are known,[26] the latter usually gives rise to mixed-valent complexes often presenting high-spin ground states and SMM behavior, which makes them interesting building blocks. In addition, a structural survey[27] shows that in the butterfly-like $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ systems the external Mn ions, in general divalent, often have labile terminal ligands. This characteristic offers an ideal opportunity to assemble the tetranuclear core into extended coordination networks through exchange of these terminal ligands by judiciously selected moieties. Indeed, some examples (described in this microreview) of compounds based on the same structural motif have demonstrated that these positions can be used to construct, in a rather controlled manner, extended networks of these interesting building blocks. We will first describe in this section the isolated $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ systems. In manganese–oxido coordination chemistry, comproportionation reactions or preformed complexes, especially triangular oxido-centered ones, are very often used to obtain mixed-valent species. This is particularly valid for compounds containing Mn^{III}, as this ion is useful as a source of uniaxial magnetic anisotropy. This is also true for the $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ system that could be isolated from trinuclear $[Mn_3O(O_2CR)_6](O_2CR)$ (vide infra, compounds **15**–**16**), although, in most cases, the reported complexes could also be obtained from simple Mn precursor salts and the components of the final complexes.

Rhombic Mixed-Valent $[Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ Systems

This system is by far the most extended family of complexes presenting the $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ butterfly core. In this tetranuclear core, the inner Mn ions are trivalent, while external ones are divalent. The inner Mn^{III} ions are connected through two μ_3-alkoxido bridges from an alcohol-based ligand [2-hydroxymethylpyridine (Hhmp), 2,6-dihydroxymethylpyridine (H_2pdm), or polyalcohols; see Scheme 2 and below], and four μ-alkoxido groups from the same ligands bridge each Mn^{III} ion to the two external Mn^{II} ones (see Scheme 1). An additional carboxylate bridge between Mn^{II} and Mn^{III} ions is also found in some cases, with H_2pdm and polyalcohol ligands. In all cases, the resulting metal core has a defective dicubane topology. The coordination sphere of the external Mn^{II} ions is completed by the



Scheme 2. Ligands discussed in this review: from top to bottom, N-aromatic alcohols, salen-type ligands, aliphatic polyalcohols, and others.

chelating N-donor-containing ligands, coordinated anions, and/or solvent molecules. The latter two have been found to be labile and thus easily exchanged by species present in the reaction mixture, resulting in many variations in which the Mn^{II} is either hexacoordinate or heptacoordinate. On the other hand, the internal Mn^{III} are always hexacoordinate and present the Jahn–Teller elongation typical of a +3 oxidation state. As shown by many reported examples, this [Mn_4] defective dicubane core is very stable and is best formed from Mn^{II} salts under aerobic, and thus oxidative, conditions. The solvent of choice is acetonitrile, while an organic base such as tetraethylammonium hydroxide (TEAOH) is used to deprotonate the alcohol ligands. Despite the variations in synthetic conditions (ligands, anions, solvent), the structural features of the [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core are in most cases preserved. The Mn^{III}–Mn^{III} separation ranges from 3.29 to 3.40 Å, with Mn–O–Mn angles of 99 to 101°. One of the Mn^{III}–O distance is always much longer (2.17 to 2.27 Å for axial positions with respect to 1.94 to 2.04 Å for equatorial ones), corresponding to the Jahn–Teller elongation axis. The Mn^{II}–Mn^{III} separation lies in the 3.24–3.31 Å range, with Mn–μ_3-O–Mn angles from 94 to 96° and Mn–O–Mn angles that are larger and more variable between 106 and 114°. In almost all the examples, the resulting magnetic interactions, J_{wb} (for wing-body) and J_{bb} (for body-body), are both ferromagnetic and lead to a high-spin ground state of $S_T = 9$. The values derived for these two interactions (see Table 1),[29] are not very sensitive to the ligand used; nor are they sensitive to the presence of an additional Mn^{III}–Mn^{II} bridge. Because the Jahn–Teller elongation axes of the two anisotropic Mn^{III} ions are almost or strictly parallel (usually by molecular symmetry), the high-spin states of the complexes present a significant magnetic anisotropy (D). This parameter has been evaluated in many cases for the $S_T = 9$ ground state to be negative and uniaxial, in the range –0.1 to –0.45 K (see Table 1). Note that the evaluation of D can be done either by using the first step due to quantum tunneling of magnetization (QTM) in low-temperature hysteresis loops, from HF-EPR data, or from the fit of the M vs. H/T data. In all cases discussed in this section, these [Mn_4] complexes are well isolated from each other. Indeed, most are cationic species surrounded by uncoordinated anions and lattice solvent molecules resulting in at most very weak intercomplex interactions. As a result, most of the reported examples behave as SMM. The following paragraphs briefly describe, by groups, all reported examples, together with, when relevant, their structural singularities and deviations from the magnetic properties described above.

So far, the most widely used bridging ligand to build these tetranuclear cores is Hhmp. Note, nevertheless, that this ligand has also allowed the isolation of higher-nuclearity Mn complexes,[20b,20j–20l,30] as well as Fe or Co complexes[31] or heterometallic systems.[32] Indeed, the deprotonated form, hmp^-, is able to form μ_3-alkoxido bridges while chelating one metal ion, thus limiting the growth of a metal-oxido and/or -alkoxido core. All these complexes have in a common a [$Mn_4(hmp)_6]^{4+}$ core, in which the hmp^- provides all μ_3-O Mn^{III}–Mn^{III} and μ-O bridges Mn^{III}–Mn^{II}. The outer Mn^{II} ions are heptacoordinate in the first group of complexes. These are chelated by either a η^2-O,O′ nitrate anion, e.g. in [$Mn_4(hmp)_6(NO_3)_2(MeCN)_2](ClO_4)_2\cdot 2MeCN$ (**1**), [$Mn_4(hmp)_6(NO_3)_2(NO_3)_2]\cdot MeCN$ (**2**),[33] [$Mn_4(hmp)_6(NO_3)_2(H_2O)_2](NO_3)_2\cdot 2.5H_2O$ (**3**, see Figure 1),[34] [$Mn_4(hmp)_6(H_2O)_2(NO_3)_2](ClO_4)_2\cdot 4H_2O$ (**4**),[35] and [$Mn_4(hmp)_6(NO_3)_2(dcn)_2]\cdot 2MeCN$ (**5**),[36] or a carboxylic group in the η^2-O,O′ coordination mode, e.g. in [$Mn_4(hmp)_6(MeCO_2)_2(H_2O)_2](ClO_4)_2\cdot 4H_2O$ (**6**) and [$Mn_4(hmp)_6(PhCO_2)_2(H_2O)_2](ClO_4)_2\cdot 4MeCN\cdot 2H_2O$ (**7**).[37]

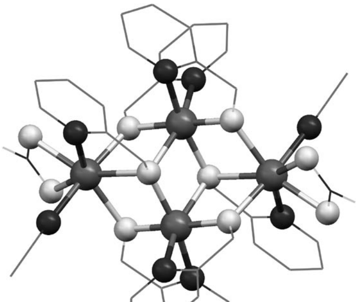


Figure 1. A view of the [Mn_4] complex in [$Mn_4(hmp)_6(NO_3)_2(H_2O)_2](NO_3)_2\cdot 2.5H_2O$ (**3**), with heptacoordinate terminal Mn^{II} ions. Color and size code used throughout this review: Mn (or M) gray, O light gray, and N dark gray. Only the atoms involved in coordination and the metal centers are represented as balls and sticks; hydrogen atoms are omitted for clarity.

A smaller group of complexes with the same core mostly built from the Hhmp ligand possesses hexacoordinate outer Mn^{II} ions, namely [$Mn_4(hmp)_6(acac)_2(MeOH)_4](ClO_4)_2$ (**8**),[33] [$Mn_4(hmp)_6(H_2O)_4](ClO_4)_4\cdot 2H_2O$ (**9**),[34] [$Mn_4(hmp)_6(Hhmp)_2](ClO_4)_4\cdot 2MeCN$ (**10**),[34] and [$Mn_4(hmp)_6(Cl_3CCO_2)_2(H_2O)_2](ClO_4)_2$ (**11**, see Figure 2).[37] Except for **9**, hexacoordination arises from steric reasons. A too bulky group on a terminal ligand (CCl_3 in **11**) or a large chelate (acac in **8** or Hhmp in **10**) impedes the coordination of an additional terminal ligand. In **10**, the presence of additional terminal Hhmp neutral ligands arises from the use of excess Hhmp in the synthesis.

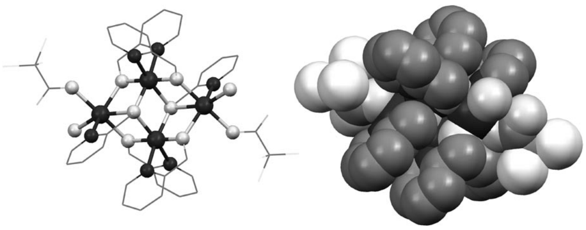


Figure 2. Representations of the [Mn_4] complex in [$Mn_4(hmp)_6(Cl_3CCO_2)_2(H_2O)_2](ClO_4)_2$ (**11**), in which the outer Mn^{II} ions are hexacoordinate. The space-filling view (right) highlights the role of the bulky trichloroacetate group in preventing heptacoordination and further assembly as a 1D chain (see text). Hydrogen atoms are omitted for clarity.

Compound $[Mn_4(hmp)_6(MeCN)_2(H_2O)_2](ClO_4)_4$·2MeCN (**12**)[38] demonstrates that, if no specific constraint is present in the synthetic system (coordinating anion, sterically hindered ligand, stoichiometry), the outer Mn^{II} ions prefer to be heptacoordinate. Indeed, **12** is crystallized extremely fast in high yield out of an acetonitrile solution containing $Mn(ClO_4)_2$, Hhmp, and TEAOH in H_2O. Under these experimental conditions, complex $[Mn_4(hmp)_6(MeCN)_2(H_2O)_2]^{4+}$ is therefore present in solution and represents a good candidate for building extended networks of the $[Mn_4O_6]$ core. These extended systems can be achieved through exchange of the labile MeCN and H_2O terminal ligands on the external Mn^{II} ions (see Figure 3) by selected bridging species that can be added to the solution. It is worth mentioning that **12** presents the highest D (S_T = 9) of this series of $[Mn_4(hmp)_6]^{4+}$ complexes (see Table 1).

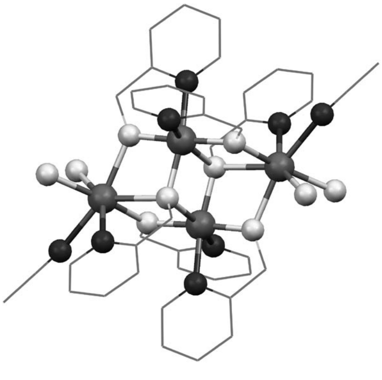


Figure 3. A view of the simplest $[Mn_4(hmp)_6]^{4+}$ cation, in $[Mn_4(hmp)_6(MeCN)_2(H_2O)_2](ClO_4)_4$·2MeCN (**12**), obtained when no coordinating anion or additional bridging moiety is used. External Mn^{II} ions are heptacoordinate with three labile terminal ligands (2H_2O and 1MeCN) that can be replaced for further coordination assembly of the $[Mn_4]$ complex (vide infra).

The first reported compound with the rhombic mixed-valent defective dicubane $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ core was obtained with a ligand similar to Hhmp, but with two hydroxymethyl arms: H_2pdm. As for Hhmp, this ligand is also able to produce higher-nuclearity complexes.[39] In $[Mn_4(Hpdm)_6(MeCO_2)_2](ClO_4)_2$·2MeCN·2$Et_2O$ (**13**) and its analogue, $[Mn_4(Hpdm)_6(MeCO_2)_2](ClO_4)_2$·2.5$H_2O$ (**13b**), obtained by exchange of lattice solvent molecules in air, the H_2pdm ligand is only monodeprotonated and provides all μ_3-O and μ-O bridges.[40] As shown in Figure 4, four of the $Hpdm^-$ ligands have their protonated hydroxymethyl arm uncoordinated and pending outward the complex core, while the deprotonated ligands form the four μ-O bridges. The two remaining $Hpdm^-$ ligands have their deprotonated hydroxy oxygen atom in μ_3-bridging mode, the protonated one being coordinated as a terminal ligand to the outer Mn^{II} ions. $Hpdm^-$ is therefore quite similar to the hmp^- anion in terms of chelation and bridging properties. Nevertheless, each central Mn^{III} ion is additionally bridged to only one of the outer Mn^{II} ions by an acetate group. The tridentate coordination mode of two of the ligands results in the efficient chelation of the outer Mn^{II} ions. Two of their terminal positions are thus blocked, while some steric constraints arise for the remaining position. As a consequence, compound **13** is not a good candidate for building extended assemblies.

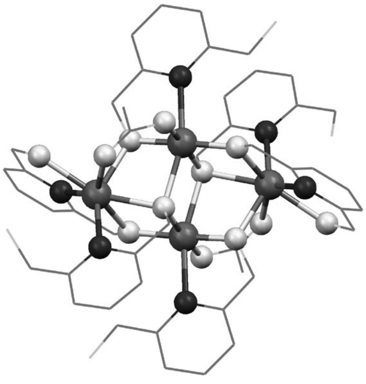


Figure 4. The structure of the $[Mn_4]$ complex in $[Mn_4(Hpdm)_6(MeCO_2)_2](ClO_4)_2$·2MeCN·2$Et_2O$ (**13**). Note the additional acetate bridges, the pending uncoordinated hydroxymethyl arms of two of the $Hpdm^-$ ligands, and the chelating *N*,*O*,*O′* coordination mode of $Hpdm^-$ on the terminal Mn^{II} ions.

The use of different flexible polyalcoholamines has allowed in recent years the isolation of many high-nuclearity complexes, for some of them with SMM properties.[41] Again, the conjunction of chelating capabilities and the potential bridging modes of alkoxido groups limit the expansion of the metal-oxido (or -alkoxido) core. Thus several isolated complexes presenting the $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4]$ core have been obtained with ethanolamine-based ligands. With *N*-methyldiethanolamine (Hmda), the compound $[Mn_4(mda)_2(mdaH)_2(PhCO_2)_4]$·$CH_2Cl_2$·$Et_2O$ (**14**, Figure 5) is obtained,[42] in which the deprotonated mda^{2-} ligands provide the μ_3-O Mn^{III}–Mn^{III} bridges, as well as two of the μ-O Mn^{III}–Mn^{II} bridges, through a *N*,*O*,*O′* bridging-chelating moiety similar to the coordination mode adopted by the deprotonated $Hpdm^-$. On the other hand, the monodeprotonated $mdaH^-$ ligands chelate the outer Mn^{II} ions and provide the two other μ-O Mn^{III}–Mn^{II} bridges. The Mn^{II}–Mn^{III} pairs are further connected through benzoate bridges, while monocoordinated benzoate groups complete the heptacoordinate environment of the Mn^{II} ions. Overall, the $[Mn_4]$ units are well-isolated, as the remaining proton on $mdaH^-$ is only involved in intramolecular hydrogen bonds with the terminal benzoate. With *N*-butyldiethanolamine, two compounds very similar to **14** were isolated either with benzoate or pivalate as carboxylate bridge and terminal ligand: $[Mn_4(bdea)_2(bdeaH)_2(tBuCO_2)_4]$ (**15**) and $[Mn_4(bdea)_2(bdeaH)_2(PhCO_2)_4]$ (**16**).[43] For these two complexes, the sources of carboxylate are trinuclear $[Fe_3O(O_2CR)_6](O_2CR)$, $[Mn_3O(O_2CR)_6L_3]$, or $[Mn_3O(O_2CR)_6L_3](O_2CR)$ complexes, often used in the synthesis of high-nuclearity iron or manganese oxido-carboxylato complexes. With respect to the Hhmp systems, the use of these complexes as building blocks seems to be less adequate, as the chelating *N*,*O*,*O′* moiety of the ligand blocks in a stable manner the coordination sphere of the outer Mn^{II} ions. The use of triethanolamine also yields $[Mn_4(\mu_3$-

$O)_2(\mu\text{-}O)_4$] cores, but the corresponding compounds present extended hydrogen-bonding networks that will be discussed below.

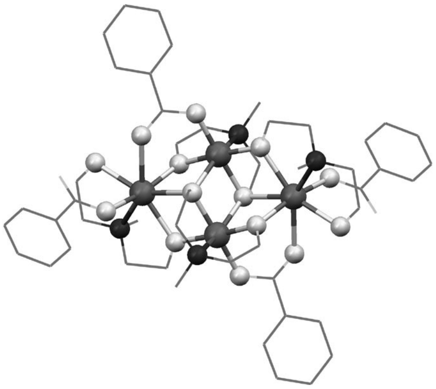


Figure 5. A typical view of the structure of the [Mn_4] complex obtained by the use of polyalcoholamines as ligands in combination with carboxylates, here in [$Mn_4(mda)_2(mdaH)_2(PhCO_2)_4$]·$CH_2Cl_2$·$Et_2O$ (**14**), showing the *N*,*O*,*O′* chelating coordination of the polyalcoholamine.

Other [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] Systems with Different Valencies

The mixed-valent complex [$Mn_4(HL^1)_2(OH)_2(MeO)_2(bpy)_2$] (**17**) is obtained from a Mn^{III} precursor bearing the chelating 1,2-bis(2-hydroxybenzamido)benzene ligand (HL^1) that is able to further coordinate through its phenol groups and thus produces the μ-O bridges of the [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core upon reaction with Mn^{II}.[44] The μ_3-O bridges in the resulting [Mn_4] complex arise from hydroxido ligands. In this complex, however, the central ions are divalent and low-spin ($S = 1/2$), while the external ones are trivalent. Their coordination environment is completed by bipyridine and methanol molecules, respectively. This complex could therefore be considered for the construction of extended systems through the replacement of the terminal methanol molecule on the external Mn^{III} ions. Nevertheless, both Mn^{III}–Mn^{III} and Mn^{II}–Mn^{III} magnetic interactions are antiferromagnetic, inducing an $S_T = 1$ ground state, and thus SMM properties are absent.

The rest of the known tetranuclear manganese complexes possessing the considered [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core are not mixed-valent. The neutral catecholate complex [$Mn_4(t\text{Bu}_2\text{cat})_4(py)_6$] (**18**)[45] has all its manganese ions in the +2 oxidation state. Two of the catecholates have one μ_3-bridging and one terminal oxygen, while the other two catecholates have two μ-bridging oxygen atoms. One (on the central Mn^{II} ions) or two (on the external Mn^{II} ions) pyridine molecules complete the coordination sphere of all Mn^{II} ions, yielding distorted trigonal bipyramidal or octahedral environments, respectively, and a basket-like [Mn_4] core. While replacement of the terminal pyridine ligands could be considered to use **18** as a building block, its magnetic properties, although not reported, are likely dominated by antiferromagnetic interactions on basis of the Mn–O–Mn angles, and this should result in an $S_T = 0$ ground state.

Eventually, the considered core can be isolated with all manganese ions being trivalent. The μ_3-bridges are then oxido ions, as observed in [$Mn_4(L^2)_2(O)_2$]$(PF_6)_2$·4MeCN (**19**),[46] [$Mn_4(L^2)_2(O)_2$]($MnCl_4$)·MeCN (**20**),[47] [$Mn_4(L^3)_2(O)_2(MeCO_2)_2$]·$4H_2O$·2MeOH (**21**),[48] and [$Mn_4(L^4)_2(O)_2(MeCO_2)_2$]·2MeCN (**22**).[49] In the first two related complexes **19** and **20**, the flexible salicylaldimine ligand $N(CH_2CH_2N{=}CHC_6H_4OH)_3$ (H_3L^2) acts as a heptadentate bridging-chelating ligand (the tripodal N is involved in a coordination bond with the external Mn^{III} ion), providing the rest of the axially elongated octahedral coordination environment for both central and external Mn ions. Although no structure was reported, perchlorate, trifluromethanesulfonate, and tetraphenylborate salts of complex **20** were also isolated.[46] In **21**, only one of the salicylphenol oxygen atoms of each L^3 [H_3L^3: 1,5-bis(salicylidenamino)pentan-3-ol] forms a μ-O bridge, the other one acting as a terminal ligand for an external Mn^{III} ions. The other two μ-O bridges arise from the alkoxido moiety. A similar structure is observed in **22**, with the phenoxido group of L^4 [H_3L^4: 2,6-bis(salicylidenaminomethyl)-4-methylphenol]. In both **21** and **22**, an acetato group additionally bridges central and external Mn^{III} ions. The Mn–Mn separation is shorter in these four complexes, e.g. below 3 Å, as observed in the WOC complex of PSII. Nevertheless, the intramolecular magnetic interactions in these four [Mn^{III}_4] compounds are all antiferromagnetic, which leads to an $S_T = 0$ ground state.

Assembling [Mn_4] Single-Molecule Magnets

Hydrogen-Bonded and π-Stacked Networks of [Mn_4] Units

Weak intermolecular interactions (hydrogen-bonding, π-stacking, anion–π, halogen–halogen, etc.) are often present in coordination compounds without being particularly highlighted in the papers. Nevertheless, these can have non-negligible effects, in particular on the magnetic properties. Therefore, compounds with the [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core in which these weak intermolecular interactions are significant and form extended networks of the molecular complexes are first considered here. The resulting magnetic properties are briefly summarized in comparison with the isolated systems previously described.

In [$Mn_4(hmp)_6Br_2(H_2O)_2$]Br_2·$4H_2O$ (**23**),[50] shown in Figure 6, the molecular structure of the [Mn_4] core is very similar to those of the isolated systems **8**–**11**. The outer Mn^{II} ions are hexacoordinate, most likely due to steric limitations arising from the coordinated bromide anion. These bromide anions interact directly with a Br···Br separation of 4.91 Å between neighboring [Mn_4] moieties, resulting in the formation of 1D chains of interacting [Mn_4] units (see Figure 6). In addition, a 3D hydrogen-bonding network, which connects these coordinated bromide anions, uncoordinated ones, and lattice water molecules, is observed. Altogether, these intermolecular interactions are at the origin of a transition to an antiferromagnetic ordered phase observed at 1.33 K.[51] Single-molecule-magnet behavior is nevertheless observed in **23** above this temperature. It is interesting to note that this compound was in fact the first [Mn_4] SMM isolated with the Hhmp ligand.

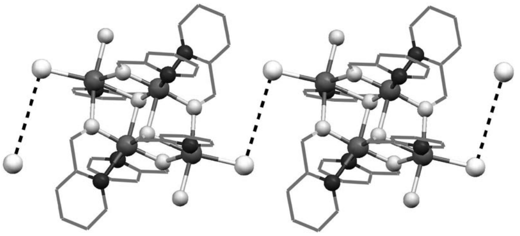


Figure 6. A view of the structure of [$Mn_4(hmp)_6Br_2(H_2O)_2$]Br_2·$4H_2O$ (**23**), highlighting with dashed bold lines the one-dimensional Br–Br contacts among [Mn_4] units.

As mentioned in the previous section, the use of triethanolamine as a bridging-chelating ligand indeed yields the expected [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core, which is similar to that in **14**–**16**, but uncoordinated ethanolamine arms form intermolecular hydrogen bonds with uncoordinated anions. These result in extended hydrogen-bonding networks linking the [Mn_4] units. In [$Mn_4(teaH_2)_2(teaH)_2(PhCO_2)_2$]$(PhCO_2)_2$·MeCN(**24**)[52]and[$Mn_4(teaH_2)_2(teaH)_2(PhCO_2)_2$]$(PhCO_2)_2$·0.7MeCN·0.3EtOH (**24b**),[43] the uncoordinated oxygen of the free ethanolamine arm is hydrogen-bonded to the uncoordinated benzoate anion, which also forms hydrogen bonds with the μ-O atoms of the coordinated ethanolamine arms. These hydrogen bonds link the [Mn_4] complexes into chains as shown in Figure 7. The same chain network is observed in [$Mn_4(teaH_2)_2(teaH)_2(t\text{BuCO}_2)_2$]$(t\text{BuCO}_2)_2$ (**25**) through the uncoordinated pivalate anions; in this case additional hydrogen bonds are formed with coordinated pivalate ions.[53] In **24** and **24b**, the intermolecular interactions among the [Mn_4] units were found to have no apparent influence on the magnetic properties. Only in the case of **25**, some indications of antiferromagnetic intermolecular interactions were found in susceptibility measurements. In the temperature region studied, the three compounds nevertheless behave as paramagnetic species with SMM behavior at low temperatures.

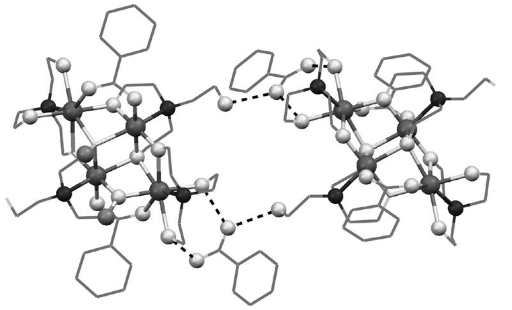


Figure 7. A view of the structure of [$Mn_4(teaH_2)_2(teaH)_2(PhCO_2)_2$]$(PhCO_2)_2$·MeCN (**24**), emphasizing the 1D hydrogen-bonding network (dashed bold lines) among [Mn_4] units.

In [$Mn_4(teaH_2)_2(teaH)_2(MeCO_2)_2$]$(MeCO_2)_2$·$2H_2O$ (**26**),[52] similar hydrogen bonds with an uncoordinated acetate anion are observed; but they also involve an uncoordinated lattice water molecule. The result is a 2D sheet-like network of [Mn_4] units. Nevertheless, no indication of significant intermolecular magnetic interactions were detected. In [$Mn_4(teaH_2)_2(teaH)_2(EtCO_2)_2$]$(ClO_4)_2$ (**27**),[52] each [Mn_4] complex is directly connected to four neighbors through hydrogen bonds between the free ethanolamine oxygen atoms and coordinated ethanolamine terminal oxygen atoms, which also results in a 2D network, shown in Figure 8. These more direct contacts in **27** result in significant inter-[Mn_4] antiferromagnetic interactions of the order of –0.06 K. As observed in **23**, some indications of a possible transition to an antiferromagnetic ordered phase were obtained from M vs. H data.[51]

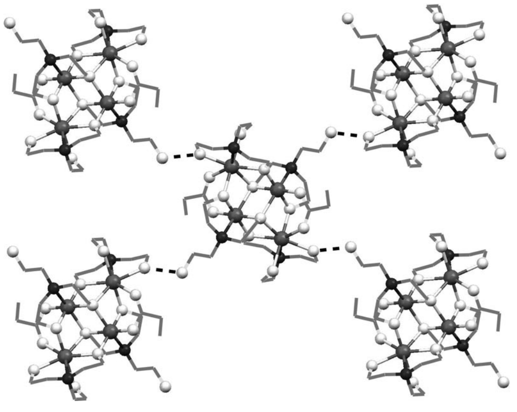


Figure 8. Direct hydrogen bonds (dashed bold lines) connect the [Mn_4] units in [$Mn_4(teaH_2)_2(teaH)_2(EtCO_2)_2$]$(ClO_4)_2$ (**27**) into a 2D network.

In [$Mn_4(L^5)_2(MeO)_2(MeOH)_2$] {**28**, H_3L^5 is the Schiff base 1,5-bis(3-chloro-5-nitro-salicylideneamino)pentan-3-ol}, the [$Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4$] core is built through two μ_3-methoxide ligands connecting two dinuclear units that are themselves bridged (μ-O of the central alkoxido ligand) and chelated by the trianionic pentadentate Schiff base.[54] The salicyl oxygen atoms provide the additional μ-O bridges among the dinuclear units. Each one of the coordinated methanol molecules forms a strong hydrogen bond with the nitro group of one of the $(L^5)^{3-}$ ligands of a neighboring [Mn_4], thus generating a supramolecular chain. The ability of the nitro group of this kind of ligand to induce intermolecular interactions was previously documented in a Fe^{III} spin-crossover system, in which the supramolecular assembly through hydrogen bonds was shown to have a strong influence on the magnetic properties.[55] Unfortunately, the magnetic properties of **28** were not investigated.[54]

Compounds [$Mn_4(HL^6)_4Cl_2(MeOH)_4$]·$2Et_2O$ (**29**) and [$Mn_4(HL^6)_4Br_2(MeOH)_4$]·$2Et_2O$ (**30**) are obtained under similar conditions from MnX_2 salts (X = Cl or Br) and 2,6-bis(hydroxymethyl)-4-methylphenol (H_3L^6) in methanol.[56] Their [$Mn^{II}_2Mn^{III}_2O_6$] core is very similar to those of compounds **8**–**11**, **13**, and **23**, whose outer Mn^{II} ions are hexacoordinate, likely for steric reasons, as for **23**. Similarly to $Hpdm^-$ in **13**, the $(L^6)^{2-}$ ligand is either tridentate, providing a μ_3-alkoxido bridge, a μ-phenoxido link, and a terminal protonated alcohol donor, or bidentate ligand then providing a μ-alkoxido and a terminal phenoxido donor. The coordinated methanol molecules are involved in hydrogen bonds with the protonated uncoordinated hydroxymethyl arm of the bidentate $(L^6)^{2-}$ ligand, while the coordinated halides also form hydrogen bonds with the oxygen atom of the protonated terminal hydroxymethyl arm of the tridentate $(L^6)^{2-}$ ligands. The result is a 2D network of the [Mn_4] units. Both **29** and **30** behave as SMMs, and no indication of intermolecular magnetic interactions has been found, although data were only given down to 1.8 K.[56]

$[\{Mn_4(hmp)_6(MeCN)_2\}\{Pt(mnt)_2\}_4][Pt(mnt)_2]_2$ (**31**) has been obtained by electrochemical oxidation from the reaction of **12** with $(NBu_4)[Pt^{III}(mnt)_2]$ in a 1:3 ratio.[57] It is thus an example of rationally designed material by using the [Mn_4] SMM as a precursor building block. Its structure reveals four $[Pt(mnt)_2]^{n-}$ units coordinated to the terminal heptacoordinate Mn^{II} ions of [Mn_4] through one of the mnt^{2-} nitrile moieties, forming a discrete $\{[Pt(mnt)_2]_2$-[Mn_4]-$[Pt(mnt)_2]_2\}$ complex. The reaction was designed to allow the formation of a conducting system that would keep the magnetic properties of the [Mn_4] SMM. Indeed, the coordinated and uncoordinated $[Pt(mnt)_2]^{n-}$ are mutually π-stacked along the *a* axis into segregated columns (see Figure 9, Pt–Pt distances of 3.46 and 3.57 Å), thus weakly connecting the [Mn_4] complexes in a 2D arrangement. The Pt ions were found to have an average charge of +3.33, corresponding to $[Pt(mnt)_2]^{0.66-}$ moieties. As a result, semiconducting transport properties are detected when probing along the *a* axis. The conductivity at room temperature is 0.22 S/cm, and the compound behaves as a semiconductor at room temperature, with an average energy gap of 136 meV. Below 100 K, **31** is an insulator with $\rho > 10^7\ \Omega\cdot\text{cm}$. Although SMM properties of the [Mn_4] units were maintained as expected, no coexistence of a reasonable electric conductivity and "magnet" properties was achieved. Nevertheless, **31** represents the first step towards superparamagnetic/conductive hybrid materials.

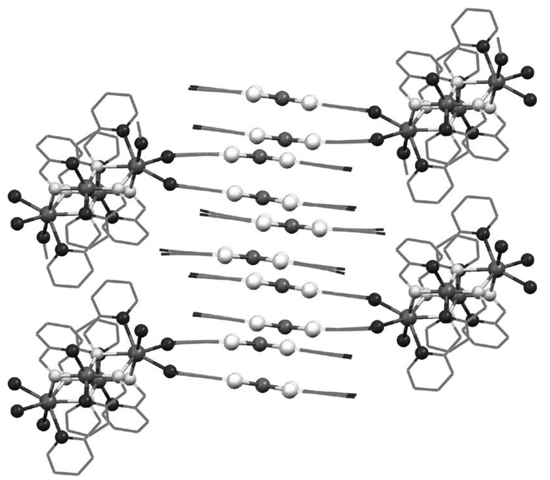
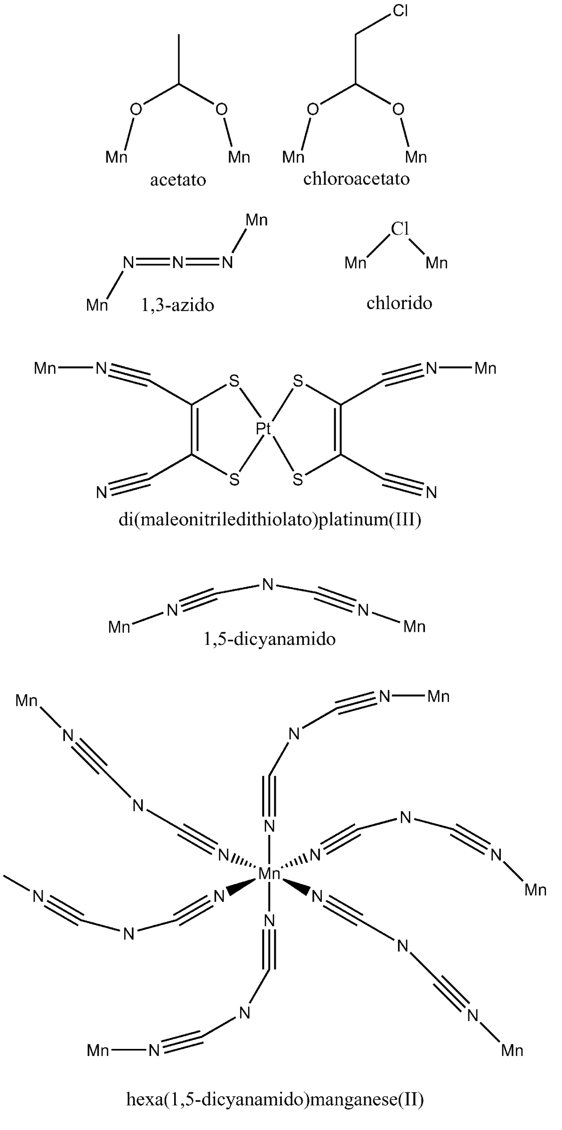


Figure 9. The conductive packing of coordinated and uncoordinated $[Pt(mnt)_2]^{0.66-}$ in $[\{Mn_4(hmp)_6(MeCN)_2\}\{Pt(mnt)_2\}_4]$-$[Pt(mnt)_2]_2$ (**31**) resulting in a π-stacked 2D supramolecular assembly of [Mn_4] units.

One-Dimensional Coordination Assemblies of [Mn_4] SMM

As evidenced in the Hhmp system, the $[Mn_4(hmp)_6]^{4+}$ core is formed efficiently under many conditions, and it crystallizes in different final forms depending on the species present in solution. It therefore seems possible to modulate this final form, by starting from the simplest reagents that allow the $[Mn_4(hmp)_6]^{4+}$ unit to be prepared in solution, e.g. those used to obtain **12**, and *then* only to add the reagent necessary for the planed extended system. The $[Mn_4(hmp)_6]^{4+}$ system is actually perfect for 1D assembly, as double bridges can be expected through two terminal ligands on the Mn^{II} outer ions, which would make them hexacoordinate. Obviously, from structural analyses of the [Mn_4] core, these interconnecting ligands should not be too sterically demanding (Scheme 3).



Scheme 3. The moieties used so far to connect [Mn_4] SMMs into infinite coordination networks.

These considerations are well evidenced by the products obtained when using as the additional reagent a source of the potentially bridging acetate, chloroacetate, and trichloroacetate anions.[37] In the latter case, with the bulky trichloromethyl group, the isolated [Mn_4] complex **8** is crystallized (see Figure 2), while in the two former cases, chains of [Mn_4] units connected through double *syn-syn* carboxylic bridges are crystallized, in [$Mn_4(hmp)_6(MeCO_2)_2](ClO_4)_2\cdot H_2O$ (**32**) and [$Mn_4(hmp)_6(ClCH_2CO_2)_2](ClO_4)_2\cdot 2H_2O$ (**33**, Figure 10), respectively.[37] Given that the bridging moiety is sufficiently small, this synthetic strategy is versatile. Indeed, a very similar compound is obtained when using a source of azido ligands, namely [$Mn_4(hmp)_6(N_3)_2](ClO_4)_2$ (**34**), in which the [Mn_4] units are linked one-dimensionally by double μ-1,3-azido bridges (so-called end-to-end bridging mode, see Figure 11).[34] Finally, adding NaCl under the same synthetic conditions,[58] or starting from $MnCl_2$ salt,[59] yields the related chlorido chain compound [$Mn_4(hmp)_6Cl_2](ClO_4)_2$ (**35**). In all these four chain compounds, the [Mn_4] unit is almost identical to that in isolated complexes, in which the terminal Mn^{II} ions are hexacoordinate. The chains are well-isolated in the four structures by perchlorate anions and lattice water molecules, with no significant intermolecular interactions. In all four cases, the bridges propagate weak antiferromagnetic interactions, as expected for such *syn-syn* carboxylato, end-to-end azido, and chlorido bridges. The four compounds therefore behave as antiferromagnetically coupled chains of $S_T = 9$ [Mn_4] units. The weak inter-[Mn_4] interaction (J) has been evaluated to be –0.13, –0.10, –0.15, and –0.07 K for **32**, **33**, **34**, and **35**, respectively. Apparently, the coupling along the chain in chlorido compound **35** is sufficiently weak to allow the observation of the slow relaxation of the magnetization of the [Mn_4] SMM units, as if they were isolated. Nevertheless, the existence of two types of chains with two different orientations of the Mn^{III} Jahn–Teller elongation axis (ca. 45°) results in a complex behavior at low temperatures, which has been assigned to spin-canting.[58] Interestingly, in the three chains with stronger intrachain antiferromagnetic interactions, **32**, **33**, and **34**, the typical responses of isolated SMMs, e.g. slow relaxation of the magnetization and QTM, are not observed as a result of the overall cancellation of the spins along the antiferromagnetic chains. Nevertheless, the presence of varying amounts of defects in these crystalline materials has allowed for the first time the measurement and full modeling of the relaxation of the staggered magnetization of such antiferromagnetic chains, through the relaxation signal of chains with an odd number of [Mn_4] units.[35,37]

Eventually, instead of small inorganic or organic linkers, larger bridging moieties such as coordination complexes can be considered. For a linear chain assembly, these linkers should present two available donors or two labile coordination sites in *trans* positions. Indeed, when **12** is reacted in acetonitrile with (NBu_4)[$Pt^{III}(mnt)_2$] in a 1:4 ratio, compound [$\{Mn_4(hmp)_6(MeCN)_2\}\{Pt(mnt)_2\}_2][Pt(mnt)_2]_2\cdot 2MeCN$ (**36**) is obtained, in which the coordinated [$Pt(mnt)_2]^-$ moieties doubly bridge the [Mn_4] units into a $\{–[Mn_4]–[Pt(mnt)_2]_2\}_\infty$ 1D coordination assembly through one terminal cyanido group of each mnt^{2-} ligand (Figure 12).[57] Uncoordinated [$Pt(mnt)_2]^-$ anions are located between these chains, packing in a broken stair-like column with coordinated ones. Unlike those in **31**, the platinum cations in **36** are trivalent, and **36** is an insulator at room temperature. The magnetic behavior of **36** is that of isolated paramagnetic [$Pt(mnt)_2]^-$ and SMM [Mn_4] units, as only extremely weak antiferromagnetic interunit interactions could be observed. These interactions were evaluated to be about $zJ/k_B \approx -0.001$ K from the shift of the central step from zero-field in the hysteresis loop measured on an oriented single crystal at 470 mK.[57]

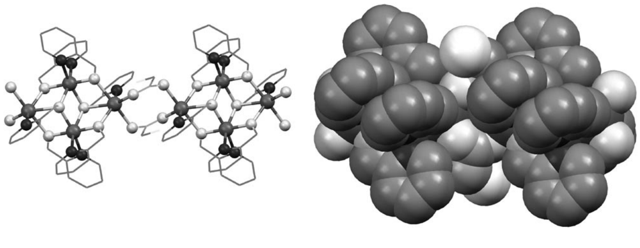


Figure 10. Representations of a portion of the 1D assembly of [Mn_4] units in [$Mn_4(hmp)_6(ClCH_2CO_2)_2](ClO_4)_2\cdot 2H_2O$ (**33**), in which the outer Mn^{II} ions of two neighboring [Mn_4] units are doubly bridged by *syn-syn* chloroacetate groups. The space-filling view (right) highlights the steric limitations in such an assembly, as well as a weak Cl–π interaction between the bridging chloroacetate group and one of the hmp⁻ rings.

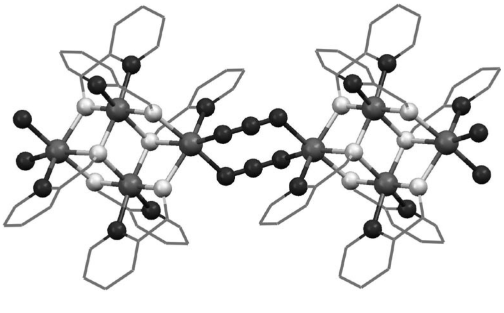


Figure 11. Representation of a portion of the 1D assembly of [Mn_4] units in [$Mn_4(hmp)_6(N_3)_2](ClO_4)_2$ (**34**), in which the outer Mn^{II} ions of two neighboring [Mn_4] units and the two μ-1,3-azido anions form a chair-like bridge.

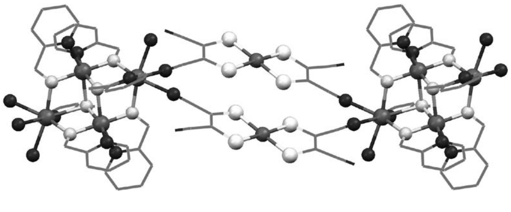


Figure 12. A view of the structure of compound **36** showing the connection among neighboring [Mn_4] units into chains through double [$Pt(mnt)_2]^-$ bridges.

Given the current interest for chains of anisotropic spins, arising from the discovery of single-chain magnets,[15,16,60] the present [$Mn_4(hmp)_6]^{4+}$ building block should allow the isolation of new SCM systems. Of particular interest along this line is the use of a ferromagnetic short linker, or intrachain antiferromagnetic coupling, as observed so far, but with a paramagnetic low-spin bridge, which would induce ferromagnetic arrangements of the SMM spin carriers. Obviously, higher dimensionality may also be attained. If instead of short double bridges, one uses sufficiently long and flexible linkers or a coordination complex with more available donors or labile coordination sites, then the units may be connected not to two, but to four (2D assembly) or even six (3D assembly) neighboring [Mn_4] moieties. The few known examples reported so far are described in the next two sections.

2D Coordination Assemblies of [Mn_4] Units

The dicyanamide anion $N(CN)_2^-$ (dcn$^-$) has allowed the isolation of a number of extended magnetically coupled compounds by reaction with simple transition-metal salts.[61] It usually acts as a bidentate linear μ-1,5-bridging ligand, although other bridging modes are possible.[61] It is therefore not sterically demanding, rather flexible, and thus represents a good candidate for the assembly of the [Mn_4] units into higher coordination assemblies. Indeed, three 2D compounds have been isolated, in which each terminal hexacoordinate Mn^{II} ion bears only two dcn$^-$ anions that bridge two separate [Mn_4] neighbors.[36] A view of the layers in these three related compounds is sketched in Figure 13. $[Mn_4(hmp)_6(dcn)_2](ClO_4)_2$ (**37**) is simply obtained from compound **12** in situ by adding, as the last step of the reaction, a limited amount of Na[dcn] (Mn/Hhmp/Na[dcn] = 1:2.5:0.4). Another way of limiting the number of dcn$^-$ anions per terminal Mn^{II} ions is to use a mixture of Hhmp and H_2pdm in a similar reaction that yields $[Mn_4(hmp)_4(Hpdm)_2(dcn)_2](ClO_4)_2 \cdot 2H_2O \cdot 2MeCN$ (**38**). Indeed, as in compound **13**, the two monodeprotonated Hpdm$^-$ ligands afford the μ_3-O bridges but also act as terminal ligands for the Mn^{II} ions through their protonated hydroxymethyl arm, thus blocking one coordination site of these outer Mn^{II} ions. In $[Mn_4(hmp)_4Br_2(MeO)_2(dcn)_2] \cdot 0.5H_2O \cdot 2thf$ (**39**), which is obtained from compound **23** and Na[dcn] in MeOH, the dcn$^-$ anions have replaced the coordinated water molecules, and together with methoxide ions (that provide the μ_3-O bridges), two hmp$^-$ ligands. In **39**, it is the coordinated bromide ion that limits the number of dcn$^-$ anions per Mn^{II}.

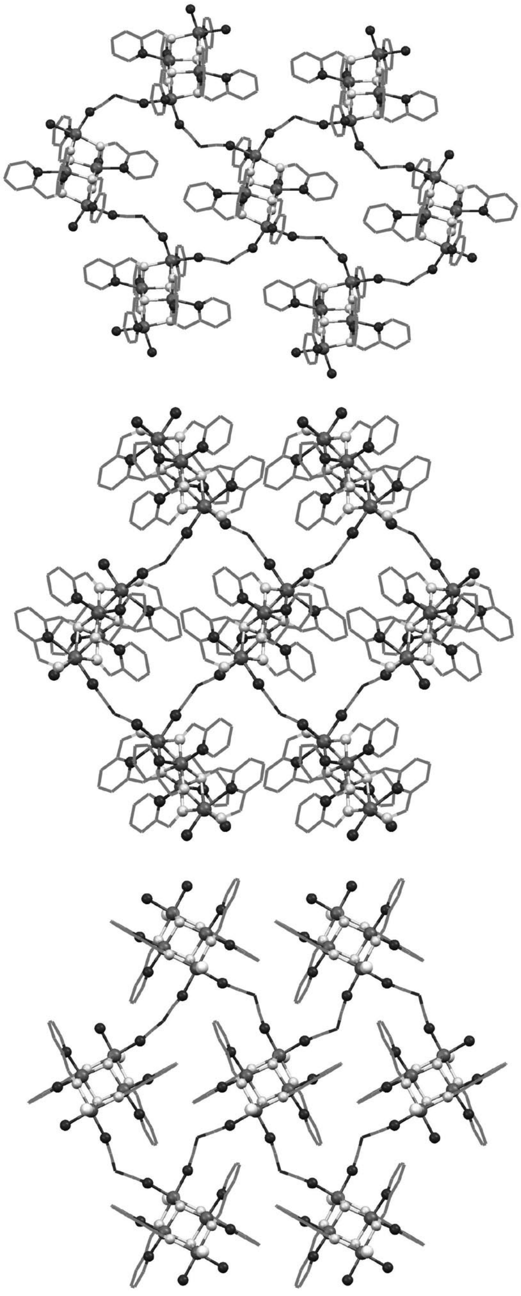


Figure 13. Views of the 2D sheets of [Mn_4] units in $[Mn_4(hmp)_6(dcn)_2](ClO_4)_2$ (**37**, top), $[Mn_4(hmp)_4(Hpdm)_2(dcn)_2](ClO_4)_2 \cdot 2H_2O \cdot 2MeCN$ (**38**, middle), and $[Mn_4(hmp)_4Br_2(MeO)_2(dcn)_2] \cdot 0.5H_2O \cdot 2thf$ (**39**, bottom), in which the [Mn_4] easy axes of magnetization (Jahn–Teller elongation axis of the Mn^{III} ions) have two orientations separated by 9, 80, and 63°, respectively.

As can be seen in Figure 13, despite a very similar 2D structure of dicyanamido-bridged [Mn_4] units, compounds **37**, **38**, and **39** strongly differ in the two orientations presented by the [Mn_4] easy axes of magnetization within these sheets, which form angles of 9, 80, and 63°, respectively. The low-temperature magnetic properties are strongly influenced by this simple structural difference. The weak antiferromagnetic interaction ($zJ/k_B \approx -0.05$ K, with $z = 4$) propagated through the dicyanamido bridges implies theoretically a canted antiferromagnetic ground state in the three compounds, with expected T_C values of 0.8 K for **38**, ca. 2.1 K for **39** and ca. 4.4 K for **37**. If the angle is small, as in **37**, the magnetic order is observed normally as it occurs in the temperature range (at 4.6 K for **37**) where the dynamics of the [Mn_4] units is fast. On the other hand, for larger angles, the *effective* magnetic interactions are reduced, and the magnetic order is stabilized at lower temperatures, which makes its achievement difficult within the timescale of the experiments because of the intrinsic slow dynamics of the [Mn_4] SMM units. Indeed, compound **38** behaves as a classical SMM, while interplay between slow relaxation of magnetization (SMM) and the ordering phenomenon is observed in **39**. These three 2D compounds, obtained by controlling the number of bridging dicyanamido ligands per

[Mn_4], have thus led to new magnetic behaviors resulting from the competition between dynamic properties of the [Mn_4] units and thermodynamic behavior induced by the coordination networks.[36]

A Unique 3D Coordination Assembly of [Mn_4] Units

Under similar synthetic conditions as those used to obtain the 2D assemblies above, the three potentially available coordination sites on each external Mn^{II} ions of the [Mn_4] units can be occupied by bridging dcn^- anions. Indeed, when using dicyanamide in a higher Mn/dcn^- ratio {namely $Mn(ClO_4)_2·6H_2O$, hmp^-, and Na[dcn] in a 1:2:1 molar ratio}, the six positions are occupied by dcn^- connecting the [Mn_4] units into a 3D assembly, namely $[Mn_4(hmp)_4(OH)_2Mn(dcn)_6]·2MeOH·2thf$ (**40**).[62] This arises at the expense of the hmp^- ligand, which normally provides the μ_3-O bridge and is terminally coordinated to the Mn^{II} ion. In **40**, it is replaced by one of the dcn^- anions and a μ_3-hydroxido moiety. The six dcn^- ligands per [Mn_4] bind in the μ-1,5 mode to a Mn^{II} ion, thus forming a $[Mn^{II}(dcn)_6]^{4-}$ unit, interconnecting the [Mn_4] into a 3D coordination network (see Figure 14). At low temperatures, the antiferromagnetic interactions mediated by dicyanamido anions between the [Mn_4] units ($S_T = 9$) and the Mn^{II} ($S = 5/2$) result in a ferrimagnetic order observed at $T_C = 4.1$ K. These interactions are overcome at a critical field H_C of 23 kOe. Both T_C and H_C allow a consistent estimation of the interaction (J_{3D}) through the dicyanamido anion at ca. –0.03 K. Compound **40** was the first material to show that anisotropic classical magnets can be designed with SMM building blocks.[62]

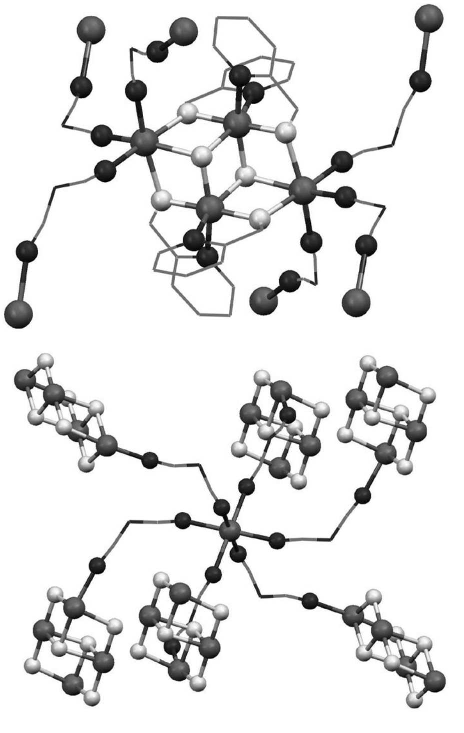


Figure 14. Two simplified views of the structure of **40** showing the connection of the [Mn_4] unit to six Mn^{II} ions (top) and the connection of each Mn^{II} ion to six [Mn_4] units (bottom) through dicyanamido ligands.

Potential Outcomes of the Assembly of Magnetic Complexes and Selected Examples

Designed Assemblies of Magnetic Complexes: from Weakly Interacting to Magnetically Correlated Systems of High-Spin Complexes

The first goal of selecting building blocks and linkers through their coordination acceptor and donor abilities is to control the way these elements are going to self-assemble into extended networks of varying dimensionalities, and thus to be able, in fine, to predesign the final assembly in order to obtain premeditated physical properties. The example of the [Mn_4] unit considered here shows that this crystal engineering strategy is indeed possible with SMM building blocks. Almost all types of networks, e.g. coordination 1D, 2D, 3D networks, but also hydrogen-bonded systems, have been obtained with simple synthetic considerations. The first outcome of these coordination assemblies is thus basic knowledge on the coordination potential, as acceptor or donor, of certain high-spin complexes. However, further studies are still necessary to gain a real control over the way these SMM or high-spin complex building blocks assemble and to extend the rational assembly to other building blocks and linkers. Indeed, a number of reports in the literature illustrate that this type of synthetic rationalization, made by using the [Mn_4] SMM building block, is applicable to other systems. As shown in the next paragraphs with some selected examples, a variety of magnetic building blocks and linkers have already been used to design new materials. The magnetic properties of these coordination assemblies are also briefly discussed.

When magnetic properties are targeted, not only the dimensionality but also the orientation of the anisotropic building blocks in the assembly should be controlled, which has so far not been fully possible. A way to achieve such geometrical control is to use the complex-as-ligand strategy,[18] by which rather strict geometric constraints can be achieved. As an example, reacting an out-of-plane $S = 4$ dimer $[Mn_2(saltmen)_2(H_2O)_2](ClO_4)_2$ {**41**, $saltmen^{2-}$ = *N*,*N'*-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)} with the neutral mononuclear unit $[Ni(pao)_2(py)_2]$ (**42**, pao^- = pyridine-2-aldoximate) results in the replacement of axial water molecules of **41** by the O donor of pao^-, which are disposed *trans* to each other in **42**. Thus, with these geometric constraints, infinite heterometallic chains of the anisotropic Mn^{III} and Ni^{II} ions are formed.[16] In $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$ (**43**), the repeating unit is $[–Mn–(O)_2–Mn–ON–Ni–NO–]_n$ (see Figure 15). The dominant magnetic interaction along the chains (which are well isolated from each other in the structure) is that mediated by the aldoxime bridge (J/k_B = –21 K), resulting in Mn···Ni···Mn trinuclear units with an $S = 3$ ground state that are ferromagnetically coupled via the biphenolate bridge. As a result of this combination of high-spin magnetic units, strong interunit interactions, and uniaxial anisotropy, **43** shows hysteresis loops as well as slow relaxation of the magnetization, at low temperature, indicating the presence of a metastable state without magnetic long-range order. This material was the second example of a SCM and the first heterometallic one with a ferromagnetic interaction among the spins along the chain. A whole family of SCMs could be isolated and studied by using the same designed assembly with various building blocks.[63] Also to be mentioned are the assemblies of dinuclear complexes similar to **41**, albeit with salen-based ligands, into one-dimensional arrays through hydrogenocyanamide single bridges, exhibiting various types of low-temperature magnetic properties.[64]

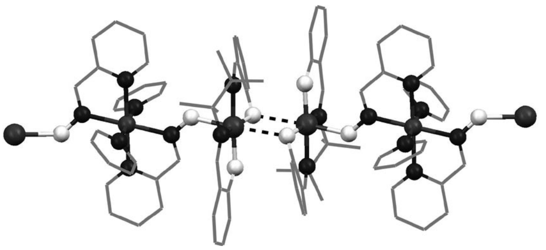


Figure 15. A view of the linear Mn···Ni···Mn(O)$_2$Mn···Ni···Mn sequence within the chains in [$Mn_2(saltmen)_2Ni(pao)_2(py)_2$]($ClO_4$)$_2$ (**43**). The out-of-plane biphenolate bridge is shown as dashed bold lines.

Oxido-centered triangular [$M_3O(O_2CR)_6L_3$]$^{n+}$ (n = 0, 1) complexes have often been used to construct molecular magnetic materials, and especially SMMs.[43] Nevertheless, these planar compounds act more as sources of M-oxido and/or carboxylates rather than as building blocks. Indeed, they usually present antiferromagnetic interactions yielding a low-spin ground state, and, most importantly, the easy axes of magnetization of the metal ions in the [M_3O] unit are not parallel to each other. Nevertheless, a neutral oxido-centered Mn^{III} triangular complex with all Jahn–Teller elongation axes of the Mn^{III} ions parallel to each other has been isolated with the bulky 3,5-di-*tert*-butylsalicylaldoxime (*t*Bu-saoH_2): [Mn_3O(*t*Bu-sao)$_3$Cl(MeOH)$_5$] (**44**).[65] Interestingly, the apical positions are all occupied by the chlorido and methanol terminal ligands, thus making **44** an interesting building block for assembly into infinite chains through replacement of some of the apical donors. Indeed, replacement of the chlorido ligand by either formato or azido ligands results in the isolation of chains of very similar [Mn_3O] units bridged by the *anti-anti* formato ligand in [Mn_3O(*t*Bu-sao)$_3$(HCOO)(MeOH)$_5$]·MeOH·0.5H_2O (**45**) or the end-to-end azido ligand in [Mn_3O(*t*Bu-sao)$_3$(N_3)(MeOH)$_5$]·0.5MeOH (**46**).[65] In both compounds, the *t*Bu groups isolate the chains well, and in both cases slow relaxation of the magnetization, typical of SCM behavior, is observed. In **45**, the interaction between [Mn_3O] units through the *anti-anti* formato bridge is weak and antiferromagnetic, while that in **46** through the end-to-end azido bridge is ferromagnetic and stronger, resulting in the observation of relaxation at higher temperatures (7 K at 1500 Hz), related to a larger energy gap, Δ_τ/k_B = 96.6 K. A similar chain with *anti-anti* acetato bridges [Mn^{III}_3O(Meppz)$_3$(EtOH)$_4$(OAc)] {**47**, Meppz = 3-(5-methyl-2-phenolate)pyrazolate, see Figure 16} was obtained by another group from a predesigned triangular complex, [Mn^{III}_3O(Meppz)$_3$(EtOH)$_5$Cl] (**48**), similar to **44**.[66] As in **45**, the interaction through the *anti-anti* acetato bridge is antiferromagnetic, and **47** behaves nevertheless as a SCM. Interestingly, its noncentrosymmetric structure results in dielectric relaxation.[66b]

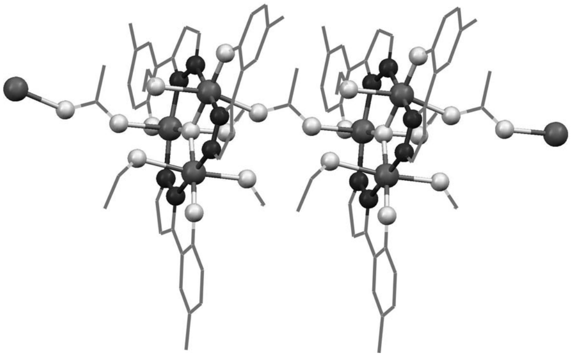


Figure 16. A view of the structure of compound **47** showing the connection among neighboring triangular [Mn_3] units into chains through a single acetato bridge.

Another example with similar bridges is obtained from $MnCl_2 \cdot 2H_2O$ and the polyalcohol 1,1,1-tris(hydroxymethyl)ethane (H_3thme). In the presence of sodium azide and under aerobic conditions, necessary for oxidation of Mn^{II} to Mn^{III}, the original μ_6-oxido-centered hexanuclear mixed-valent complex Na_2[$Mn^{II}Mn^{III}_5(\mu_6$-O)(thme)$_3(N_3)_5(H_2O)$]·5H_2O (**49**), shown in Figure 17, is isolated.[67] Compound **49** presents an octahedral [Mn_6] core with the μ_6-O^{2-} ion at the centre, the four thme^{3-} ligands completing this very symmetric core through three μ-O bridges. The azido or water terminal ligands that complete the octahedral environment of all six Mn ions could then be used either to form end-to-end intercomplex bridges or to be replaced by

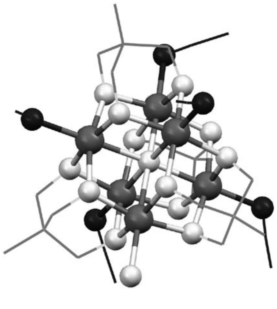


Figure 17. A view of the μ_6-oxido centered [Mn_6] complex present in **49** and **50**, showing the water and azido terminal ligands.

another bridging ligand, respectively. Indeed, under very similar synthetic conditions, the use of higher temperatures favors the formation of azido end-to-end bridges among similar octahedral [Mn_6] complexes, resulting in compound $Na_2[Mn_6(\mu_6\text{-}O)(thme)_4(N_3)_5]\cdot(H_3thme)_2$ (**50**).[67] In **50**, neighboring [Mn_6] units are connected through one sole shared azido ligand to form infinite zigzag coordination chains, while the rest of the azido ligands remain terminal. Nevertheless, the magnetic properties of both compounds are very similar and are dominated by antiferromagnetic interactions, resulting in the case of **49** in a $S = 2$ ground state.

Finally, when the linker propagates a more significant magnetic coupling, magnetic correlations among the high-spin complexes assembled may yield various kinds of properties. As shown in **41**, **47**, or **48**, if the correlations are 1D (even if the interactions are not very strong), then the final assembly can be a magnetically arranged chain of uniaxial anisotropic spins that should, if well isolated, present slow dynamics typical of SCMs, as first predicted by R. J. Glauber for an Ising chain.[68] On the other hand, classical ferro- or antiferromagnets may be attained when these correlations are 3D or 2D, the intrinsic magnetic anisotropy of SMM building blocks being an advantage to potentially favor relatively large coercivity. As shown by the 2D systems obtained from the [Mn_4] SMM considered here, the orientation of the magnetic complexes and therefore of their anisotropy axes can drastically affect the final bulk properties. As a result of various orientations in the assembly, canted magnets may also be isolated. Although some examples of such assemblies of correlated magnetic complexes have been reported, some obtained in a rational manner, their number is still very limited, and one can expect that promising new systems would be obtained in the near future. A good example arises from the use of nitroxide as a magnetic linker. Indeed, 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl (NIT-Me) can replace terminal thf molecules in the [Mn_6] complex $[Mn_6O_2(tBuCO_2)_{10}(thf)_4]\cdot thf$ (**51**) to connect two neighboring [Mn_6] units through its two oxygen atoms.[69] This results in extended heterospin networks in which the [Mn_6] units remain but interact magnetically through and with the NIT-Me moiety. Interestingly, in this system, it is not the stoichiometry but the solvent in which the reaction is conducted that controls the number of replaced thf molecules and therefore the dimensionality of the final assembly. In dichloromethane, only two thf terminal ligands on opposite sides of the [Mn_6] complex are replaced, resulting in infinite chains in $[Mn_6O_2(tBuCO_2)_{10}(thf)_2(NIT\text{-}Me)Mn_6O_2(tBuCO_2)_{10}(thf)(CH_2Cl_2)(NIT\text{-}Me)]$ (**52**). On the other hand, in heptane or CCl_4, all four thf positions are replaced by NIT-Me, forming $[Mn_6O_2(tBuCO_2)_{10}(NIT\text{-}Me)_2]$ (**53**), which possesses a diamond-like framework structure. Views of the connectivity between [Mn_6] units in these two compounds are sketched in Figure 18. As a result of the antiferromagnetic interaction between NIT-Me and the [Mn_6] units and noncompensation of spins, **53** presents a ferrimagnetic order at $T_C = 3.5$ K.

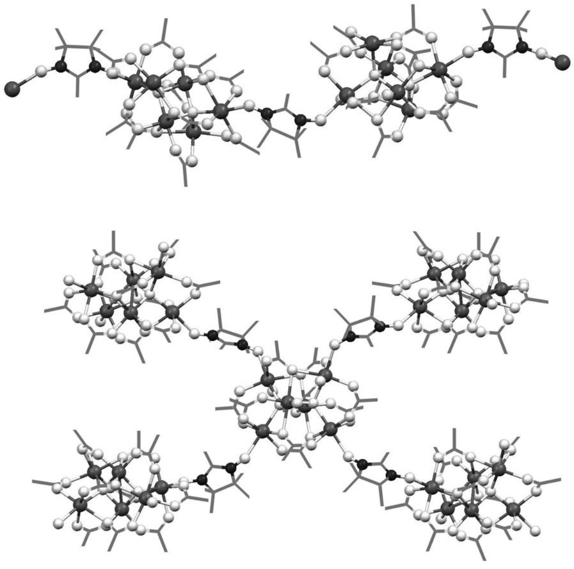


Figure 18. The connections between neighboring [Mn_6] units through NIT-Me in **52** (top) and **53** (bottom), respectively.

Isolated High-Spin Building Blocks in Coordination Networks through “Innocent” Bridges

When the linker does not mediate any significant magnetic interaction (e.g. “innocent” bridge), the assembly results in well-ordered connected magnetic complexes, which can nevertheless be considered to be isolated high-spin complexes from the magnetic viewpoint. This may lead to materials with improved SMM or more general magnetic properties, as the linker may force a better isolation and orientation of the molecular magnets than by simple traditional crystal packing through weak interactions. Several groups have attempted to anchor or deposit isolated SMM molecules on different surfaces for the use of their individual properties at the nanoscale.[70] Following this goal, extended networks of connected and organized but magnetically isolated SMMs may be useful to form crystalline deposits directly on the surface. An example of large mixed-valent Mn complexes connected into an infinite coordination network, but isolated from the magnetic point of view, is observed in a 3D coordination polymer based on [Mn_{19}] units, namely in $[Mn_{19}Na(\mu_4\text{-}O)_9(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(O_2CMe)_9(pd)_9(H_2O)_3][OH]$ (**54**).[71] Although obtained by serendipitous assembly from 1,3-propanediol (H_2pd), this compound shows a connection among the mixed-valent [$Mn^{II}_7Mn^{III}_{12}$] aggregates that is different from those seen so far in this review: each [Mn_{19}] is connected to three sodium cations through μ_3-acetate groups. Each [Mn_{19}] is thus bridged through the sodium cations, as well as through direct μ_3-acetato links (see Figure 19), to three similar units. The resulting highly ordered framework presents large channels of ca. 12×16 Å^2. The $[Mn_{19}(\mu_4\text{-}O)_9(\mu_3\text{-}O)(\mu_3\text{-}OH)_3]$ core has a triangular-pyramidal topology, possesses a large $S = 23/2$ ground state and behaves as SMM below 1.1 K. Nevertheless, the linker in **54** does not mediate a significant magnetic coupling so as to affect the molecular behavior of the pseudo-isolated [Mn_{19}] units.

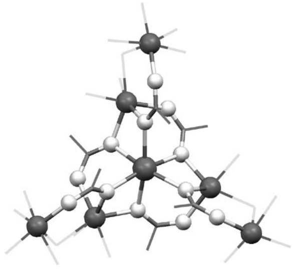


Figure 19. The connection between three neighboring [Mn_{19}] units (only the two Mn ions involved in the connection and their coordination spheres are drawn for clarity) through a Na^+ cation (here at the center) and μ_3-acetato bridges in [$Mn_{19}Na(m_4\text{-}O)_9(m_3\text{-}O)(m_3\text{-}OH)_3(O_2CMe)_9(pd)_9(H_2O)_3$][OH] (**54**).

Similar diamagnetic bridges are obtained from polycarboxylic acid ligands, in conjunction with a source of hydroxido, oxido, or short alkoxido bridges, which also favor the serendipitous assembly of large transition-metal aggregates.[72] For example, with the carboxyphenyliminodiacetic acid (H_3cpida) ligand, triethylamine as a base, and a source of Cu^{II}, a "ferrimagnetic"[73] isolated dodecanuclear complex formulated as [$Cu_{12}(\mu_3\text{-OMe})_2(\mu\text{-OMe})_6(cpida)_6$]$^{2-}$ is obtained. Interestingly, by using alkali metal hydroxide bases (M = Na, K, Rb, Cs), these [Cu_{12}] aggregates can be assembled by mono-, di-, or tetraalkali bridges, through carboxylate groups, into 1D, 2D, and 3D networks of the unmodified [Cu_{12}] unit.[74] Note, nevertheless, that this strategy is not limited to diamagnetic alkali bridges, since, when using an excess of the Cu^{II} source, the [Cu_{12}] aggregates are linked into a zigzag chain through magnetic [$Cu_2(\mu\text{-OMe})_2$]$^{2+}$ bridges (see Figure 20), in [{$Cu_{12}(\mu_3\text{-OMe})_2(\mu\text{-OMe})_6(cpida)_6$}{$Cu_2(\mu\text{-OMe})_2$}] (**55**). Although the magnetic properties of **55** were not reported, given the Cu–O–Cu angles, the [Cu_2] bridge is likely antiferromagnetically coupled, which means that it will in fact be quasidiamagnetic at low temperatures.[75]

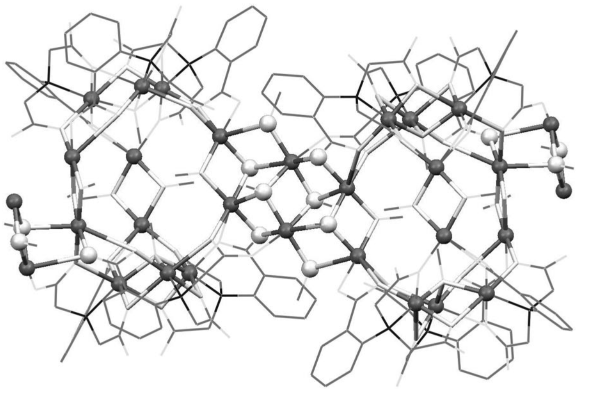


Figure 20. The connection of two [Cu_{12}] units through [$Cu_2(\mu\text{-OMe})_2$]$^{2+}$ moieties along the zigzag chains in [{$Cu_{12}(\mu_3\text{-OMe})_2(\mu\text{-OMe})_6(cpida)_6$}{$Cu_2(\mu\text{-OMe})_2$}] (**55**). For clarity, only the Cu^{II} ions and the oxygen atoms involved in the bridging of the [Cu_{12}] aggregates are shown as balls and sticks.

Bipyridine ligands are often used to build metal–organic frameworks and represent other potential nonmagnetic linkers for high-spin-building-block complexes, as each pyridine can act as a terminal N-donor ligand. With 4,4′-bipyridine (4,4′-bipy), two such assemblies, namely [$Mn_4O_2(PhCO_2)_6(dbm)_2$(4,4′-bipy)] (**56**)[76] and [$Mn_6O_2(t\text{BuCO}_2)_{10}(t\text{BuCO}_2\text{H})_2$(4,4′-bipy)] (**57**),[77] have been reported starting from the butterfly core (NBu_4)[$Mn_4O_2(PhCO_2)_7(dbm)_2$] (**58**) and the mixed-valent [Mn_6] complex [$Mn_6O_2(t\text{BuCO2})_{10}(t\text{BuCO}_2\text{H})_4$] (**59**), respectively.[78] In the first system, the only carboxylate group bridging the Mn ions in the central body in the starting complex can be replaced, after treatment with Me_3SiCl, by two 4,4′-bipy ligands in *anti* position, thus resulting in a staircase-like linear infinite arrangement of the initial [Mn_4] units. In the latter case, two of the terminal pivalic acid tBuCO$_2$H ligands on neighboring Mn^{II} ions of **57** are replaced by 4,4′-bipy ligands, this disposition resulting in zig-zag chains of [Mn_6] units in **59**, as shown in Figure 21. In both cases, the magnetic properties of the 1D-assembled systems are identical to those of the starting building blocks.

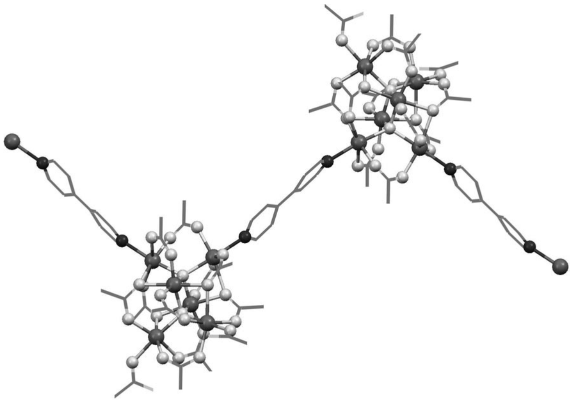


Figure 21. The connection through 4,4′-bipy in [$Mn_6O_2(t\text{BuCO}_2)_{10}(t\text{BuCO}_2\text{H})_2$(4,4′-bipy)] (**59**), yielding a 1D arrangement of [Mn_6] units, which are nevertheless magnetically isolated.

Original Physical Behaviors or Multifunctional Materials

The assembly of high-spin complexes may also allow the isolation of multifunctional materials with an unprecedented coexistence of specific physical properties. A good example is the first case of coexistence of conductive and SMM properties, as in **31**. Original physical properties may also be observed thanks to a controlled assembly of high-spin complexes. Indeed, the slow relaxation of the staggered magnetization of antiferromagnetic chains has been observed for the first time thanks to finite-size effects in antiferromagnetically coupled chains of [Mn_4] SMM, e.g. **32**, **33** and **34**. Quantum relaxation was also observed recently in a SCM.[79] Overall, one can expect to obtain new materials with novel physical properties as a result of more studies on molecular nanomagnets and their assemblies. So far, magnetic interactions within the magnetic complexes used as building blocks is usually larger than those occurring through the linkers. The case of strong correlations, especially in 1D systems, has in fact been very sparsely documented experimentally;[80] nevertheless, original behaviors may arise. Eventually, the use of light-sensitive linkers may allow to tune both the dimensionality and topology of an extended network of magnetic units as well as the magnetic carriers themselves.[81] The first point might be achieved with an organic linker that is able, upon adequate irradiation, either to create/break the magnetic pathway between the magnetic carriers, or to change its conformation. The second point would be achieved with a diamagnetic transition-metal-containing linker, which, upon irradiation, would participate with a neighboring metal of the magnetic complex in a metal-to-metal electron transfer as acceptor. The resulting phenomenon would then be a photoinduced switch from a system with isolated magnetic complexes to a magnetically coupled extended network.

Conclusions

The assembly of high-spin polynuclear coordination complexes into extended coordination or hydrogen-bonded frameworks may give access to original and interesting magnetic properties such as single-chain magnets, molecular-based classical magnets, or systems possessing an interplay between modified quantum and bulk thermodynamic properties. Multifunctional materials may also be constructed from building blocks with adequate conductive, optical, or other properties. For this purpose, the rational design or selection of the starting complexes and of the linkers is of paramount importance in controlling the dimensionality of the desired coordination network. The way the magnetic units are disposed and interact in the solid state are also prime parameters that the chemist can intend to adjust by judiciously selecting the components of the assembly. The use of a [Mn_4] single-molecule magnet as building block illustrates well the different strategies and outcomes in terms of physical properties that can be attained. Although many coordination frameworks based on polynuclear metal complexes have been reported, very few have been obtained from isolated, well-characterized building blocks, allowing a rationalization of the synthetic strategies. In this respect, if one considers that these few rationally designed systems have been synthesized in the last six years, one can suppose that the present subject has an eventful and promising future ahead. We hope that this review, exhaustive with regard to the [Mn_4] system, will be useful for scientist eager to develop new strategies and new framework materials based on high-spin coordination complexes.

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[1] O. Kahn (Ed.), *Molecular Magnetism*, Wiley-VCH, New York, **1991** .
[2] *MRS Bull.* **2000**, *25*, issue 11.
[3] a) R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816; b) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141–143.
[4] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66–71; b) D. Gatteschi, R. Sessoli, *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297.
[5] See, for example, reviews on biomimetics of Cu, Fe, and Ni: a) E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563–2605; b) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, *Chem. Soc. Rev.* **2006**, *35*, 814–840; c) E. Bouwman, J. Reedijk, *Coord. Chem. Rev.* **2005**, *249*, 1555–1589; d) M. A. Halcrow, G. Christou, *Chem. Rev.* **1994**, *94*, 2421–2481.
[6] a) V. L. Pecoraro (Ed.), *Manganese Redox Enzymes*, VCH Publishers, New York, **1992**; b) For a recent update, see: V. L. Pecoraro, H.-Y. Hsieh, *Inorg. Chem.* **2008**, *47*, 1765–1778.
[7] R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* **2002**, 1–10.
[8] For a recent review of transition-metal SMMs, see: G. Aromí, E. K. Brechin, *Struct. Bonding (Berlin)* **2006**, *122*, 1–67.
[9] For a recent example with polytopic diazine ligands, see: L. N. Dawe, T. S. M. Abedin, L. K. Thompson, *Dalton Trans.* **2008**, 1661–1675.
[10] For examples with polydiketones, see: a) G. Aromí, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, S. J. Teat, E. MacLean, H. Stoeckli-Evans, J. Reedijk, *Chem. Eur. J.* **2004**, *10*, 6476–6488; b) G. Aromí, P. Gamez, J. Reedijk, *Coord. Chem. Rev.* **2008**, *252*, 964–989.
[11] G. Wu, I. J. Hewitt, S. Mameri, Y. Lan, R. Clérac, C. E. Anson, S. Qiu, A. K. Powell, *Inorg. Chem.* **2007**, *46*, 7229–7231.
[12] Mononuclear precursors bearing various numbers of cyanides allow the construction of various metal complex topologies, see, for example: a) F. Karadas, E. J. Schelter, M. Shatruk, A. V. Prosvirin, J. Basca, D. Smirnov, A. Ozarowski, J. Krzystek, J. Telser, K. R. Dunbar, *Inorg. Chem.* **2008**, *47*, 2074–2082; b) E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer, K. R. Dunbar, *J. Am. Chem. Soc.* **2007**, *129*, 8139–8149; c) C. F. Wang, J. L. Zuo, B. M. Bartlett, J. R. Long, X. Z. You, *J. Am. Chem. Soc.* **2006**, *128*, 7162–7163; d) D. Li, R. Clérac, O. Roubeau, E. Harté, C. Mathonière, R. Le Bris, S. M. Holmes, *J. Am. Chem. Soc.* **2008**, *130*, 252–258.
[13] For a review of grid-type systems, see: M. Ruben, J. Rojo, F. J. Romero-Salguero, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662.
[14] W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature* **2002**, *416*, 406–409.
[15] C. Coulon, H. Miyasaka, R. Clérac, *Struct. Bonding (Berlin)* **2006**, *122*, 163–206.
[16] R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837–12844.
[17] a) For a review of extended Ni and Mn cyanide-based systems, see: J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *195*, 1027–1068; b) For a review of azido isolated complexes, see: A. Escuer, G. Aromí, *Eur. J. Inorg. Chem.* **2006**, 4721–4736.
[18] E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret, M. Julve, *Dalton Trans.* **2008**, 2780–2805.
[19] For simplicity, the metal complex cores are only given with the metals and the types of bridging oxygen atoms. These are not necessarily oxides, but can be alkoxides, hydroxides, etc., although the format used does not indicate the corresponding chemical group bearing the oxygen atom.
[20] A nonexhaustive list with varying [Mn_x] nuclearities ($x > 4$): a) M. D. Godbole, O. Roubeau, R. Clérac, H. Kooijman, A. L. Spek, E. Bouwman, *Chem. Commun.* **2005**, 3715–3717; b) L. F. Jones, E. K. Brechin, D. Collison, J. Raftery, S. J. Teat, *Inorg. Chem.* **2003**, *42*, 6971–6973; c) A. J. Tasiopoulos, W.

Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 6338–6342; d) S. Maheswaran, G. Chastanet, S. J. Teat, T. Mallah, R. Sessoli, W. Wernsdorfer, R. E. P. Winpenny, *Angew. Chem. Int. Ed.* **2005**, *44*, 5044–5048; e) M. Soler, W. Wernsdorfer, K. Folting, M. Pink, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 2156–2165; f) E. K. Brechin, E. C. Sañudo, W. Wernsdorfer, C. Boskovic, J. Yoo, D. N. Hendrickson, A. Yamaguchi, H. Ishimoto, T. E. Concolino, A. L. Rheingold, G. Christou, *Inorg. Chem.* **2005**, *44*, 502–511; g) H.-C. Yao, Y.-Z. Li, Y. Song, Y.-S. Ma, L.-M. Zheng, X.-Q. Xin, *Inorg. Chem.* **2006**, *45*, 59–65; h) R. W. Saalfrank, T. Nakajima, N. Mooren, A. Scheurer, H. Maid, F. Hampel, C. Trieflinger, J. Daub, *Eur. J. Inorg. Chem.* **2005**, 1149–1153; i) C. Papatriantafyllopoulou, C. P. Raptopoulou, A. Escuer, C. J. Milios, *Inorg. Chim. Acta* **2007**, *360*, 61–68; j) E. C. Sañudo, E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, T. R. Concolino, K. A. Abboud, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson, G. Christou, *Polyhedron* **2003**, *22*, 2267–2271; k) C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, D. N. Hendrickson, G. Christou, *Chem. Commun.* **2001**, 467–468; l) N. C. Harden, M. A. Bolcar, W. Wernsdorfer, K. A. Abboud, W. E. Streib, G. Christou, *Inorg. Chem.* **2003**, *42*, 7067–7076; M. D. Godbole, O. Roubeau, A. M. Mills, H. Kooijman, A. L. Spek, E. Bouwman, *Inorg. Chem.* **2006**, *45*, 6713–6722.

[21] See, for example: a) C. Philouze, G. Blondin, J.-J. Girerd, J. Guilhem, C. Pascard, D. Lexa, *J. Am. Chem. Soc.* **1994**, *116*, 8557–8565; b) H. Chen, M.-N. Collomb, C. Duboc, G. Blondin, E. Rivière, J. W. Faller, R. H. Crabtree, G. W. Brudvig, *Inorg. Chem.* **2005**, *44*, 9567–9573; c) H. Y. Chen, J. W. Faller, R. H. Crabtree, G. W. Brudvig, *J. Am. Chem. Soc.* **2004**, *126*, 7345–7349.

[22] See, for example: a) M. L. Kirk, M. K. Chan, W. H. Armstrong, E. I. Solomon, *J. Am. Chem. Soc.* **1992**, *114*, 10432–10440; b) S. Mukhopadhyay, H. J. Mok, R. J. Staples, W. H. Armstrong, *J. Am. Chem. Soc.* **2004**, *126*, 9202–9204.

[23] S. Mukhopadhyay, R. J. Staples, W. H. Armstrong, *Chem. Commun.* **2002**, 864–865.

[24] G. Aromí, S. Badhuri, P. Artús, K. Folting, G. Christou, *Inorg. Chem.* **2002**, *41*, 805–817 and references cited therein.

[25] C. E. Dubé, S. Mukhopadhyay, P. J. Bonitatebus, R. J. Staples, W. H. Armstrong, *Inorg. Chem.* **2005**, *44*, 5161–5175 and references cited therein.

[26] a) E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1991**, *30*, 3486–3495; b) E. Bouwman, M. A. Bolcar, E. Libby, J. C. Huffman, K. Folting, G. Christou, *Inorg. Chem.* **1992**, *31*, 5185–5192; c) S. Wang, K. Folting, W. E. Streib, E. A. Schmitt, J. K. McCusker, D. N. Hendrickson, G. Christou, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 305–306; d) J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1989**, *111*, 2086–2097; e) C. Cañada-Vilalta, J. C. Huffman, G. Christou, *Polyhedron* **2001**, *20*, 1785–1793; f) G. Aromí, S. Badhuri, P. Artús, J. C. Huffman, D. N. Hendrickson, G. Christou, *Polyhedron* **2002**, *21*, 1779–1786.

[27] A search using the core described in Scheme 1 in CCDC version 5.28; references given throughout this microreview.

[28] Note that an exception to this classification corresponds to the case where the butterfly core is made of two μ_3-oxido bridges together with μ-1,1-azido ligands. Although the azido ligands act as N-mononuclear bridges, the corresponding compound will not be considered here; see: G. S. Papaeftstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, R. Vicente, *Eur. J. Inorg. Chem.* **2001**, 1567–1574.

[29] Experimental susceptibility data are usually reproduced by using the Heisenberg–Van Vleck model derived from the spin Hamiltonian $H = -2J_{bb}(s_a s_b) - 2J_{wb}(S_a+S_b)(s_a+s_b)$, to derive the wing–body and body–body interaction constants. S_a and S_b represent the Mn^{II} $S = 5/2$ spins, while s_a and s_b stand for Mn^{III} $S = 2$ spins. The letters a and b differentiate between the two Mn ions with the same valence.

[30] For other recent Mn/hmp systems, see: a) T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2006**, *45*, 4134–4137; b) T. C. Stamatatos, K. M. Poole, K. A. Abboud, W. Wernsdorfer, T. A. O'Brien, G. Christou, *Inorg. Chem.* **2008**, *47*, 5006–5021.

[31] a) T. C. Stamatatos, A. K. Boudalis, K. V. Pringouri, C. V. Raptopoulou, A. Terzis, J. Wolowska, E. J. L. McInnes, S. Perlepes, *Eur. J. Inorg. Chem.* **2007**, 5098–5104; b) T. Taguchi, T. C. Stamatatos, K. A. Abboud, C. M. Jones, K. M. Poole, T. A. O'Brien, G. Christou, *Inorg. Chem.* **2008**, *47*, 4095–4108.

[32] a) P. L. Feng, C. C. Beedle, W. Wernsdorfer, C. Koo, M. Nakano, S. Hill, D. N. Hendrickson, *Inorg. Chem.* **2007**, *46*, 8126–8128; b) P. L. Feng, C. C. Beedle, W. Wernsdorfer, C. Koo, M. Nakano, S. Hill, D. N. Hendrickson, *Inorg. Chem.* **2008**, *47*, 3188–3204.

[33] E.-C. Yang, N. Harden, W. Wernsdorfer, L. Zakharov, E. K. Brechin, A. L. Rheingold, G. Christou, D. N. Hendrickson, *Polyhedron* **2003**, *22*, 1857–1863.

[34] L. Lecren, W. Wernsdorfer, Y.-G. Li, O. Roubeau, H. Miyasaka, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 11311–11317.

[35] L. Lecren, O. Roubeau, C. Coulon, Y.-G. Li, X. F. Le Goff, W. Wernsdorfer, H. Miyasaka, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 17353–17363.

[36] H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fijisaki, K.-I. Sugiura, M. Yamashita, R. Clérac, *J. Am. Chem. Soc.* **2006**, *128*, 3770–3783.

[37] L. Lecren, O. Roubeau, Y.-G. Li, X. F. Le Goff, H. Miyasaka, F. Richard, W. Wernsdorfer, C. Coulon, R. Clérac, *Dalton Trans.* **2008**, 755–766.

[38] L. Lecren, Y.-G. Li, W. Wernsdorfer, O. Roubeau, H. Miyasaka, R. Clérac, *Inorg. Chem. Commun.* **2005**, *8*, 626–630.

[39] see: a) E. K. Brechin, *Chem. Commun.* **2005**, 5141–5153; b) M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 4766–4767; c) M. Murugesu, W. Wernsdorfer, K. A. Abboud, G. Christou, *Polyhedron* **2005**, *24*, 2894–2899; d) T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2007**, *46*, 884–888.

[40] a) E. K. Brechin, J. Yoo, M. Nakano, J. C. Huffman, D. N. Hendrickson, G. Christou, *Chem. Commun.* **1999**, 793–794; b) J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maneiro, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2000**, *39*, 3615–3623.

[41] See, for example: a) G. Rajaraman, M. Murugesu, E. C. Sañudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S. J. Teat, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2004**, *126*, 15445–15457; b) M. Murugesu, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2005**, *44*, 892–896; c) M. Cavaluzzo, Q. Chen, J. Zubieta, *J. Chem. Soc., Chem. Commun.* **1993**, 131–132; d) C. J. Milios, F. P. A. Fabbiani, S. Parsons, M. Murugesu, G. Christou, E. K. Brechin, *Dalton Trans.* **2006**, 351–356; e) C. J. Milios, M. Manoli, G. Rajaraman, A. Mishra, L. E. Budd, F. White, S. Parsons, W. Wernsdorfer, G. Christou, E. K. Brechin, *Inorg. Chem.* **2006**, *45*, 6782–6793.

[42] D. Foguet-Albiol, T. A. O'Brien, W. Wernsdorfer, B. Moulton, M. J. Zaworotko, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2005**, *44*, 897–901.

[43] A. M. Ako, V. Mereacre, I. J. Hewitt, R. Clérac, L. Lecren, C. E. Anson, A. K. Powell, *J. Mater. Chem.* **2006**, *16*, 2579–2586.

[44] Y. Sunatsuki, H. Shimada, T. Matsuo, M. Nakamura, F. Kai, N. Matsumoto, N. Re, *Inorg. Chem.* **1998**, *37*, 5566–5574.

[45] S. C. Shoner, P. P. Power, *Inorg. Chem.* **1992**, *31*, 1001–1010.

[46] a) S. K. Chandra, A. Chakravorty, *Inorg. Chem.* **1991**, *30*, 3796–3798; b) S. K. Chandra, P. Chakraborty, A. Chakravorty, *J. Chem. Soc., Dalton Trans.* **1993**, 863–869.

[47] C. Gedye, C. Harding, V. McKee, J. Nelson, J. Patterson, *J. Chem. Soc., Chem. Commun.* **1991**, 392–394.

[48] a) M. Mikuriya, Y. Yamato, T. Tokii, *Chem. Lett.* **1991**, 1429–1432; b) M. Mikuriya, Y. Yamato, T. Tokii, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2624–2637.

[49] M. Mikuriya, K. Nakadera, T. Kotera, T. Tokii, W. Mori, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3077–3083.

[50] J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L.-C. Brunel, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, *40*, 4604–4616.

[51] A. Yamaguchi, N. Kusumi, H. Ishimoto, H. Mitamura, T. Goto, N. Mori, M. Nakano, K. Awaga, J. Yoo, D. N. Hendrickson, G. Christou, *J. Phys. Soc. Jpn.* **2002**, *71*, 414–417.

[52] L. M. Wittick, K. S. Murray, B. Moubaraki, S. R. Batten, L. Spiccia, K. J. Berry, *Dalton Trans.* **2004**, 1003–1011.

[53] L. M. Wittick, L. F. Jones, P. Jensen, B. Moubaraki, L. Spiccia, K. J. Berry, K. S. Murray, *Dalton Trans.* **2006**, 1534–1543.

[54] L. Stelzig, A. Steiner, B. Chansou, J.-P. Tuchagues, *Chem. Commun.* **1998**, 771–772.

[55] a) D. Boinnard, A. Bousseksou, A. Dworkin, J. M. Savariault, F. Varret, J. P. Tuchagues, *Inorg. Chem.* **1994**, *33*, 271–281; b) H. Spiering, T. Kohlhaas, H. Romstedt, A. Hauser, C. Bruns-Yilmaz, J. Kusz, P. Gütlich, *Coord. Chem. Rev.* **1999**, *192–192*, 629–647.

[56] C.-I. Yang, G.-H. Lee, C.-S. Wur, J. G. Lin, H.-L. Tsai, *Polyhedron* **2005**; *24*, 2215–2221.

[57] H. Hiraga, H. Miyasaka, K. Nakata, T. Kajiwara, S. Takaichi, Y. Oshima, H. Nojiri, M. Yamashita, *Inorg. Chem.* **2007**, *46*, 9661–9671.

[58] L. Lecren Ph. D Thesis, ***2006***, Bordeaux 1 University, France.

[59] J. Yoo, W. Wernsdorfer, E.-C. Yang, M. Nakano, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.* **2005**, *44*, 3377–3379.

[60] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760–1763.

[61] S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* **2003**, *246*, 103–130.

[62] H. Miyasaka, K. Nakata, K.-I. Sugiuara, M. Yamashita, R. Clérac, *Angew. Chem. Int. Ed.* **2004**, *43*, 707–711.

[63] a) H. Miyasaka, R. Clérac, K. Mizushima, K.-I. Sugiura, M. Yamashita, W. Wernsdorfer, C. Coulon, *Inorg. Chem.* **2003**, *42*, 8203–8213; b) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K.-I. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090–3099.

[64] M. Yuan, F. Zhao, W. Zhang, F. Pan, Z.-H. Wang, S. Gao, *Chem. Eur. J.* **2007**, *13*, 2937–2952.

[65] H.-B. Xu, B.-W. Wang, F. Pan, Z.-M. Wang, S. Gao, *Angew. Chem. Int. Ed.* **2007**, *46*, 7388–7392.

[66] a) J. Tao, Y.-Z. Zhang, Y.-L. Bai, O. Sato, *Inorg. Chem.* **2006**, *45*, 4877–4879; b) Y.-L. Bai, J. Tao, W. Wernsdorfer, O. Sato, R.-B. Huang, L.-S. Zheng, *J. Am. Chem. Soc.* **2006**, *128*, 16428–16429.

[67] K. C. Mondal, M. G. B. Drew, P. S. Mukherjee, *Inorg. Chem.* **2007**, *46*, 5625–5629.

[68] R. J. Glauber, *J. Math. Phys.* **1963**, *4*, 294.

[69] V. Ovcharenko, E. Fursova, G. Romanenko, V. Ikorskii, *Inorg. Chem.* **2004**, *43*, 3332–3334.

[70] a) For a review up to 2006, see: A. Cornia, A. F. Costantino, L. Zobbi, A. Caneschi, D. Gatteschi, R. Sessoli, *Struct. Bonding (Berlin)* **2006**, *122*, 133–161 and references cited therein; b) K. Kim, A. Ford, V. Meenakshi, W. Teizer, H. Zhao, K. R. Dunbar, *J. Appl. Phys.* **2007**, *102*, 094306; c) J. Gomez-Segura, J. Veciana, D. Ruiz-Molina, *Chem. Commun.* **2007**, 3699–3707; d) G. G. Condorelli, A. Motta, G. Pellegrino, A. Cornia, L. Gorini, L. L. Fragala, C. Sangregorio, L. Sorace, *Chem. Mater.* **2008**, *20*, 2405–2411; e) E. Coronado, L. Marti-Gastaldo, S. Tatay, *Appl. Surf. Sci.* **2007**, *254*, 225–235.

[71] E. E. Moushi, T. C. Stamatatos, W. Wernsdorfer, V. Nastopoulos, G. Christou, A. J. Tasiopoulos, *Angew. Chem. Int. Ed.* **2006**, *45*, 7722–7725.

[72] See, for example: M. Murugesu, R. Clérac, C. E. Anson, A. K. Powell, *Inorg. Chem.* **2004**, *43*, 7269–7271.

[73] The term ferrimagnetic has been coined for polynuclear magnetic complexes for cases where the conjugation of antiferromagnetic interactions between the individual pairs of paramagnetic centers in the complex results in an increase in magnetic moment with decreasing temperature, see: D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054.

[74] M. Murugesu, C. E. Anson, A. K. Powell, *Chem. Commun.* **2002**, 1054–1055.

[75] The use of other transition-metal ions with less tendency to dimerize antiferromagnetically than Cu^{II} would nevertheless probably yield paramagnetic bridges.

[76] S. Wang, H.-L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson, G. Christou, *J. Chem. Soc., Chem. Commun.* **1994**, 671–673.

[77] K. Nakata, H. Miyasaka, K. Sugimoto, T. Ishii, K.-I. Sugiura, M. Yamashita, *Chem. Lett.* **2002**, 658–659.

[78] A. R. E. Baikie, A. J. Jowes, M. B. Hursthouse, A. B. Quick, P. Thornton, *J. Chem. Soc., Chem. Commun.* **1986**, 1587–1588.

[79] W. Wernsdorfer, R. Clérac, C. Coulon, L. Lecren, H. Miyasaka, *Phys. Rev. Lett.* **2005**, *95*, 237203.

[80] H. Miyasaka, T. Madanbashi, K. Sugimoto, Y. Nakazawa, W. Wernsdorfer, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *Chem. Eur. J.* **2006**, *12*, 7028–7040.

[81] H. Miyasaka, M. Yamashita, *Dalton Trans.* **2007**, 399–406.

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