

Functionalization of polyoxometalates by carboxylato and azido ligands: macromolecular complexes and extended compounds

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Polyoxometalate compounds continue to be widely studied due to their relevance in various fields such as catalysis or magnetochemistry. In this article, we will focus on two topics we recently developed, the functionalization of rare earth polyoxometalates by organic ligands, which has led to compounds ranging from magnetic macromolecular complexes to a 3D open-framework system, and the functionalization of first row transition metal substituted polyoxometalates by azido ligands, which has allowed the isolation of complexes exhibiting the largest ferromagnetic exchange couplings observed to date in polyoxometalate chemistry.

Introduction

Polyoxometalates¹ (POMs) are metal–oxygen anionic clusters which can act as multidentate inorganic ligands. They can bind most of the transition metal and rare earth cations, leading to a family of compounds exhibiting a huge diversity of structures. Their morphology (size and shape) and their electronic, electrochemical and acido–basic properties can be finely tuned, making them useful in various fields ranging from catalysis² to magnetochemistry.³ Concerning this last topic, the ability of POM complexes to encapsulate magnetic clusters between diamagnetic fragments makes them especially valuable for the quantification of magnetic interactions. Moreover, for two decades, the functionalization of POM species by organic or inorganic groups has been heavily investigated, resulting in a new class of molecular complexes, but also to extended POM compounds. Several approaches have been developed to obtain such systems. Particularly, numerous studies have been devoted to the direct grafting of organic substrates on the nucleophilic oxygen atoms of the POM core and to the introduction of organometallic fragments into vacant POM

complexes.⁴ If most of these molecular systems have been synthesized using usual bench conditions, hybrid multidimensional materials have been obtained mainly by means of the one pot hydrothermal technique.⁵ Nevertheless, the rationalized synthesis of extended solids from isolated POM precursors remains a challenge. This article focuses on two topics recently developed in our laboratory. First, we have shown that the controlled functionalization of rare earth polyoxometalates by organic ligands can be achieved in soft conditions. The synthesis of such species involves either a monovacant POM building unit (Scheme 1a) or a reduced saturated POM building unit (Scheme 1b). A series of macromolecular and multidimensional compounds have been synthesized, the exogenous ligands acting as intermolecular linkers. Such a strategy has allowed the isolation of the first hybrid open framework based on Keggin building blocks. This compound belongs to the metal–organic frameworks class of materials,⁶ which attracts much interest because of potential applications in catalysis, gas storage and separation. Secondly, if as pointed out above, the magnetic properties of POM clusters have been widely studied, in all cases the superexchange interactions were mediated *via* oxo, hydroxo or *via* phosphato bridges. Recently, we started to explore the synthesis of magnetic POMs where exogenous azido ligands are introduced in the metal–oxide cluster, acting either

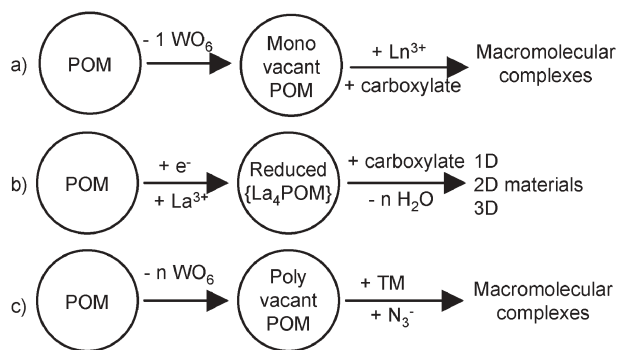
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Scheme 1 Summary of the three synthetic pathways used for the elaboration of the functionalized rare earth or transition metal POMs presented in this article.

as intra- or intermolecular linkers between the paramagnetic centers. In this case, multivacant POMs have been used as inorganic chelating ligands as represented in Scheme 1c. This approach led us to obtain a new family of ferromagnetic species, including complexes exhibiting the largest exchange constants observed to date in polyoxometalate chemistry. These two families of compounds are presented here.

Hybrid organic/inorganic rare earth POM compounds

The study of the interaction of the Keggin-type $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and the Dawson-type $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ monovacant polyoxotungstates with Ln(III) cations was initiated at the beginning of the seventies by Peacock and Weakley,⁷ but it was only in 2000 that Pope *et al.* reported the structure of the $\{\text{Ln}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_3\}_n$ (Ln = La(III), Ce(III)) monodimensional compounds.⁸ A ¹⁸³W NMR study carried out by the same group on the lanthanum derivative showed that, in solution, these species decompose in molecular $[\text{La}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_n]^{5-}$ units. Later, the reactivity of the same monovacant POM with various rare earth cations (Ln = Nd(III), Eu(III), Gd(III), Yb(III)) was studied in our group, confirming that these systems adopt, in all cases, multidimensional arrangements, but also that the arrangements of the polyoxometalate building units, the Ln(III):POM ratios, and the dimensionalities of these compounds are strongly dependent on the nature of the rare earth cation. Nevertheless, luminescence studies performed on the europium derivative revealed that monomeric species are formed in aqueous media. Indeed, while in the solid state two terminal water ligands are connected to the europium center, in agreement with the single-crystal XRD data, four terminal water ligands are evidenced in aqueous solution, which implies the absence of any Eu(III)–O(W) intermolecular interactions in this medium.⁹ Considering the solution studies performed on the La(III) and Eu(III) derivatives, it can be reasonably assessed that this decomposition into monomeric species occurs whatever the nature of the Ln(III) cation. The terminal water ligands connected to the rare earth cation embedded in the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ unit are labile enough to be potentially exchangeable by organic substrates. Due to their high affinity for lanthanide cations, mono- and dicarboxylate ligands have

been considered, and indeed, in acetate–acetic acid buffer solution the $[\{\text{Ln}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2]^{12-}$ (Ln = Eu(III) (1), Gd(III) (2), Yb(III) (3)) dimeric species have been obtained (Fig. 1).¹⁰ In these complexes, each Ln(III) center is eight-coordinated within a distorted Archimedean antiprism geometry (pseudo- D_{4h}), the two Ln(III) centers being doubly bridged by two $(\eta^2, \mu\text{-}1, 1)$ -acetato ligands. Surprisingly, while related complexes with lighter Ln(III) cations (Ln = Ce(III), Pr(III)) could not be obtained in analogous experimental conditions, Körtz concomitantly reported the characterization of the lanthanum Dawson-type $[\{\text{La}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2]^{16-}$ POM, obtained by decomposition of the hexalacunary $[\alpha\text{-H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ polyanion in the presence of La(III) ions in acetate buffer.¹¹ The $\chi_{\text{M}}T = f(T)$ curve of complex 2 has been fitted using the spin Hamiltonian $\hat{H} = -J\hat{S}_{\text{Gd}(1)}\hat{S}_{\text{Gd}(2)}$, leading to a J value of -0.02 cm^{-1} . This value, although slightly lower than for the previously reported dinuclear gadolinium complexes,¹² confirmed the connection of the two paramagnetic centers *via* the acetato ligands. A tetradentate linker was then considered. The reactivity of the $[\text{Yb}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_4]^{5-}$ and $[\text{Yb}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})(\text{H}_2\text{O})_4]^{7-}$ precursors with oxalato ligands has been investigated, and in both cases the linear tetrameric $[\{\text{Yb}(\text{POM})\}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]^{n-}$ (POM = $\alpha\text{-SiW}_{11}\text{O}_{39}$ (4), $n = 26$; $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}$ (5), $n = 34$) clusters were obtained (Fig. 2).¹³ All the ytterbium ions adopt the same Archimedean antiprism arrangement as in the carboxylato compound. The two central Yb(III) centers are coordinated to two oxalato groups and the two terminal Yb(III) ions are coordinated to one oxalato ligand and to two terminal water molecules, resulting in a well-isolated linear tetranuclear $\{\text{Yb}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4\}$ magnetic cluster. Despite the high affinity of the Yb(III) ions for the $\text{C}_2\text{O}_4^{2-}$ ligands, ³¹P NMR studies indicate that equilibria involving several unidentified species occur in aqueous media.

These two examples illustrate the possibility of obtaining clusters with magnetically interacting rare earth centers by condensation of lanthanide POMs *via* organic ligands. Considering the diversity of polydentate oxygenated ligands, this synthetic strategy should lead to a family of complexes of various nuclearities and topologies. Nevertheless, it appears that the functionalization of rare earth monosubstituted POMs by exogenous ligands has not led to multidimensional

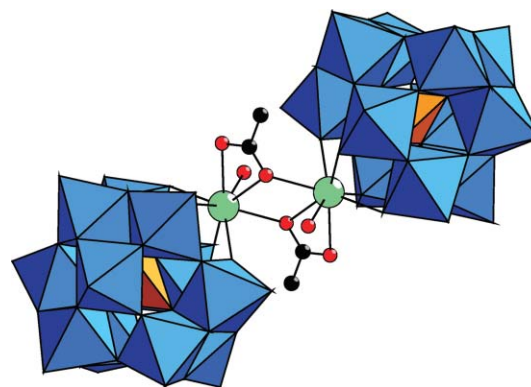


Fig. 1 Structure of complex $[\{\text{Yb}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2\}_2(\mu\text{-CH}_3\text{COO})_2]^{12-}$ (3) (blue octahedra = WO_6 , orange octahedra = SiO_4 , black spheres = C, red spheres = O, green spheres = Yb).

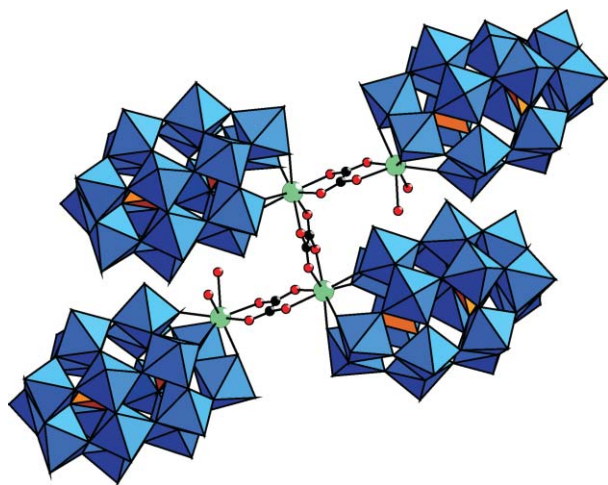


Fig. 2 Structure of complex $[\{Yb(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]^{34-}$ (**5**) (blue octahedra = WO_6 , orange octahedra = PO_4 , black spheres = C, red spheres = O, green spheres = Yb).

materials. In order to access such species, it was necessary to consider a new POM precursor which must (i) possess several accessible rare earth centers coordinated to exchangeable water ligands, (ii) be soluble in the usual solvents and (iii) be stable in solution. As, to the best of our knowledge, such a compound was not available, we synthesized a complex possessing these three qualities. Polyoxomolybdate compounds can easily be obtained in a reduced form, leading to highly negatively charged compounds exhibiting a strong affinity for metallic ions. Müller *et al.* reported that an ϵ -Keggin isomer capped by Ni(II) ions, the complex $[\text{Mo}_{12}\text{O}_{30}(\text{OH})_{10}\text{H}_2\{\text{Ni}(\text{H}_2\text{O})_3\}_4]$, could be obtained.¹⁴ However, this neutral molecular species is insoluble, preventing any further chemical reactions on this compound. We have prepared a soluble ϵ -Keggin species by reaction of sodium molybdate, phosphoric acid, lanthanum chloride and hydrazine as reducing agent. The complex $[(\epsilon\text{-PMo}_{12}\text{O}_{36})(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ (**6**) is represented in Fig. 3.¹⁵ It has to be noted that, although the $[\alpha\text{-PMo}_{12}\text{O}_{40}]^{3-}$ polyanion has been known for almost 200 years, this was the first characterization of its

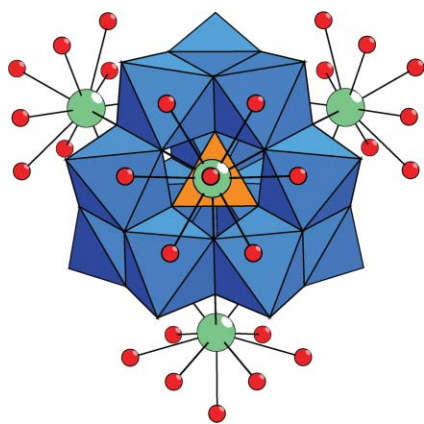


Fig. 3 Structure of complex $[(\epsilon\text{-PMo}_{12}\text{O}_{36})(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ (**6**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , red spheres = O, green spheres = La). The water ligands are disordered.

related ϵ -isomer derivative. The overall T_d symmetry of the $\{\epsilon\text{-PMo}_{12}\text{O}_{40}\}$ structure is maintained by the grafting of four stabilizing $\{\text{La}(\text{H}_2\text{O})_4\}$ units on the four faces of the truncated tetrahedron defined by the twelve molybdenum centers. Potentiometric titrations confirmed the presence of 8 Mo(V) and 4 Mo(VI) centers. As no intervalence Mo(V) \rightarrow Mo(VI) charge transfer band has been observed by electronic absorption spectroscopy, it is assumed that the Mo(V) centers form Mo(V)–Mo(V) diamagnetic pairs. **6** is soluble in water and methanolic media. ³¹P NMR data agree with an equilibrium between two species, the $[(\epsilon\text{-PMo}_{12}\text{O}_{36})(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ precursor and the $[(\epsilon\text{-PMo}_{12}\text{O}_{36})(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_3]^{2+}$ species ($K = 2.4 \times 10^{-4} \text{ mol L}^{-1}$), showing that the $\{\text{La}(\text{H}_2\text{O})_4\}$ groups capping the ϵ -Keggin entity are labile. The recrystallization of complex **6** from a KCl solution afforded the $\text{K}_3[\epsilon\text{-PMo}_{12}\text{O}_{32}(\text{OH})_8\{\text{La}(\text{H}_2\text{O})_{4.25}(\text{Cl})_{0.75}\}_4][\alpha\text{-PMo}_{12}\text{O}_{40}]$ salt (**7**), confirming the relative instability of this precursor. The ionic compound **7**, represented in Fig. 4, consists of ϵ - and α -Keggin ions playing the role of counterions to each other, an unprecedented feature in the chemistry of polyoxometalates. Nevertheless, even if the formation of the ionic salt indicates the decomposition of complex **6**, the degradation process is slow. Moreover, ³¹P NMR studies indicate that this precursor is stabilized in solution in the presence of acetate. Then, its functionalization by exogenous ligands has been envisaged, and indeed, this precursor reacts with polydentate organic anions (Scheme 2) to afford hybrid organic–inorganic multi-dimensional materials.

The 1D $[(\epsilon\text{-PMo}_{12}\text{O}_{37})(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_{0.5}\}_4]$ compound (**8**) has been obtained using the glutarate dianion as a linker.¹⁶ Each lanthanum ion is coordinated to carboxylate groups which act as chelating groups (Fig. 5). Two, almost parallel, bidentate ligands connect the polyoxocations one by one, leading to zig-zag chains. In the presence of squarate, the 2D compound $[(\epsilon\text{-PMo}_{12}\text{O}_{39})(\text{OH})\{\text{La}(\text{H}_2\text{O})_5(\text{C}_4\text{O}_4)_{0.5}\}_2\{\text{La}(\text{H}_2\text{O})_6\}_2]$ (**9**) has been isolated. In this case, only two of

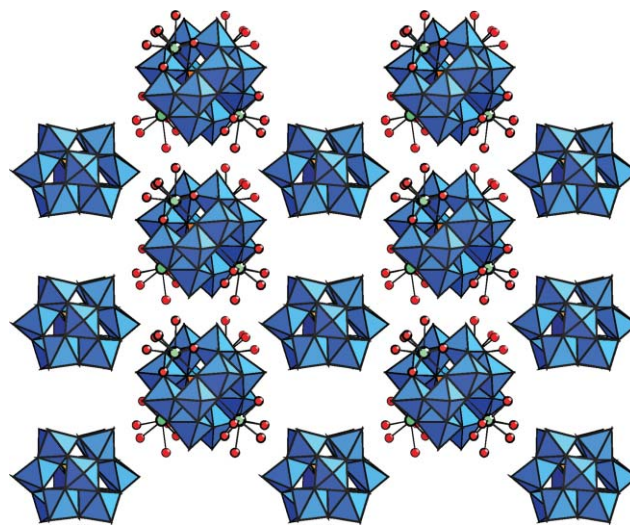
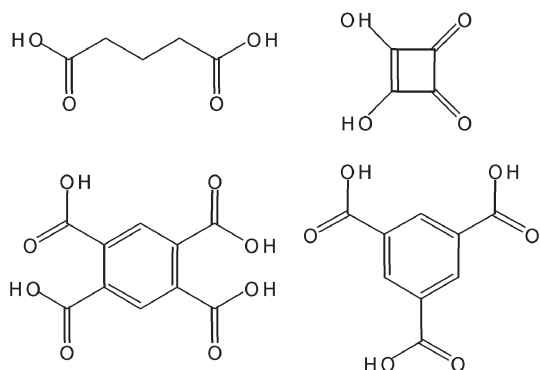


Fig. 4 Ionic structure of compound $\text{K}_3[\epsilon\text{-PMo}_{12}\text{O}_{32}(\text{OH})_8\{\text{La}(\text{H}_2\text{O})_{4.25}(\text{Cl})_{0.75}\}_4][\alpha\text{-PMo}_{12}\text{O}_{40}]$ (**7**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , red spheres = O, green spheres = La). The potassium counterions are not shown.



Scheme 2 Organic ligands used as linkers for the preparation of compounds **8**, **9**, **10** and **11** (from left to right and from top to bottom).

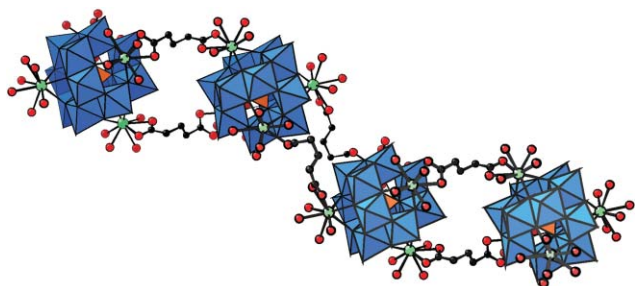


Fig. 5 View of the 1D chain in compound $[(\epsilon\text{-PMo}_{12}\text{O}_{37})(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_{0.5}\}_4]$ (**8**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , black spheres = C, red spheres = O, green spheres = La).

the four lanthanum ions are bound to an organic ligand. The dianion bridges two $\text{La}(\text{III})$ cations through two *trans*-located oxygen atoms, leading to the formation of a straight POM–La–squarate–La–POM chain (Fig. 6). The cohesion within sheets is ensured by hydrogen bonding interactions occurring between water molecules coordinated to the lanthanum centers of a chain and terminal oxygen atoms of an ϵ -Keggin core of an adjacent chain. By increasing the anchoring potentiality of the ligand using the pyromellitate tetraanion and the trimellate trianion as linkers, 3D systems are generated.¹⁷ In the pyromellitate $[(\epsilon\text{-PMo}_{12}\text{O}_{37})(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4(\text{C}_{10}\text{H}_2\text{O}_8)]$

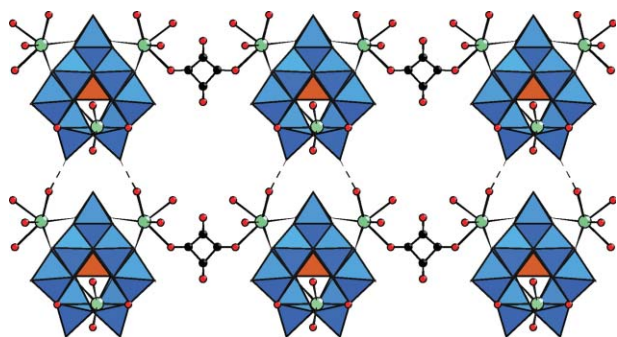


Fig. 6 View of the 2D layer in compound $[(\epsilon\text{-PMo}_{12}\text{O}_{39})(\text{OH})\{\text{La}(\text{H}_2\text{O})_5(\text{C}_4\text{O}_4)_{0.5}\}_2\{\text{La}(\text{H}_2\text{O})_6\}_2]$ (**9**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , black spheres = C, red spheres = O, green spheres = La). The dotted lines represent the $(\text{La})\text{OH}_2^+\cdots\text{O}(\text{W})$ hydrogen bonds.

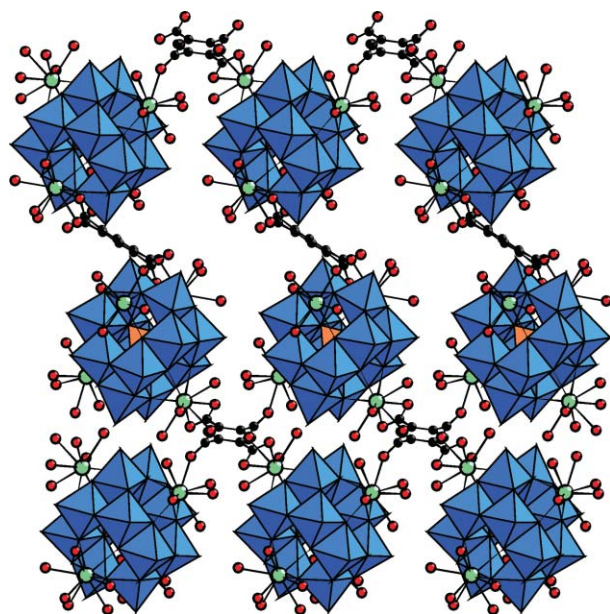


Fig. 7 View of the 3D network in compound $[(\epsilon\text{-PMo}_{12}\text{O}_{37})(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4\}_4(\text{C}_{10}\text{H}_2\text{O}_8)]$ (**10**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , black spheres = C, red spheres = O, green spheres = La).

compound (**10**), each ligand is bound to four lanthanum ions from four distinct polyoxocations, generating a neutral 3D framework with small empty 1D channels (Fig. 7). In the $[(\epsilon\text{-PMo}_{12}\text{O}_{35})(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3(\text{C}_9\text{H}_3\text{O}_6)_{0.5}\}_4]$ compound (**11**), one trimellate ligand connects three different polyoxocations through La–O bonds, also leading to a 3D arrangement. In this case, the channels have relatively large rectangular apertures of $6.1 \times 7.2 \text{ \AA}$, containing only water molecules (Fig. 8). The lability of these water molecules has been demonstrated using X-ray powder diffraction. Indeed, the powder pattern of a freshly filtered sample of **11** progressively evolves with time over a period of two hours, but is recovered if a drop of water is added to the powder sample. This

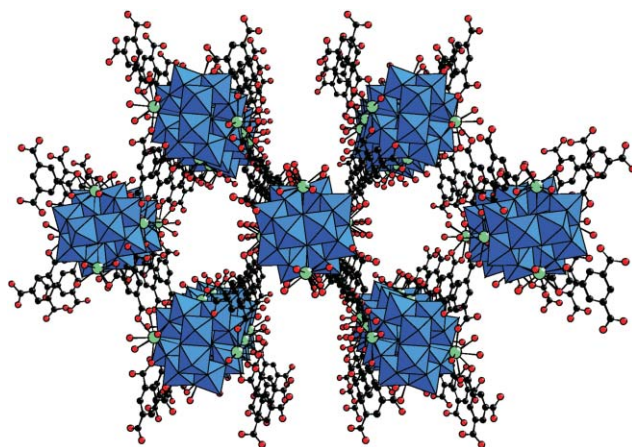


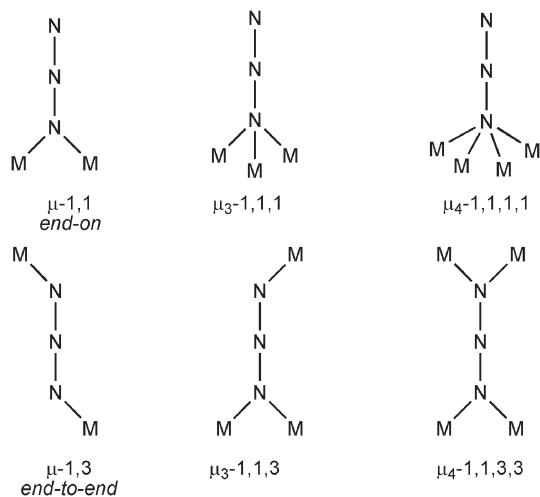
Fig. 8 View of the 3D network in compound $[(\epsilon\text{-PMo}_{12}\text{O}_{35})(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3(\text{C}_9\text{H}_3\text{O}_6)_{0.5}\}_4]$ (**11**) (blue octahedra = MoO_6 , orange octahedra = PO_4 , black spheres = C, red spheres = O, green spheres = La).

experiment shows that the dehydration at room temperature is reversible. Both the hydrated and dehydrated powder patterns have been simulated using lattice energy minimizations.¹⁸ This allows the conclusion that the channels shrink upon dehydration, in agreement with the hydrophobic character of the aromatic linkers. TGA measurements indicate the loss of 32 water molecules per polycationic unit. Nevertheless, X-ray thermodiffraction experiments show that this compound is not stable at high temperature, the 3D structure starting to collapse at 70 °C. This is probably due to the loss of the water molecules coordinated to the La(III) centers upon heating. The replacement of the La(III) ions by cations with lower coordination numbers could improve the stability of the framework.

In conclusion POM systems with one rare earth cation or four non-interacting lanthanide ions localized at the vertices of a tetrahedron have been used as building units in order to obtain macromolecular or extended systems. In both cases, obviously, the exogenous ligands functionalizing the POM compound induce only intermolecular linkage. In the following section, we will see that, when cations are inserted in adjacent vacant sites of a POM matrix, the exogenous ligands can also induce intramolecular linkage, leading to POM complexes with unusual properties.

Functionalization of magnetic polyoxometalates by azido ligands

The azido ion is well-known to be a very versatile ligand. It can bridge two, three or even four paramagnetic transition metals (Scheme 3),¹⁹ the most common azido bridging modes being μ -1,1 (*end-on*) and μ -1,3 (*end-to-end*). It is generally assumed that an *end-on* coordination mode gives rise to ferromagnetic coupling while an *end-to-end* coordination mode leads to antiferromagnetic behavior. Since ferromagnetism in molecular complexes is much less frequent than antiferromagnetism, the *end-on* azido-bridged transition metal species have been hugely studied. Nevertheless, the nature of the magnetic exchange and the absolute J value is strongly dependent on the structural parameters. For example, it has been determined



Scheme 3 Main coordination modes of an azido ligand.

that two Cu(II) ions connected by an *end-on* azido ligand are ferromagnetically coupled for a Cu(II)–N(N₂)–Cu(II) θ bridging angle lower than 108° and antiferromagnetically coupled for a θ angle higher than 108°. ²⁰ Moreover, this magneto-structural relationship is valid only for *basal-basal* coordination modes,²¹ and antiferromagnetic Cu(II) complexes with *basal-apical end-on* azido bridging ligands exhibiting very low θ angles have been characterized.²² If, obviously, several thousands of compounds where first row transition metal cations are coordinated to an organic ligand and magnetically coupled *via* an exogenous ligand (carboxylate, cyanide, azide, diazenido, ...) have been characterized, only one analogous POM complex had been reported when we started our study in 2003. In this species, two Cr(III) centers embedded in the divacant [γ -SiW₁₀O₃₆]⁸⁻ POM are connected by two acetato ligands.²³ Beside the complexes presented in this article, to date, only one other example has been published.²⁴ Several reasons can explain the very low number of such POM complexes. Firstly, POMs are sterically hindered ligands. This does not favor the connection of the transition metals inserted in the vacancies to large ligands, such as aromatic carboxylates. Secondly, POMs exhibit little flexibility, and the exogenous ligand(s) introduced must perfectly fit the rigid paramagnetic cluster. Thirdly, POM–transition metal systems are generally highly negatively charged. Then, for simple electrostatic reasons, it can be unfavorable to introduce negatively charged ligands, and especially polyanionic ligands, in the POM matrix. The monoanionic azido ligand was thus chosen not only since it represents one of the most efficient magnetic coupling agents, but also for its small size, making it very adaptable to the host system.

The first transition metal azido POM characterized possesses a {Ni(μ -1,1-N₃)Ni} core.²⁵ This complex, formulated [(PW₁₀O₃₇)(Ni(H₂O))₂(μ -1,1-N₃)]⁶⁻ (**12**) (Fig. 9a), has been synthesized in water. Each Ni(II) center is tetracoordinated to the {PW₁₀O₃₇} polyanionic ligand, the coordination spheres of the Ni(II) centers being completed by two terminal water molecules. Very interestingly, the Ni–Ni bridging angle ($\theta = 129.3^\circ$) is by far the largest ever observed for *end-on* azido bridged Ni(II) compounds ($85.0^{26} \leq \theta \leq 104.3^{27}$ for the previously reported complexes). While empirical $J = f(\theta)$ magneto-structural correlations have been proposed for *end-on* azido bridged Cu(II)²⁰ and Mn(II)²⁸ compounds, the situation is much less clear for analogous Ni(II) complexes. The present species thus provided a unique opportunity to study the magnetic behavior of a Ni(II) *end-on* azido complex exhibiting a very large θ angle. The $\chi_M T = f(T)$ curve (Fig. 9b) was then simulated using the $\hat{H} = -J\hat{S}_{\text{Ni}(1)}\hat{S}_{\text{Ni}(2)} - D(\hat{S}_z^2 - \hat{S}(\hat{S} + 1))$ Hamiltonian, revealing a ferromagnetic interaction between the two Ni(II) centers ($J = 36.4 \text{ cm}^{-1}$, $g = 2.13$ and $|D| = 5.1 \text{ cm}^{-1}$). This provides empirical evidence that the species possessing a {Ni(μ -1,1-N₃)Ni} core must exhibit ferromagnetic behavior whatever the θ angle is. Moreover, considering the analogous complexes previously reported,¹⁹ no evident relationship between θ and the absolute J value can be found, even if the number of bridging azido ligands is taken into account.²⁹ Even though, in agreement with the experimental data, DFT B3LYP calculations predict a positive J value for the whole experimentally-accessible θ range for *end-on* diazido bridged

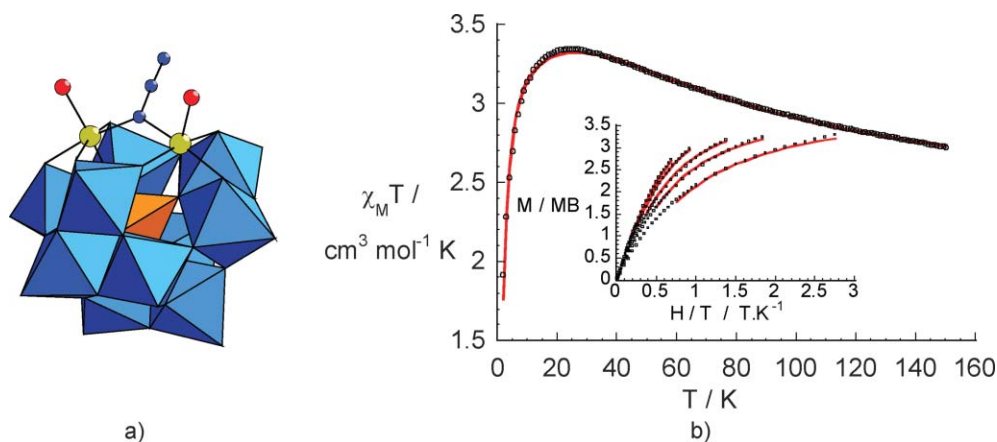


Fig. 9 (a) Structure of complex $[(\text{PW}_{10}\text{O}_{37})(\text{Ni}(\text{H}_2\text{O}))_2(\mu\text{-}1,1\text{-N}_3)]^{6-}$ (**12**) (blue octahedra = WO_6 , orange octahedra = PO_4 , blue spheres = N, red spheres = O, yellow spheres = Ni); (b) $\chi_M T$ vs. T for compound **12**. Inset: M vs. H/T at 8, 6, 4, 3 and 2 K (from left to right) of complex **12**. The red lines were generated from the best fit parameters given in the text.

dinuclear Ni(II) complexes,³⁰ and no negative electronic densities have been found on the nitrogen atoms bridging the two Cu(II) centers in the $[\text{Cu}_2(p\text{-tert-butylpyridine})_4(\mu\text{-}1,1\text{-N}_3)_2]^{2+}$ complex,³¹ it would be very interesting to perform a polarized neutron diffraction study on a complex possessing the $\{\text{Ni}(\mu\text{-}1,1\text{-N}_3)_n\text{Ni}\}$ core in order to determine if a spin polarization effect is superimposed on spin delocalization in these systems.

Due to the coordination mode of the $[\alpha\text{-PW}_{10}\text{O}_{37}]^{9-}$ POM, the two paramagnetic centers in **12** are bridged by only one azido ligand. In order to increase the ferromagnetic coupling between the magnetic ions, the divacant $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ POM has been considered. Indeed, this anion can accommodate two first row transition metal cations, dibridged by two potentially exchangeable hydroxo ligands.³² Three tetranuclear azido polyoxometalate compounds have thus been obtained.

The complex $\{[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Mn}_2(\mu\text{-OH})_2(\text{N}_3)_{0.5}(\text{H}_2\text{O})_{0.5}]_2(\mu\text{-}1,3\text{-N}_3)\}^{10-}$ (**13**) has been synthesized in methanol–acetonitrile medium.³³ It can be described as two sub-units, similar to the entities present in the monomeric complex $[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Mn}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_2]^{4-}$ previously reported by Pope *et al.*,^{32a} dimerized *via* an *end-to-end* azido ligand (Fig. 10). Each Mn(III) ion is in a distorted octahedral environment, the POM sub-units acting as a tridentate ligand for each paramagnetic center. In each sub-unit, two hydroxo anions connect the two Mn(III) ions. The two peripheral paramagnetic centers of the linear tetranuclear cluster are coordinated to a water molecule and a terminal azido ligand, respectively, these two ligands interacting *via* a strong hydrogen bond ($d_{\text{N}\cdots\text{O}} = 2.487(1)$ Å). The experimental $\chi_M T = f(T)$ curve of compound **13** is characteristic of antiferromagnetic behavior, as expected for such a system. The data have been fitted using the Hamiltonian $\hat{H} = -J_1(\hat{S}_{\text{Mn}(1)}\hat{S}_{\text{Mn}(2)} + \hat{S}_{\text{Mn}(1^*)}\hat{S}_{\text{Mn}(2^*)}) - J_2(\hat{S}_{\text{Mn}(1)}\hat{S}_{\text{Mn}(1^*)})$,³⁴ neglecting the zero field splitting (ZFS) effects on the low-lying excited states. The best fit parameters are $J_1 = -25.5$ cm^{-1} , $J_2 = -19.6$ cm^{-1} and $g = 1.98$. The J_1 value is much lower than that observed for di- μ -oxo-Mn(III) species ($-173 \leq J \leq -201$ cm^{-1}),³⁵ confirming the nature of the hydroxo bridges. Moreover, the magnitude of J_1 is in relatively

good agreement with the exchange parameter found for the isolated $[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Mn}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_2]^{4-}$ sub-unit ($J_1 = -34$ cm^{-1}). The J_2 value reflecting the coupling *via* the azido ligand is higher than those found for the three other structurally and magnetically characterized *end-to-end* azido Mn(III) systems. Even if the low number of reported $\{\text{Mn(III)}(\mu\text{-}1,3\text{-N}_3)\text{Mn(III)}\}$ species³⁶ precludes any quantitative magneto-structural correlation, it is observed that for these four compounds the coupling constant decreases continuously as the Mn(III)–N(N_2) distance increases, from $J = -19.6$ cm^{-1} ($d_{\text{Mn-N}} = 2.208(7)$ Å) to $J = -8.6$ cm^{-1} ($d_{\text{Mn-N}} = 2.33$ Å).

Attempts to substitute the two hydroxo bridges by azido groups in **13** have failed, even in a large excess of N_3^- ligand, but the synthesis of *end-on* diazido bridged POM complexes has been achieved successfully using Cu(II) as a paramagnetic ion.

The tetranuclear linear Cu(II) complex $\{[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Cu}_2(\text{H}_2\text{O})(\mu\text{-}1,1\text{-N}_3)_2]_2\}^{12-}$ (**14**) (Fig. 11), made of two $[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Cu}_2(\text{H}_2\text{O})(\mu\text{-}1,1\text{-N}_3)_2]^{6-}$ sub-units, has been synthesized in aqueous medium.³⁷ In each sub-unit, the Cu(II) cations are tricoordinated to the POM ligand and bridged by two *basal-basal end-on* azido groups ($\theta_{\text{av}} = 96.7^\circ$). The sixth positions of the external Cu(II) centers are occupied by an aquo ligand, while the apical positions of the central Cu(II) ions ensure the connection between the two dinuclear

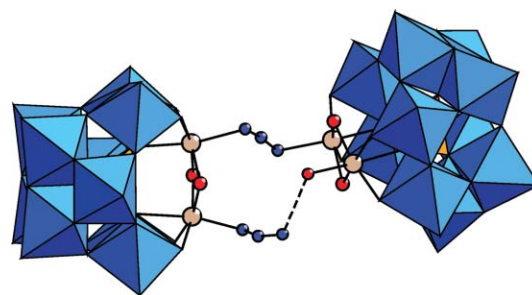


Fig. 10 Structure of complex $\{[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Mn}_2(\mu\text{-OH})_2(\text{N}_3)_{0.5}(\text{H}_2\text{O})_{0.5}]_2(\mu\text{-}1,3\text{-N}_3)\}^{10-}$ (**13**) (blue octahedra = WO_6 , orange octahedra = SiO_4 , blue spheres = N, red spheres = O, light brown spheres = Mn). The dotted line represents the $(\text{N}_2)\text{N}\cdots\text{H}_2\text{O}$ hydrogen bond.

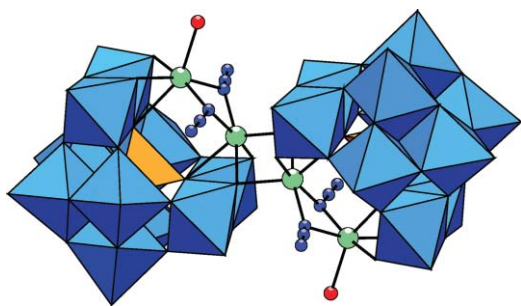


Fig. 11 Structure of complex $[(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Cu}_2(\text{H}_2\text{O})(\mu\text{-}1,1\text{-N}_3)_2]^{12-}$ (**14**) (blue octahedra = WO_6 , orange octahedra = SiO_4 , blue spheres = N, red spheres = O, green spheres = Cu).

units *via* Cu–O(W) bonds ($d_{\text{Cu-O(W)}} = 2.273(5)$ Å). The $\chi_{\text{M}}T$ vs. T plot of complex **14** is characteristic of a strong ferromagnetic coupling, the $\chi_{\text{M}}T$ product increasing when the temperature decreases, a plateau being reached around 60 K. A fit of the magnetic data using the Hamiltonian $\hat{H} = -J_1(\hat{S}_{\text{Cu}(1)}\hat{S}_{\text{Cu}(2)} + \hat{S}_{\text{Cu}(1)^*}\hat{S}_{\text{Cu}(2)^*}) - J_2(\hat{S}_{\text{Cu}(1)}\hat{S}_{\text{Cu}(1)^*})$ has afforded $J_1 = +224$ cm^{-1} , $J_2 = 0$ cm^{-1} and $g = 2.20$. This indicates that the studied system can be seen as two non-interacting magnetic pairs. The value of the J_2 parameter can be justified considering that (i) this coupling constant reflects magnetic interactions involving the non-magnetic d_{z^2} orbitals of the central Cu(II) ions and (ii) superexchange interactions occurring *via* $\mu\text{-O(=W)}$ bridges in $\{\text{Cu}(\mu\text{-O(=W)})_2\text{Cu}\}$ have been found to be very weak, even though the bridging oxygen atoms bridge in a *basal-basal* fashion.³⁸ Moreover, the nature of the ground state has been confirmed by the fit of the magnetization $M = f(H/T)$ curves and by multifrequency high-field-EPR spectroscopy. Indeed, the EPR spectra at 95, 190, 230 and 285 GHz can be reproduced in the 5–30 K temperature range with a unique set of parameters related to a triplet state by full diagonalization using the ZFS spin Hamiltonian $\hat{H}_s = D[\hat{S}_z^2 - \frac{1}{3}\hat{S}(\hat{S} + 1)] + E(\hat{S}_x^2 - \hat{S}_y^2)$.³⁹ Finally, for such *basal-basal end-on* diazido bridged Cu(II) species, it is confirmed that the exchange parameter is strongly correlated to the θ angle, the J_2 value determined for complex **14** being similar to that determined for the complex $[\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2(3\text{-aminopyridine})_4(\mu\text{-NO}_3)_2]$ reported by Escuer *et al.*⁴⁰ ($J = +223$ cm^{-1}), which exhibits a θ bridging angle of 97.5° .

The complex $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Cu}_4(\mu\text{-}1,1,1\text{-N}_3)_2(\mu\text{-}1,1,1\text{-N}_3)_2]^{12-}$ (**15**) (Fig. 12) has been obtained in similar conditions to **14**, but in acetonitrile–methanol medium.³⁷ The dimeric compound **15** is based on the same sub-unit as **14**, but two $\mu\text{-}1,1,1\text{-N}_3$ ligands connect the four Cu(II) ions, which form a lozenge. This illustrates the crucial role played by the nature of the solvent on the organization of the building units in these systems. In **15**, two Cu(II) centers are in a highly distorted octahedral environment, being coordinated to two $\mu\text{-}1,1,1\text{-N}_3$ ligands, while the remaining two copper centers adopt a distorted square pyramidal arrangement, being connected to only one $\mu\text{-}1,1,1\text{-N}_3$ ligand. The $\chi_{\text{M}}T$ vs. T plot of compound **15** (Fig. 13) has been fitted using the spin Hamiltonian $\hat{H} = -J_1(\hat{S}_{\text{Cu}(1)}\hat{S}_{\text{Cu}(2)} + \hat{S}_{\text{Cu}(1)^*}\hat{S}_{\text{Cu}(2)^*}) - J_2(\hat{S}_{\text{Cu}(2)}\hat{S}_{\text{Cu}(2)^*})$, the J_1 constant reflecting the exchange interaction between the Cu(II) embedded in the same $\{\gamma\text{-SiW}_{10}\text{O}_{36}\}$ sub-unit. The best fit

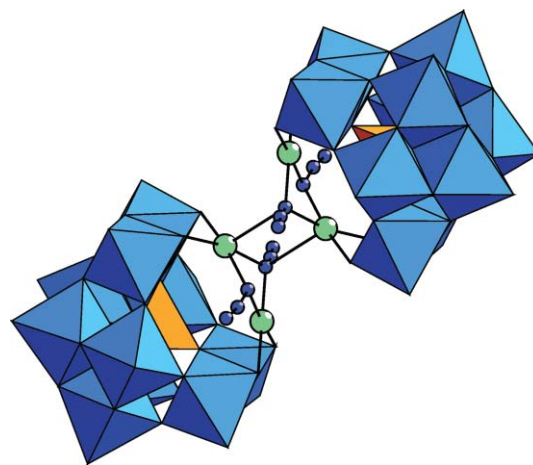


Fig. 12 Structure of complex $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Cu}_4(\mu\text{-}1,1,1\text{-N}_3)_2(\mu\text{-}1,1\text{-N}_3)_2]^{12-}$ (**15**) (blue octahedra = WO_6 , orange octahedra = SiO_4 , blue spheres = N, red spheres = O, green spheres = Cu).

parameters are $J_1 = +294.5$ cm^{-1} , $J_2 = +1.6$ cm^{-1} and $g = 2.085$, indicating that the ground state is a quintet with a first excited state $S = 1$ close in energy. The J_1 value corresponds to the strongest ferromagnetic coupling ever observed in a POM compound but also in any azido bridged complex. This result can be understood in the light of the Thompson *et al.* studies on dinuclear *basal-basal end-on* azido bridged complexes. For these compounds, the exchange coupling constant increases from *ca.* -920 cm^{-1} for a Cu–N(N_2)–Cu angle of 123° to $+170$ cm^{-1} for an average angle of 100° .²⁰ Then, our result is not surprising as complex **15** possesses the lowest θ_{av} angle ($\theta_{\text{av}} = 94.5^\circ$) for this family of compounds. Moreover, to the best of our knowledge, such strong ferromagnetic coupling between two Cu(II) ions has never been observed experimentally up to now.⁴¹ Considering the previously reported structurally and magnetically characterized *basal-basal end-on* diazido bridged complexes where the Cu(II) centers are not connected by other efficiently magnetically coupled

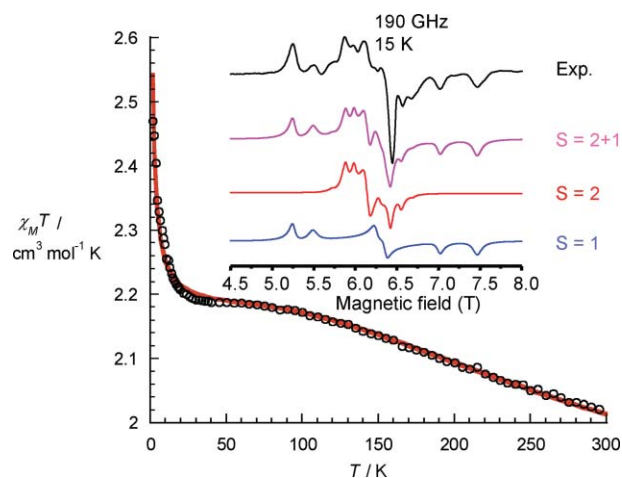


Fig. 13 $\chi_{\text{M}}T$ vs. T for compound **15**. The red line was generated from the best fit parameters given in the text. Inset : experimental powder 190 GHz HF-EPR spectrum of complex **15** recorded at 15 K and simulated spectra of the $S = 1$ and $S = 2$ spin states. The parameters used for the simulations are given in the text.

bridges,^{42,20} we have proposed the new empirical linear magneto-structural correlation $J_1 = 2639.5 - 24.95\theta_{av}$. This experimental $J_1 = f(\theta)$ relation is in good agreement with that proposed by Ruiz *et al.* based on DFT B3LYP calculations.³⁰ Concerning the J_2 exchange parameter, its small absolute value can be easily understood considering that the exchange pathway occurs *via* the non-magnetic d_{z^2} orbitals with very long Cu–N distances ($d_{Cu-N} = 2.602(13)$ Å). The presence of two $S = 1$ and an $S = 2$ state close in energy has been confirmed by multifrequency high-field EPR spectroscopy. Indeed, the experimental spectra recorded at 15 K at several frequencies can be fitted only considering the addition of a quintet and a triplet state with a 1:1 ratio (Fig. 13, inset). The electronic parameters determined for the complexes **14** and **15**⁴³ are relatively large for polynuclear Cu(II) compounds.

While complex **14** was isolated within a few minutes as a caesium salt from the aqueous reacting medium, the nonanuclear Cu(II) complex $[(\gamma\text{-SiW}_8\text{O}_{31})\text{Cu}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_2(\text{N}_3)_3(\mu\text{-}1,1,1,3,3,3\text{-N}_3)]^{19-}$ (**16**) (Fig. 14) has been obtained in similar conditions but as a potassium salt after three days, during which time the decomposition of the $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ ligand into the $[\gamma\text{-SiW}_8\text{O}_{31}]^{10-}$ unit occurred.³⁷ This unprecedented tetravacant POM species has also been characterized very recently by Kortz *et al.* in a Co(II) POM.⁴⁴ The structure of complex **16** consists of three equivalent $[(\gamma\text{-SiW}_8\text{O}_{31})\text{Cu}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_2(\text{N}_3)]^{6-}$ sub-units related *via* a C_3 axis containing the three nitrogen atoms of an encapsulated linear hexadentate $\mu\text{-}1,1,1,3,3,3$ azido group which allows the formation of the nonanuclear Cu(II) complex. So far, such a bridging coordination mode for an N_3^- ligand has been observed previously only in the diamagnetic $\text{AgN}_3 \cdot 2\text{AgNO}_3$ two-dimensional compound.⁴⁵ Each sub-unit contains the trinuclear $\{\text{Cu}_3\text{O}_7(\mu_3\text{-OH})(\text{H}_2\text{O})_2(\mu\text{-}1,3\text{-N}_3)(\text{N}_3)\}$ cluster, which can be described as a distorted defective cubane unit, where all the Cu(II) ions are in a distorted octahedral environment. The temperature dependence of the $\chi_M T$ product in the 40–300 K range is indicative of ferromagnetic interactions, the decrease

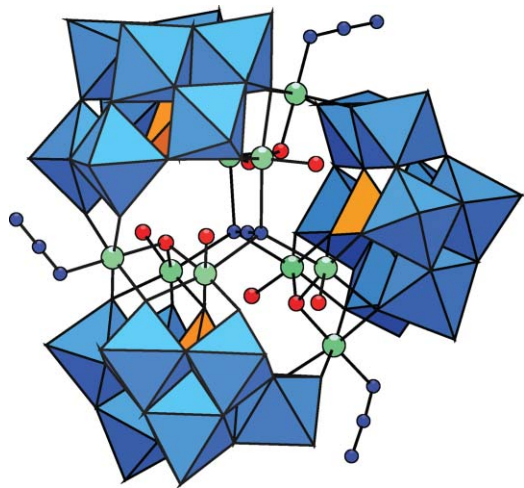
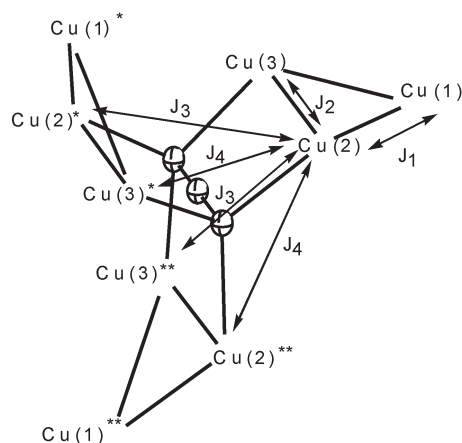


Fig. 14 Structure of complex $[(\gamma\text{-SiW}_8\text{O}_{31})\text{Cu}_3(\mu_3\text{-OH})(\text{H}_2\text{O})_2(\text{N}_3)_3(\mu\text{-}1,1,1,3,3,3\text{-N}_3)]^{19-}$ (**16**) (blue octahedra = WO_6 , orange octahedra = SiO_4 , blue spheres = N, red spheres = O, green spheres = Cu).



Scheme 4 Coupling scheme used for the fit of the magnetic data of complex **16**.

of $\chi_M T$ when T decreases at lower temperatures being attributed to weak antiferromagnetic couplings. The curve has been fitted over the whole temperature range using the exchange model presented in Scheme 4, leading to the best fit parameters $J_1 = +1.0$ cm^{-1} , $J_2 = +20.0$ cm^{-1} , $J_3 = -4.8$ cm^{-1} , $J_4 = +1.3$ cm^{-1} and $g = 2.17$. The determination from susceptibility data of exchange parameter constants using a four J model with J values of the same order of magnitude must be considered with care. Nevertheless, it has to be mentioned that the J_1 and J_2 values determined by this model are in good agreement with those found using a Hamiltonian considering the trinuclear sub-units as pseudo isolated with a Weiss correction taking into account the inter-trinuclear interactions.⁴⁶

Conclusion

This article shows that it is possible to synthesize under mild conditions not only macromolecular compounds but also extended frameworks by combining appropriate POM building units and polydentate linkers. Computational simulations using the AASBU method⁴⁷ have shown that the materials built from the connection of a tetravacant ϵ -Keggin inorganic building unit and rigid organic linkers can potentially exhibit very large pores. It is now important to check experimentally if such phases can be obtained effectively.¹⁷ The synthesis, using usual bench conditions, of new ϵ -Keggin precursors tetra-capped by low coordination number cations such as Zn(II), which could lead to extended species with higher thermal stabilities, is under study. Concerning transition metal POM compounds, it has been demonstrated that hydroxo bridging ligands can be substituted by azido ligands, which can act either as intra- or intermolecular linkers between the transition metal cations embedded in the POM matrix. Importantly, the azido systems which have been obtained using POM ligands possess structural features (bridging angles, metal–azido distances, coordination modes of the azido ligand) that are different from those exhibited by complexes where the paramagnetic ions are embedded in an organic ligand. Strongly ferromagnetically coupled systems have been characterized. We are now working on the synthesis of

complexes with higher nuclearities. The use of hexadentate POMs, such as $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$, is envisaged, as Gouzerh *et al.* showed last year that such a ligand allows the formation of large paramagnetic clusters.^{24,48} Analogously, very recently, Kortz and Mal have shown that the $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$ macrocyclic ligand is able to encapsulate 20 Cu(II) ions.⁴⁹ The study of the $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$ –transition metal–azido system is thus also under way. Finally, the connection of magnetic POM complexes by polycyanometalates, in order to impose ferromagnetic interactions between nearest neighbor magnetic centers owing to strict orthogonality of the magnetic orbitals, is also under study. Indeed, considering the large magnetic anisotropy of the paramagnetic clusters presented here, the synthesis of high spin POM species could lead to POM molecular magnets.⁵⁰

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