A novel hexanuclear ($\text{Mn}_6$) coordination complex with octahedral topology has been prepared and was subsequently used as a building unit for the construction of coordination polymers and metal–organic gels; the latter exhibit thixotropic behavior and reversible sol–gel phase transitions.

Metal–organic frameworks (MOFs) have attracted significant scientific interest due to potential applications in diverse areas such as gas adsorption, catalysis, regenerative medicine, bioengineering and drug delivery.\(^1\) Successful synthetic efforts to develop new types of MOFs highly depend on the availability of suitable organic and inorganic secondary building units (SBUs), which determine the topologies and physical properties of the materials.\(^2\) Similar to MOFs, metal–organic gels (MOGs) are a class of extended structures based on coordination complexes.\(^3\) Recently, there has been increasing interest in the studies of MOGs as these materials can be used in template synthesis, catalysis, and molecular electronics.\(^4\) The formation of MOGs involves the supramolecular self-assembly of coordination complexes through noncovalent interactions such as hydrogen-bonding, π–π stacking and van der Waals forces.\(^5\)

To improve their performances in targeted applications and create multifunctional MOF and MOG materials, there is a high demand for new multinuclear building units which endow the materials with unique electronic, magnetic and structural attributes.\(^6\) Unfortunately, the discovery of new multinuclear SBUs with appropriate topologies remains challenging and often involves serendipitous synthetic approaches. We are interested in the rational synthetic concepts and topological aspects of coordination cages and clusters\(^7\) and according to our previous studies, polynuclear Mn-organophosphonate complexes can adopt highly symmetric geometries which are necessary for qualified SBU candidates.\(^7\) More importantly, Mn coordination clusters may contain kinetically active Mn\(^{III}\) Jahn–Teller ions that can easily be functionalized by organic linkers and may facilitate the organisation of these SBUs into desired MOFs and MOGs.\(^8\)

Herein we report a new symmetric type of hexanuclear Mn coordination complex in $[\text{Cl}<\text{Mn}^{III}_6\{\text{tert-butyl-PO}_3\}_8\{4,4\text{-bipyridine}\}_6]\text{Cl\cdot}\text{H}_2\text{O}$ (6) with thixotropic properties. These materials were characterized by X-ray diffraction, scanning and transmission electron microscopy (SEM and TEM), mass spectrometry and elemental analysis.

The proportionation reaction between MnCl\(_2\)-4H\(_2\)O and KMnO\(_4\) at a molar ratio of 5 : 1 in the presence of tert-butyl-PO\(_3\)-H\(_2\)O, 4-picoline and CH\(_3\)CN gives rise to red crystals of $[\text{Cl}<\text{Mn}^{III}_6\{\text{tert-butyl-PO}_3\}_8\{4\text{-picoline}\}_6]\text{Cl\cdot}\text{H}_2\text{O}$ (1). The compound crystallizes in the cubic space group $Pm\overline{3}$. As shown in Fig. 1a, the cationic $\{\text{Mn}_6\}$ cage contains six Mn\(^{III}\) atoms in an octahedral arrangement, with a Cl\(^-\) ion located in the centre at the position of an inversion centre. The coordination environments of these six Mn\(^{III}\) can be regarded as tetragonally distorted octahedra with one N-donor originating from a 4-picoline ligand and a central Cl\(^-\) ion occupying the apical positions. Four O atoms from four different tert-butylphosphonate ligands occupy the remaining equatorial coordination sites. The 8 triangular faces of the octahedral $\{\text{Mn}_6\}$ cage are capped by 8 fully deprotonated tert-butylphosphonate ligands with each of them bridging three Mn\(^{III}\) atoms in a $\eta^1:\eta^1:\eta^3$ binding mode. Accordingly, the 8 P atoms of the tert-butylphosphonate ligands arrange into a cube (Fig. 1b). The central Cl\(^-\) ion weakly interacts with the six symmetry-related Mn centres resulting in Mn···Cl distances of 3.108(10) Å. The assigned $^3$I oxidation states of the Mn centers are confirmed by bond valence sum analyses (BVSA).
The structure of the hexanuclear Mn complex is indeed interesting in its own right as it can be regarded as a coordination chemistry analogue of the classical face-capped inorganic [Mo$_6$X$_{14}$]$^2^-$ (X = Cl, Br, I) clusters in low-valent halides or as \{Mo$_6$Y$_4$\} (Y = chalcogen) in Chevrel phases (Fig. 1c).\textsuperscript{9} In halide and chalcogenide clusters terminal monodentate ligands in the apical octahedral positions are susceptible to ligand exchange reactions. This feature is also applicable to the \{Mn$_6$\} complex.

In particular, the Jahn–Teller distorted coordination environments of these six Mn$^{III}$ centres in 1 provide kinetically labile active sites to the \{Mn$_6$\} cage, supplying possible chemical functionality through replacing the 4-picoline by other ligands. Indeed the 4-picoline ligands in 1 can formally be replaced by pyridine, H$_2$O, MeOH and 4-pyridinecarboxaldehyde ligands (2–4). The \{Mn$_6$\} cluster cores in 1–4 only reveal slight geometrical differences (see ESI†). The complexes are stable in air. Analyses of the magnetic susceptibility of the \{Mn$_6$\} complexes confirm moderate average intramolecular antiferromagnetic interactions ($|J/k_B|$ ca. 2 K) between the $S=2$ Mn$^{III}$ centres leading to $S=0$ spin ground states (the following isotropic Heisenberg spin Hamiltonian was used: $H=-2J(S_1+S_2)$; see ESI†).

Considering the octahedral symmetry of the \{Mn$_6$\} cages in 1–4 and the functionality with respect to ligand substitutions it appears plausible to use this coordination complex as a potential SBU for the preparation of extended structures (Fig. 1b). Indeed, when bifunctional 4,4′-bipyridine ligands \(4,4′\text{-bpy}\) were introduced into the reaction system, a 1D metal–organic polymer, \([\text{Cl}0_{\text{Mn}^{III}}6(\text{tert-butyl-PO}_3)8(\text{pyridine})4(4,4′\text{-bipyridine})]\text{Cl} ([5] \text{Cl})\), was obtained. X-ray diffraction analysis confirms that 5 consists of \{Mn$_6$\} cages similar to 1–4. Each of the \{Mn$_6$\} cages is connected to two adjacent ones by two 4,4′-bipyridine linkers, with the remaining four Jahn–Teller sites occupied by pyridine ligands (Fig. 1d). The compound crystallizes in the monoclinic space group \(C2/m\) and the 1D chain structure extends in the direction of the crystallographic $b$-axis. Unfortunately, the use of increased aliquots of 4,4′-bipyridine did not result in other crystalline materials and phase-pure 3D MOFs could not yet be isolated. However, interestingly, only complete substitution of pyridine by 4,4′-bipyridine results in the formation of a stable supramolecular gel that exhibits thixotropic behavior and reveals reversible sol–gel phase transitions (Fig. 2e). These MOGs settle within a period of 24 h. On agitation (e.g. intensive shaking of the...
that the formation of the liquid phase is accompanied with a
disentanglement of the fibers reducing the viscosity of the material.
As indicated by the structure of 3, it is feasible to assume that
during this process 4,4′-bipyridine moieties are replaced by MeOH
ligands. The analyses suggest that the transformation into a liquid
phase results in the degradation of the 1D assemblies producing
random aggregations of individual nanoparticles of the coordina-
tion complexes.

In summary, we report a remarkable hexanuclear MnIII complex
that is structurally related to classical octahedral face-capped cluster
compounds such as Chevrel clusters. The lability of apical ligands
of the six MnIII Jahn–Teller sites provides functionality to the system
and can be exploited for ligand substitutions allowing the prepara-
tion of a metal–organic polymer. Moreover, the synthetic approach
can be exploited for the preparation of supramolecular gels with
reversible thixotropic properties. Transformation between the liquid
and gel phase is most likely facilitated by the aggregation of
nanoparticles to form entangled 1D assemblies.

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