# A polyoxometalate-based manganese carboxylate cluster†

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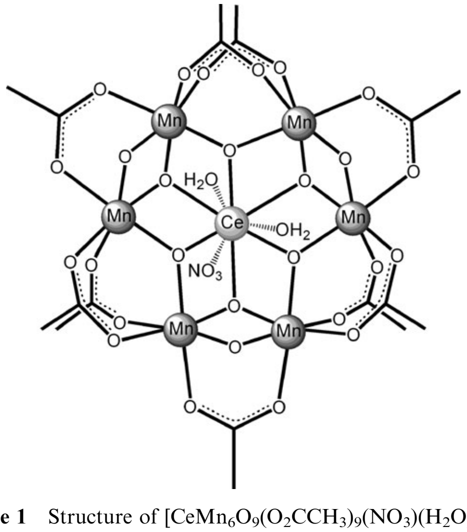
**The functionalization of a pre-formed, high oxidation state $\{Ce^{IV}Mn^{IV}{}_6\}$ cluster with a lacunary phosphotungstate, $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$, exemplifies a straightforward route for grafting redox-active building blocks to existing Mn–carboxylate clusters and modeling their deposition onto metal oxide surfaces.**

Polynuclear manganese carboxylate clusters have demonstrated promising potential in the field of molecular magnetism, especially as single-molecule magnets exhibiting spin multiplet ground states and molecular easy-axis-type anisotropy due to zero-field splitting effects.[1] Syntheses of such clusters generally involve self-assembly of manganese salts or pre-formed Mn clusters in the presence of bridging ligands such as carboxylates and alkoxides. Despite the enormous success with *organic* ligands, the utilization of discrete *inorganic* species (*e.g.* polyoxometalates, POMs[2]) as bridging units has only been explored to a very limited extent.[3,4] In this context, the ligation of redox-active and potentially magnetic polyoxoanions would doubtlessly add an important control parameter to the magnetic properties of polynuclear manganese complexes. For example, C. Duboc *et al.* recently reported an unusually high magnetic anisotropy for a mononuclear Mn(II)–POM complex.[5] The surprising scarcity of inorganic ligand-based Mn clusters may be partially attributed to the lack of easy access to coordinatively flexible inorganic ligands upon which polynuclear manganese clusters can be constructed. Furthermore, antiferromagnetic interactions between Mn spin centers often result from monoatomic bridging modes of $O^{2-}$ or $OH^{-}$ groups when inorganic ligand units are used alone, limiting the generation of high spin ground state species, as illustrated by a handful of examples.[6]

Here, we introduce an alternative hybrid approach towards this problem, and demonstrate, for the first time, that carboxylate ligands on a pre-formed Mn cluster can be partially replaced by polyoxoanion ligand(s) without altering the actual Mn cluster core. This synthetic methodology will therefore partially sustain the magnetic exchange pathways between the Mn centers; it also establishes polyoxometalate ligand environments that are known for their rich redox chemistry.

As a proof-of-concept for this methodology, we present a Mn(IV)$_6$ cluster featuring both polyoxoanion and carboxylate bridging groups, which is isolated as $[(CH_3)_2NH_2]_6H_2[\{\alpha\text{-}P_2W^{VI}{}_{16}O_{57}(OH)_2\}\{Ce^{IV}Mn^{IV}{}_6O_9(O_2CCH_3)_8\}]\cdot 20H_2O$ (**1**). **1** was directly synthesized from a heterometallic high oxidation state precursor, $[Ce^{IV}Mn^{IV}{}_6O_9(O_2CCH_3)_9(NO_3)(H_2O)_2]$ (**2**), reported by Christou and co-workers.[7] The bowl-shaped core of **2** (Scheme 1) is built from a planar Mn$_6$ hexagon with alternating Mn–Mn distances and with a basal Ce ion displaced from the Mn$_6$ plane. In addition to the acetate and oxide bridges, a monodentate nitrate and two aqua ligands are weakly attached to the Ce center. The inorganic ligand employed in the synthesis of **1** is a tri-vacant Wells–Dawson polyoxoanion, $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$, well-documented for its coordination ability towards transition metal and lanthanide ions.[2,8] The polyanion is a rare example of an 'adaptable' inorganic ligand that can undergo facile transformation into its di-vacant or mono-vacant derivatives, $[\alpha\text{-}P_2W_{16}O_{59}]^{12-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, *via* self-decomposition equilibria.[8] It is also capable of reversibly switching between different protonation states in response to solution pH and the presence of appropriate metal ions.[9] Both of these properties are key to the construction of the complex anion of **1**.

The 1 : 1 stoichiometric reaction of **2** and $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ in 1 : 3 (v/v) $CH_3COOH$–$H_2O$, in the presence of dimethylammonium, results in dark-brown crystals of **1** in 21% isolated yield after 2 days.‡ Single-crystal X-ray analysis§ of **1** reveals a POM-coordinated CeMn$_6$–carboxylate cluster (Fig. 1) with a crystallographically imposed *m* symmetry (the mirror plane is defined by the Ce and the two P positions). The CeMn$_6$ core of **2** remains intact in **1**, and bond valence sum calculations and XPS data (Mn 2p bands) indicate that all Mn and Ce centers are still in their +IV oxidation state. However, in **1** the $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ anion has gained an additional



**Scheme 1** Structure of $[CeMn_6O_9(O_2CCH_3)_9(NO_3)(H_2O)_2]$ (**2**).

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† Electronic supplementary information (ESI) available: IR, UV/Vis, XPS, solution $^{31}P$ and $^{1}H$ NMR spectra, TGA/DTA curves, control experiments with $\{P_2W_{17}\}$, packing diagram. Crystallographic data. CCDC 681991. See DOI: 10.1039/b804111c

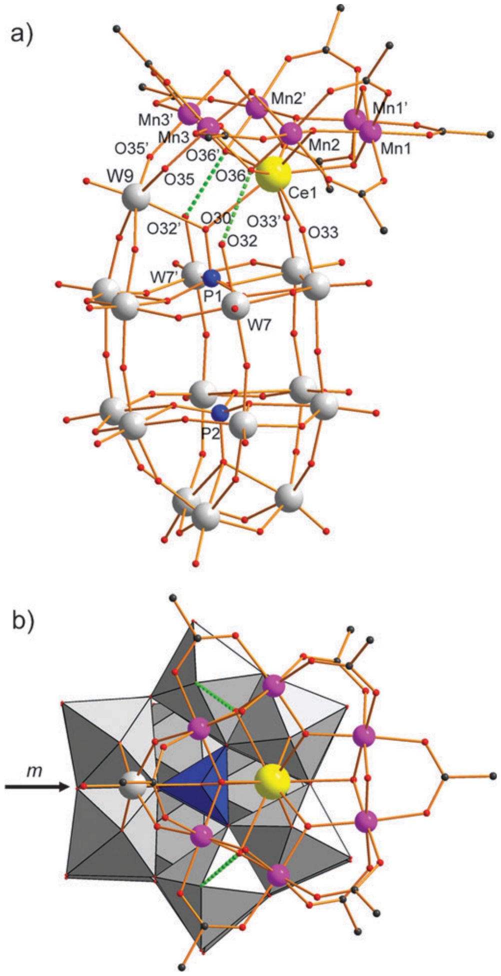

**Fig. 1** (a) A side view of the solid-state structure of the complex anion of **1** in ball-and-stick representation (W, gray; Mn, purple; Ce, yellow; P, blue; C, black; O, red; H omitted for clarity). Hydrogen bonds are highlighted as dashed green lines. (b) A perpendicular view, with the $\{P_2W_{15}\}$ moiety in polyhedral representation, highlighting the crystallographic *m* symmetry.

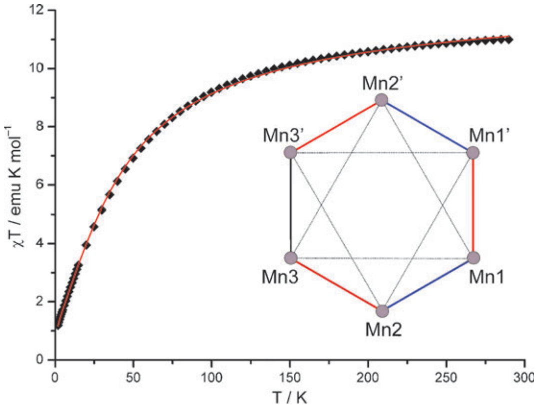

**Fig. 2** Temperature dependence of $\chi T$ for **1** at 0.1 Tesla (exp. data: black squares, best fit to isotropic Heisenberg model (see text): red graph). Inset: magnetic exchange connectivity, $J_1$ (two μ-O, one in-plane acetate bridge): red; $J_2$ (one in-plane μ-O, two acetate bridges): blue; $J_3$ (one in-plane μ-O, one acetate, one O–W–O bridge): black; $J_4$ (next-nearest neighbor interactions *via* O–Ce–O bridges): dotted lines.

tungsten site (W9) and thus is turned into a di-vacant ligand. The POM and $\{CeMn_6\}$ building blocks are connected through a number of strong and weak complementary interactions.

First, the three terminal ligands (one nitrate and two aqua groups) on Ce in **2** are now replaced by the stronger coordination of bridging (O30) and terminal (O33, O33′) oxo groups originating from the $PO_4$ tetrahedron and adjacent $WO_6$ octahedra of the polyoxoanion. As expected, the formation of stronger Ce–O–W bridges concomitantly weakens the connection between Ce and the $Mn_6$ cluster unit, increasing the average Ce···Mn distance from 3.37 Å in **2** to 3.42 Å in **1**.

A second type of connection is established *via* $\mu_2$-O bridges (O35 and O35′) between W9 and a pair of adjacent Mn ions (Mn3 and Mn3′), replacing one of the acetate groups between them. Both the structural parameters and a subsequent control experiment indicate that the Mn–O–W bridging is critical in stabilizing the overall framework. The newly formed Mn3–O35 and Mn3′–O35′ bonds (1.869(2) Å) are notably shorter than in the original Mn–acetate coordination environment (averaging 1.958(2) Å). In addition, a control experiment replacing $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with the mono-vacant $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand only produces the 2 : 1 Weakley complex $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2Ce]^{16-}$,[10] suggesting a break-down of the $CeMn_6$ core in **2** in the absence of strong Mn–O–W bridging.[11] This finding is also consistent with the above observation that Ce–polyoxoanion coordination weakens the competing Ce···Mn link.

In addition to the above coordinative bridges, intramolecular hydrogen bonding interactions also participate in connecting the two building blocks. The two non-coordinating terminal oxygen atoms (O32 and O32′) at the substitution position are mono-protonated OH groups as evidenced by their corresponding W–O distances (W7–O32 and W7′–O32′, 1.962(2) Å). They form strong H bonds (O32···O36 and O32′···O36′, 2.617(3) Å) with two of the $\mu_3$-O groups which link the Ce···Mn pairs in the $\{CeMn_6\}$ unit.

The magnetic susceptibility of **1** in the temperature range 2–290 K indicates antiferromagnetic coupling between the $s = 3/2$ Mn(IV) centers similar to **2**,[7] resulting in a singlet ground state (Fig. 2). Down to *ca.* 50 K the susceptibility data follow a Curie–Weiss expression with a Weiss temperature of −38 K. In contrast to **2**, where two Mn–Mn bridging modes alternate (resulting in two types of each of the three exchange pathways characterized by exchange energies $J_1$ and $J_2$), the coordination of the $Mn_6$ ring to W9 adds a third type of nearest-neighbor Mn–Mn exchange between Mn3 and Mn3′ ($J_3$). Indeed, a 2-*J* model[7] does not suffice to produce a satisfying fit to the susceptibility data of **1**, confirming the implication of the induced ligand change on the magnetic properties. An isotropic Heisenberg spin Hamiltonian (of the type $\boldsymbol{H} = -2\Sigma J\mathbf{S}_i\mathbf{S}_j$) based on these three interactions and a small next-nearest neighbor coupling constant ($J_4$) results in a best fit of the low-field susceptibility data for $J_1 = -4.2\ \text{cm}^{-1}$, $J_2 = -4.6\ \text{cm}^{-1}$, $J_3 = +0.4\ \text{cm}^{-1}$, and $J_4 = -0.5\ \text{cm}^{-1}$ (Fig. 2, assuming a uniform *g* factor of $g_{\text{iso}} = 2.06$).

Due to its ionic nature, **1** is insoluble in common organic solvents. The aqueous solution $^1$H NMR spectrum of **1** is not informative in distinguishing the bridging acetate groups. It displays a single acetate peak at 1.56 ppm (in 1 : 3 $CD_3COOD–D_2O$), in addition to a downfield signal attributed to $(CH_3)_2NH_2^+$ counterions (see ESI†). Analogous behavior has been observed for the prototypal $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ cluster where equatorial acetates have non-distinguishable methyl resonances due to their similar magnetic environments and flexibility in solution.[12] The $^{31}P$ NMR spectrum of **1**, on the other hand, indicates that the solid-state structure is retained in solution. It exhibits only a single resonance at −13.1 ppm ascribed to the distal P atom (P2), which is relatively sheltered from paramagnetic broadening and solvent effects. The signal for the proximal phosphorus atom (P1), however, is broadened beyond detection due to its close proximity to the paramagnetic Mn(IV) centers.

In conclusion, structural characterization of complex **1** reveals the first polyoxoanion-substituted Mn carboxylate cluster. The employed strategy opens the way to the preparation of a variety of polynuclear Mn coordination cluster derivatives by surprisingly straightforward metathesis reactions with POM ligands. Next to the implications of altering the magnetic properties of the Mn clusters, by imposed structural changes and introduction of magnetic POM groups, the preparation of such POM-stabilized complexes is also important for the design of magnetic molecule-based devices, which often require their deposition onto surfaces.[13] Much as polyoxoanions have been long proposed as soluble models of metal oxide-supported heterogeneous catalysts,[2,14] complexes such as **1** will potentially serve as tractable molecular representations for anchoring magnetic molecules onto metal and metal oxide surfaces.

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## Notes and references

‡ Synthesis of $[(CH_3)_2NH_2]_6H_2[\{\alpha\text{-}P_2W_{16}O_{57}(OH)_2\}\{CeMn_6O_9(O_2CCH_3)_8\}]\cdot 20H_2O$ (**1**): a sample of $CeMn_6O_9(O_2CCH_3)_9(NO_3)(H_2O)_2$ (**2**)[7] (0.20 g, 0.13 mmol) was dissolved in a mixture of 1 : 3 (v/v) $CH_3COOH–H_2O$ (20 mL). With vigorous stirring, solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$[15] (0.56 g, 0.13 mmol) was then added to the above solution. After stirring for 2 h at room temperature, dimethylamine hydrochloride (0.20 g) was added. The mixture was then heated to 70 °C for another 15 min, filtered hot, and left to slowly evaporate at room temperature. After two days, precipitated black crystals were collected by filtration, washed with ice-cold water, and dried *in vacuo* (yield 0.15 g, 21.7% based on W). Anal. calcd. (%) for $C_{28}H_{116}CeMn_6N_6O_{104}P_2W_{16}$: C 5.92, H 2.06, N 1.48, Ce 2.47, Mn 5.81, P 1.09, W 51.86, Na, 0.00. Found: C 5.82, H 2.11, N 1.36, Ce 2.45, Mn 5.90, P 1.10, W 49.1, Na <0.02. Selected IR bands for **1** (KBr pellet, 2000–500 $cm^{-1}$): 1713(w), 1624(m), 1549(s), 1492(m), 1466(s), 1415(vs), 1350(m), 1250(br, w), 1090(s), 1038(m), 1018(sh), 955(sh), 920(br, vs), 784(br, vs), 691(s), 670(s), 617(s), 600(sh), 524(m).

§ Crystal data for **1**, $C_{28}H_{116}CeMn_6N_6O_{104}P_2W_{16}$, $M = 5674.57$ g $mol^{-1}$, space group $C2/m$, $a = 31.003(4)$, $b = 21.508(3)$, $c = 20.162(3)$ Å, $\beta = 97.809(2)°$, $V = 13\,320(3)$ $Å^3$, $T = 173(2)$ K, $Z = 4$, $D_c = 2.830$ Mg $m^{-3}$, $F(000) = 10\,320$, $\mu$(Mo-K$\alpha$) = 14.761 $mm^{-1}$. The refinement converges with $R1 = 0.0739$ and $wR2 = 0.1954$ for 9919 reflections with $I > 2\sigma(I)$. The acetate H atoms were modeled according to idealized positions. The structures were solved and refined using SHELXTL V6.12.[16] CCDC 681991. For crystallographic data, see DOI: 10.1039/b804111c

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