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Directed assembly of nanoscale Co(II)-substituted $\{\text{Co}_9[\text{P}_2\text{W}_{15}]_3\}$ and $\{\text{Co}_{14}[\text{P}_2\text{W}_{15}]_4\}$ polyoxometalates†Claire Lydon,^a Mercè Martin Sabi,^a Mark D. Symes,^a De-Liang Long,^a Mark Murrie,^a Shunsuke Yoshii,^b Hiroyuki Nojiri^b and Leroy Cronin^{*a}

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Herein we report two structurally intriguing Co(II)-substituted polyoxometalates, a $\{\text{Co}_9[\text{P}_2\text{W}_{15}]_3\}$ and $\{\text{Co}_{14}[\text{P}_2\text{W}_{15}]_4\}$ (compounds **1** and **2**) that are formed from the same building blocks under subtly different conditions. Compound **1** displays a structure previously predicted but never before realised, whilst compound **2** is the first Co-containing Dawson-based single-molecule magnet and has a unique cruciform structure.

Polyoxometalates (POMs) are anionic molecular metal oxide clusters with a vast range of properties ranging from catalysis, magnetism and materials science to medicine.¹ Consisting of oxides of W, V or Mo with the metal in the highest oxidation state, POMs can also incorporate addenda metal atoms and non-metal heteroatoms.² Their ability to form extended assemblies, allied to the many structures and nuclearities that are possible, makes POMs attractive for developing new functional materials.³ In particular, the use of lacunary POMs as secondary building units (SBUs)⁴ in the assembly of larger architectures is one route to the rapid generation of large libraries of interesting and potentially useful structures. Of the potential POM SBUs, lacunary tungstates such as $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ ⁵ and $[\text{PW}_9\text{O}_{34}]^{9-}$ ^{6,7} and their transition metal substituted derivatives have been studied in the most detail on account of their varied and interesting electronic and catalytic properties.^{8–10} With regards to substituted Wells–Dawson clusters, some notable examples of the larger arrangements that are possible include a hexameric Dawson structure,¹¹ a titanium-substituted tetrapod¹² and an iron-substituted tetrahedron.¹³

Herein, we report the synthesis of a new ferrimagnetic trimeric ensemble $(\text{Li}_{14}\text{Na}_{11}\text{H}_2[\text{Co}_9\text{P}_8\text{W}_{45}\text{O}_{176}(\text{OH})_3(\text{H}_2\text{O})_6] \cdot 65\text{H}_2\text{O})^\ddagger$ (compound **1**), a structure corresponding to which was predicted

by Weakley in 1984, but which has not been realised before now.¹⁴ Furthermore, we show that subtle alteration of the reaction conditions yields a second structure with radically different properties, in this case a topologically interesting $\{\text{Co}_{14}\}$ bearing four pendant $\{\text{P}_2\text{W}_{15}\}$ units and with an unusual cruciform shape $(\text{Li}_{20}\text{Na}_{15}[\text{Co}_{14}\text{P}_{10}\text{W}_{60}\text{O}_{232}(\text{OH})_9(\text{H}_2\text{O})_6] \cdot 110\text{H}_2\text{O})_\S$ (compound **2**), which we show to be a single-molecule magnet (SMM).

The strategy used to synthesise compounds **1** and **2** involved dissolving simple cobalt and phosphate-containing salts in aqueous LiCl solutions and altering the pH of the reaction mixture, followed by subsequent addition of the lacunary Dawson anion $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$, obtained *via* a literature procedure.¹⁵ Using this approach and maintaining a pH of 6 (see ESI†) we were able to obtain crystals of **1** suitable for X-ray diffraction. The crystal structure of **1** (Fig. 1 and Fig. S5, ESI†) consists of three $\{\text{P}_2\text{W}_{15}\}$ fragments assembled around a core containing nine Co atoms and two phosphate (PO_4^{3-}) groups. The Co atoms are arranged in three Co_3O_4 units, or alternatively, the structure can be viewed as three tri-substituted Dawson clusters arranged around two PO_4^{3-} groups. The terminal P–O bond on the PO_4^{3-} groups is at 90° to the main structure, meaning that the PO_4^{3-} groups appear to project out of the front and back of the plane of the structure.

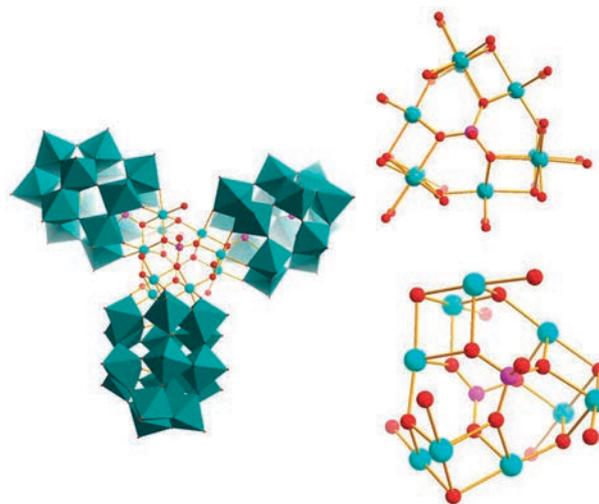


Fig. 1 Crystal structure of **1**. P = pink spheres, W = teal polyhedra, O = red spheres, Co = cyan spheres. Counterions and solvent have been omitted.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation of compounds **1** and **2**, comparison of the structures of **1** and the Weakley trimer and magnetic studies of **1** and **2**. CSD-424572 and CSD-424573 contain the supplementary crystallographic data for this paper for compounds **1** and **2** respectively. This data can be obtained free of charge from ICS, FIZ Karlsruhe (crysdata@fiz-karlsruhe.de). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34865a

The P–O_(terminal) bond lengths are 1.66(2) and 1.68(2) Å. All of the P–O bonds on the these PO₄^{3–} groups range between 1.44 and 1.68 Å (terminal oxygen). The terminal P–O bond length was determined by crystallography, and bond valence sum (BVS) calculations indicate that there is a proton associated with the oxygen (P–OH). The Co atoms in compound **1** are all in the +2 oxidation state according to BVS calculations. The Co–O bonds range between 1.98(2) and 2.23(2) Å in length. Within the core, the terminal Co–O bonds are calculated by BVS to be associated with two protons (Co–OH₂). This structure closely matches that predicted by Weakley in his paper detailing the Co₄P₂W₁₅ sandwich.¹⁴

Compound **2** contains a core of 14 Co atoms, arranged between four {P₂W₁₅} clusters and has an extended cross-like structure, which is not entirely planar (Fig. 2). There are no similarly shaped structures in the literature although some architectures containing four POM units are known, such as an H-shaped pseudo-dimer formed from Dawson clusters linked by {MoO₂S₂} units.¹⁶ The structure of compound **2** contains two Co₄O₄ cubanes on either side of a central two-tiered core. This core contains two Co₃O₄ moieties, as with compound **1**, which are linked by two phosphate groups and a shared μ₄ oxygen atom, with alternating Co and O atoms on the bottom ring and alternating Co, O and P atoms on the upper tier. All of the μ₃-oxo ligands that link three Co ions are mono-protonated, as is the central μ₄-oxo unit. The bond lengths from the μ₄-oxo ligand to the Co atoms are between 2.09(2) and 2.37(2) Å. These Co atoms have Co–O_(terminal) bond lengths of 2.14(2) and 2.17(2) Å, with BVS calculations indicating two protons associated with the oxygens (Co–OH₂).

The linking phosphorus atoms have P–O_(terminal) bond lengths of 1.51(2) and 1.50(2) Å, with BVS calculations indicating a singly protonated terminal oxo ligand (P–OH). The O–Co–O bond angles in the linked Co₃O₄ groups are between 90.1(4)° and 177.4(5)°, with the O–P–O angles being 106.8(9)° and 108.3(9)°. The Co₄O₄ cubanes are located at each end of the longest side of

the ‘cross’ and are linked by one of the Co atoms to the central two-tiered core (shown in the expansion in Fig. 2). Of the three Co atoms bonded to each {P₂W₁₅} unit in the cubane, only two have terminal Co–O bonds, and these are 2.14(2) and 2.06(2) Å in length, with the other Co–O bond lengths being between 2.00(2) and 2.37(2) Å. BVS calculations indicate that these terminal oxygen atoms have two protons associated with them (Co–OH₂). The O–Co–O bond angles in the cube are between 80.4(9)° and 84.8(9)°. The oxygens in the cubane also each appear to have a proton associated with them, according to BVS calculations, despite being bridging μ₃-oxo ligands. Alternatively, the cubanes can be considered to be capping tri-substituted {P₂W₁₅} units with an extra Co atom sitting on top of the cap, linked to a central dimer containing six Co atoms. The overall structure is slightly concave, with the POM components bending downwards (if the PO₄^{3–} groups are considered to be pointing upwards). These compounds were isolated primarily as Na⁺/Li⁺ salts, with small rectangular, dark pink crystals of tetrameric compound **2** being isolated from reaction mixtures at pH 8.5, and long pink needles of compound **1** predominating at pH 6, see ESI†¹⁷

Due to the presence of the two cubanes in compound **2**, it was thought that these compounds might be magnetically interesting as SMMs,¹⁸ and hence the magnetic properties of **2** were duly studied. Numerous elements have been used to construct SMMs, most notably manganese^{18b,c} and, to a lesser extent, cobalt.^{18e} Considering the versatility of the polyoxometalates, it is not surprising that there is interest in incorporating magnetic units into these architectures. It is considered to be advantageous to have compounds such as polyoxometalates as ligands for SMMs as they may shield the magnetic core from interaction with other molecules, creating a discrete magnet. Whilst there are many magnetically interesting polyoxometalate structures reported in the literature,^{3b,19} there are very few that may be said to exhibit single-molecule magnet behaviour. The majority of the reported examples involve Keggin-based building blocks, with Mn,^{20a} Fe,^{20b} lanthanoid^{20c} and, of particular relevance, Co substitutions.^{20d,e} There is currently one POM-SMM reported with a Dawson-based architecture, consisting of a corner sharing Mn double cubane^{20f} and there is also a Dy-based dimer exhibiting slow relaxation of magnetisation.²¹

The χ_T vs. T data for **1** and **2** at 290 K (Fig. S1, ESI†) are consistent with nine and fourteen non-interacting Co(II) centres with S_i = 3/2 and g ~ 2.3 (22.8 and 35.0 cm³ mol^{–1} K, respectively). The χ_T data for both **1** and **2** are typical of many Co(II) compounds and are dominated by strong single-ion spin-orbit coupling effects at high temperatures (deviation from the expected spin-only value). The size of the complexes and the large orbital contribution of Co(II) means that it is difficult to perform a quantitative analysis of the susceptibility data. AC susceptibility measurements for **2** are shown in Fig. 3. As the frequency is increased, the χ' T value decreases and χ'' increases, indicating that relaxation processes are present. Below 4 K, the χ' T curves for the different frequencies start to diverge and a concomitant frequency-dependent χ'' signal is observed. This behaviour is consistent with the slow magnetic relaxation observed in SMMs.

To examine the relaxation behaviour of **2**, and to verify that it is an SMM, pulsed-field measurements were performed with the sweep rate modified in the range of 24–1 T m^{–1} s^{–1} at 1 K, 1.6 K and 0.5 K (see Fig. S2–S4, ESI†). Hysteresis was

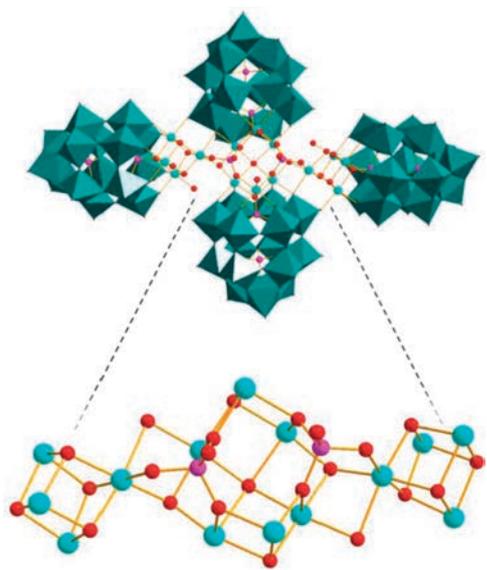


Fig. 2 Crystal structure of the tetrameric cluster, **2**, with the core separated for clarity. P = pink spheres, W = teal polyhedra, O = red spheres, Co = cyan spheres. Counterions and solvent have been omitted.

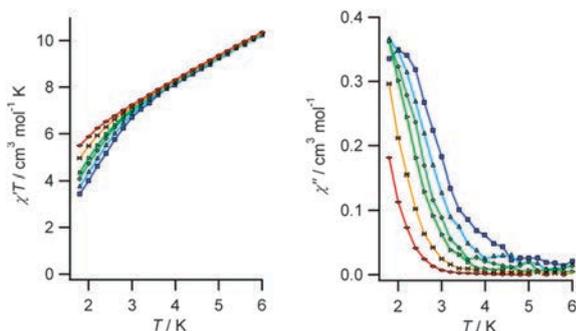


Fig. 3 AC susceptibility for **2** measured in zero dc field ($\nu = 5$ Hz (red) to 997 Hz (blue)) and plotted as $\chi''T$ versus T and χ'' versus T .

observed at 1.6 K and below, although there was little dependence on sweep rate at 0.5 K. This is similar to the first Co_4O_4 cubane SMM, which also displayed little dependence on the sweep rate, although this was attributed to the presence of intermolecular interactions.^{18d} The hysteresis curve shows a steep increase up to $\sim 12 \mu_{\text{B}}$, and does not reach a saturation point at 30 T. Compound **1** does not exhibit hysteresis at low temperatures and is not considered an SMM.

In conclusion, two novel cobalt-substituted polyoxometalate clusters were synthesised using similar reaction conditions, but raising the pH in the case of compound **2**. The structure of compound **1** was predicted by Weakley twenty eight years ago (but never previously synthesised) and compound **2** is the first example of a Dawson-based single-molecule magnet containing cobalt and is also a rare example of a polyoxometalate ensemble containing two metal-oxo cubanes in its core. Future work will focus on using other transition metals to produce analogues of these compounds and further study of the catalytic, redox and magnetic properties of these clusters.

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Notes and references

† Crystallographic data and structure refinements for compound **1**, formula $\text{Li}_{14}\text{Na}_{11}\text{H}_2[\text{Co}_9\text{P}_8\text{W}_{45}\text{O}_{176}(\text{OH})_3(\text{H}_2\text{O})_6] \cdot 65\text{H}_2\text{O}$, $M_r = 13\,549.61$; block crystal: $0.13 \times 0.08 \times 0.04 \text{ mm}^3$; triclinic, space group $P\bar{1}$ $a = 13.9749(3)$, $b = 29.2333(8)$, $c = 31.6129(6) \text{ \AA}$, $\alpha = 74.594(2)$, $\beta = 81.673(2)$, $\gamma = 89.770(2)^\circ$, $V = 12\,311.5(5) \text{ \AA}^3$, $Z = 2$, $\rho = 3.655 \text{ g cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 44.038 \text{ mm}^{-1}$, $F(000) = 12\,006$. 84 049 reflections measured, 26 793 unique ($R_{\text{int}} = 0.0567$), 2410 refined parameters, $R_1 = 0.0631$, $wR_2 = 0.1849$. Data measured on an Oxford Gemini S Ultra A diffractometer; $\text{Cu}_{\text{K}\alpha}$ radiation at 150(2) K.

§ Crystallographic data and structure refinements for compound **2**, formula $\text{Li}_{20}\text{Na}_{15}[\text{Co}_{14}\text{P}_{10}\text{W}_{60}\text{O}_{232}(\text{OH})_9(\text{H}_2\text{O})_6] \cdot 110\text{H}_2\text{O}$, $M_r = 18\,604.3$; block crystal: $0.18 \times 0.10 \times 0.06 \text{ mm}^3$; triclinic, space group $P\bar{1}$ $a = 24.8073(8)$, $b = 28.5922(9)$, $c = 29.2403(10) \text{ \AA}$, $\alpha = 112.323(3)$, $\beta = 113.172(3)$, $\gamma = 91.071(3)^\circ$, $V = 17\,289.7(10) \text{ \AA}^3$, $Z = 2$, $\rho = 3.574 \text{ g cm}^{-3}$, $\mu(\text{Mo}_{\text{K}\alpha}) = 20.703 \text{ mm}^{-1}$, $F(000) = 16\,580$. 191 079 reflections measured, 42 250 unique ($R_{\text{int}} = 0.1452$), 3060 refined parameters, $R_1 = 0.0539$, $wR_2 = 0.1254$. Data measured on an Oxford Gemini S Ultra A diffractometer; $\text{Mo}_{\text{K}\alpha}$ radiation at 150(2) K.

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