

Supporting Information for:

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†

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<i>Index</i>	<i>Page</i>
General Experimental Remarks	S2
Synthesis and Characterisation of 1 and 2	S3
Magnetic Studies and Figures S1-S4	S4-S5
Structural Comparison of the Cores of 1 and the Weakley Trimer and Figure S5	S6
UV-vis spectra for 1 and 2 and Figures S6-S8	S9
References	S10

General Experimental Remarks

Single crystal X-Ray diffraction: Suitable single crystals of **1** or **2** were selected and mounted onto the end of a thin glass fibre using Fomblin oil. X-ray diffraction intensity data were measured on an Oxford Diffraction Gemini Ultra with an ATLAS CCD detector [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$] at 150(2) K for compound **2** and an Oxford Diffraction Gemini S Ultra A diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 150(2) K for compound **1**. Data reduction was performed using the CrysAlis software package and structure solution and refinement was carried out using SHELXS-97¹ and SHELXL-97² via WinGX³. Corrections for incident and diffracted beam absorption effects were applied using analytical numeric absorption correction using a multifaceted crystal model.⁴ 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 ICSD, FIZ Karlsruhe (crysdata@fiz-karlsruhe.de). SQUEEZE was used in the final stage of structure refinement for compound **1**, producing an estimated potential solvent accessible void volume of 2068 \AA^3 and an additional electron count of 804, corresponding to a number of unidentified cations and solvated water molecules for the determination of the formula in conjunction with chemical analysis. For compound **2**, both the asymmetrical unit and void were too big to use SQUEEZE, and so the number of cations and solvent water molecules in the formula were determined by chemical analysis. Multiple unit cell checks were performed on multiple crystals from each batch of material as corroboration of general homogeneity within those samples.

Flame Atomic Absorption Data: FAAS was performed at the Environmental Chemistry Section, School of Chemistry, University of Glasgow on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

Flame Photometry: A Corning Flame Photometer 410 at the Environmental Chemistry Section, Department of Chemistry, University of Glasgow was used to determine the K and Li content of the materials.

Fourier-transform infrared (FT-IR) spectroscopy: The materials were prepared as KBr pellets and FT-IR spectra were collected in transmission mode using a JASCO FT-IR-410 spectrometer. Wavenumbers (ν) are given in cm^{-1} ; intensities as denoted as w = weak, m = medium, s = strong, br = broad, sh = sharp.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Electronic Spectra: UV-Vis spectra were collected on a TIDAS 100 spectrophotometer (J&M Analytik AG) using 1.0 cm optical path quartz cuvettes.

Synthesis of 1 and 2

Compounds 1 and 2: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.290 g, 1.22 mmol) was dissolved in LiCl (7 mL, 4 M) and sodium phosphate (0.080 g, 0.49 mmol) was added. After stirring for 5 minutes, the pH of the solution was adjusted as necessary to 6.0 for and 8.5 for **1** and **2** respectively with LiOH. Once the pH was stable, $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 24\text{H}_2\text{O}$ (3.0 g, 0.75 mmol) was added slowly in small increments and the reaction mixture was then stirred for an additional 10 minutes for **1** and 1 hr for **2**. After this time, the mixture was centrifuged for **1** and filtered for **2** to remove the precipitate and the clear solution was left in the fridge overnight. The resulting precipitate was filtered off and the mother liquor left for crystallisation. After approximately 5-6 days, long, pink, needle-shaped crystals of **1** and **2** were formed. Compound **1**: Yield: 100 mg, 5.8 % (7.38×10^{-6} mol) based on $\text{CoCl}_2 \cdot 6(\text{H}_2\text{O})$. Elemental Analysis calcd. (%) for $\text{Na}_{11}\text{Li}_{14}\text{W}_{45}\text{Co}_9\text{P}_8\text{O}_{250}\text{H}_{147}$ (13549 g mol^{-1}) W 61.06, Co 3.91, Li 0.72, Na 1.87, found: W 59.26, Co 3.43, Li 0.70, Na: 1.35. Compound **2**: Yield: 20 mg 1.2 % (1.08×10^{-6} based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$); Elemental Analysis calcd. (%) for $\text{Na}_{15}\text{Li}_{20}\text{W}_{60}\text{P}_{10}\text{Co}_{14}\text{O}_{357}\text{H}_{241}$ (18604 g mol^{-1}) W 59.29, Co 4.43, Li 0.75, Na 1.85, found: W 59.75, Co 3.51, Li 0.77, Na 2.2.

IR:

Compound **1**: (KBr, cm^{-1}): 3433 (s, b), 2922 (sh), 2852 (sh, w), 2049 (b, w), 1623 (s), 1427 (m), 1090 (s, sh) 1048 (sh, w), 934 (m), 815 (w), 723 (m, sh), 517 (sh), 451 (sh, w), 406 (sh).

Compound **2**: (KBr, cm^{-1}): 3435 (s, b), 2036 (b, w), 1627 (sh), 1090 (s, sh), 1046 (sh), 951 (m), 815 (m), 723 (m), 518.8 (w), 44 (w).

TGA:

Compound **1**: TGA weight loss: 12% (loss of water from the compound)

Compound **2**: TGA weight loss: 12% (loss of water from the compound)

Magnetism

Magnetic measurements were made on randomly oriented polycrystalline samples restrained in eicosane to prevent torquing. The data were measured using a Quantum Design MPMS XL SQUID magnetometer (dc data were measured in a field of 1 kOe and ac susceptibility data using zero dc field with 3 G ac drive field). Diamagnetic corrections have been applied to the dc susceptibility data. The magnetization was measured by a conventional inductive probe under a fast sweeping pulsed magnetic field generated by 90 kJ capacitor bank developed at IMR. A pulsed magnetic field of a full cycle was generated by inserting a diode in parallel to the main thyristor switches. Sample temperatures as low as 0.5 K were achieved by using a ^3He insert and the sample was immersed directly in liquid ^3He .⁵

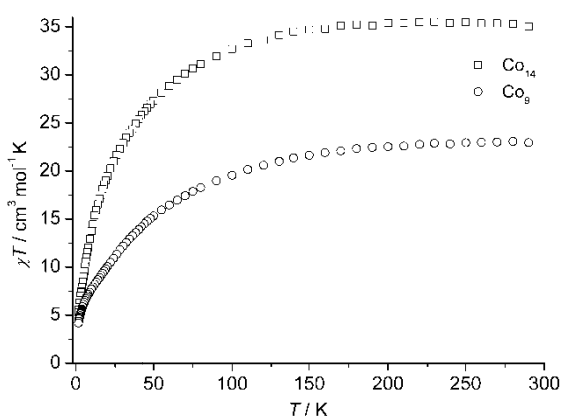


Fig. S1. Temperature dependence of χT for Co_{14} (1) and Co_9 (2) from 290 – 1.8 K.

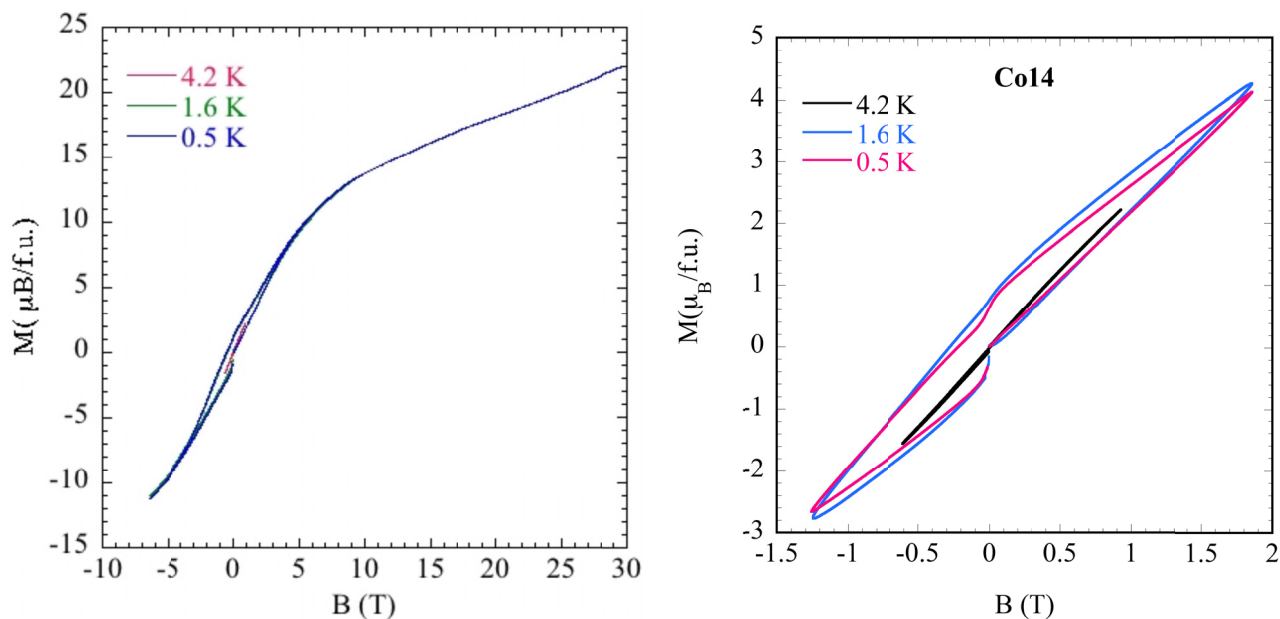


Figure S2 shows the hysteresis curve of compound 2, providing further evidence that there is some slow relaxation of magnetisation, shown in greater detail on the right hand side. Pulsed field experiments show hysteresis at 1.6 and 0.5 K

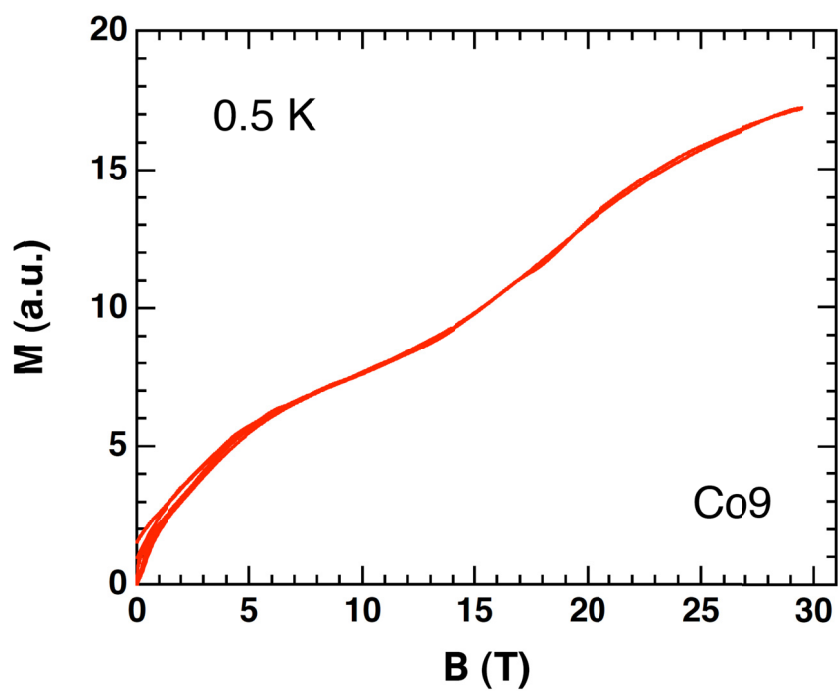


Figure S3 Pulsed field experiment for compound 1 at 0.5 K

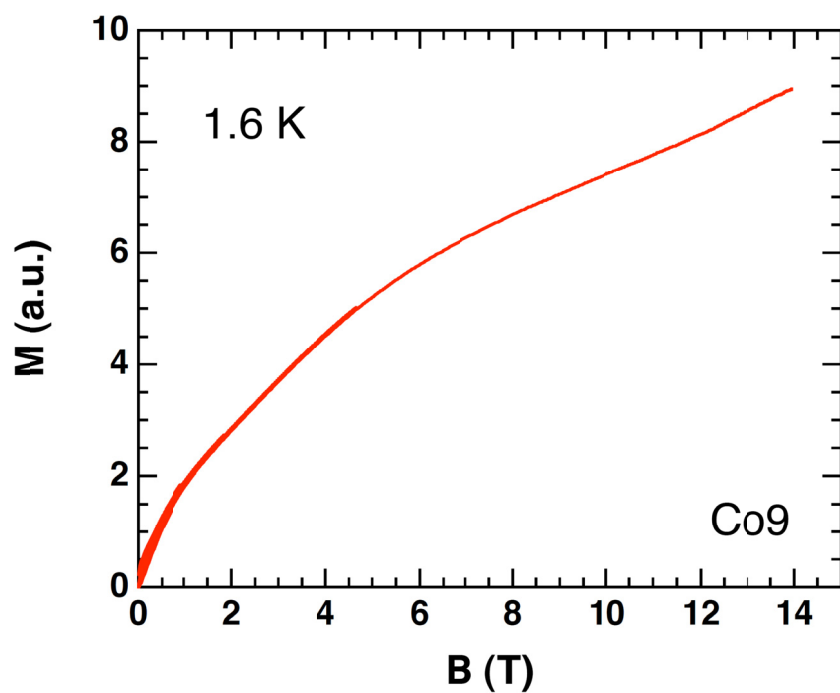


Figure S4 Pulsed field experiment for compound 1 at 1.6 K

Structural comparison of the core of compound **1** and the Weakley Co Keggin trimer#

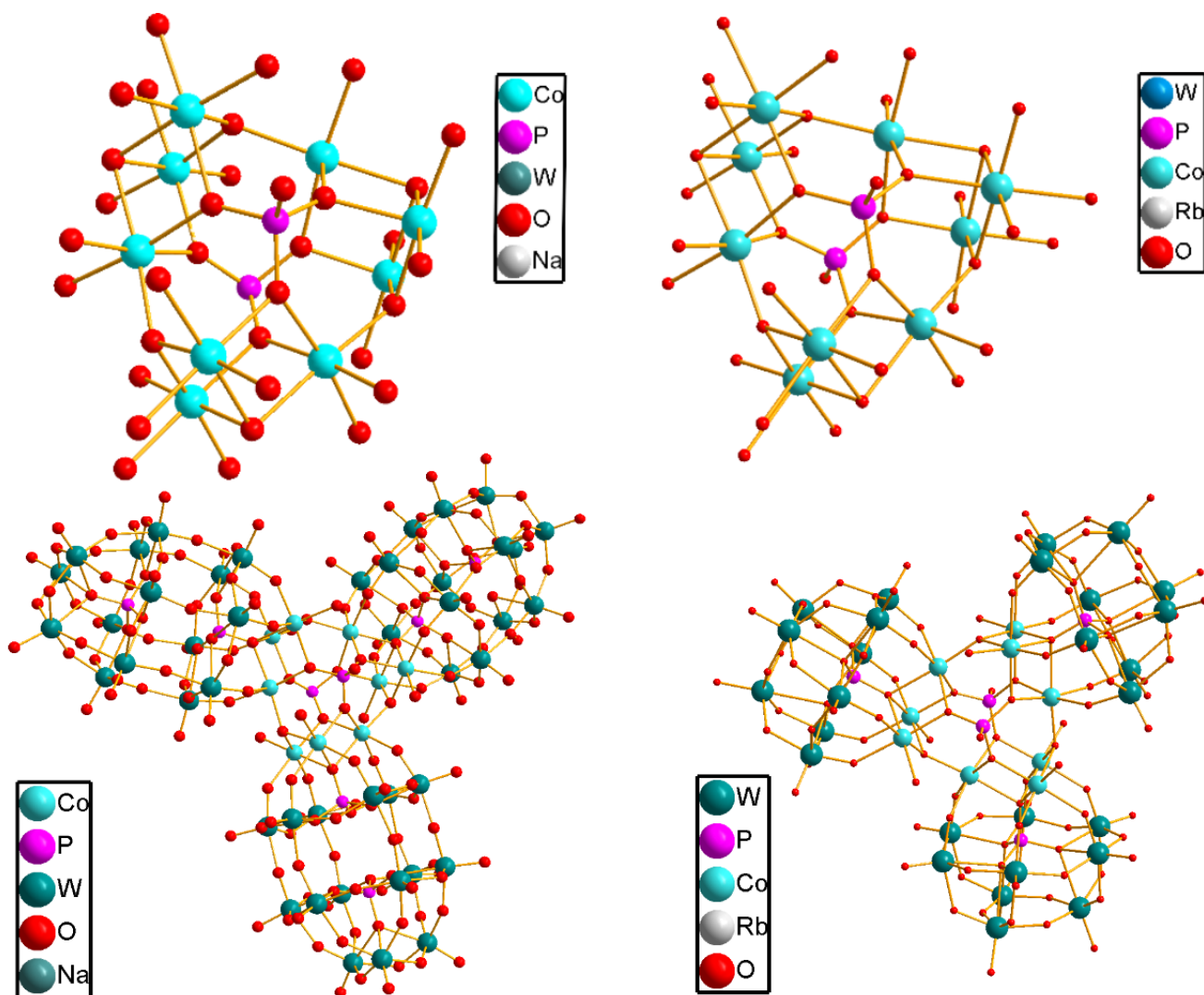
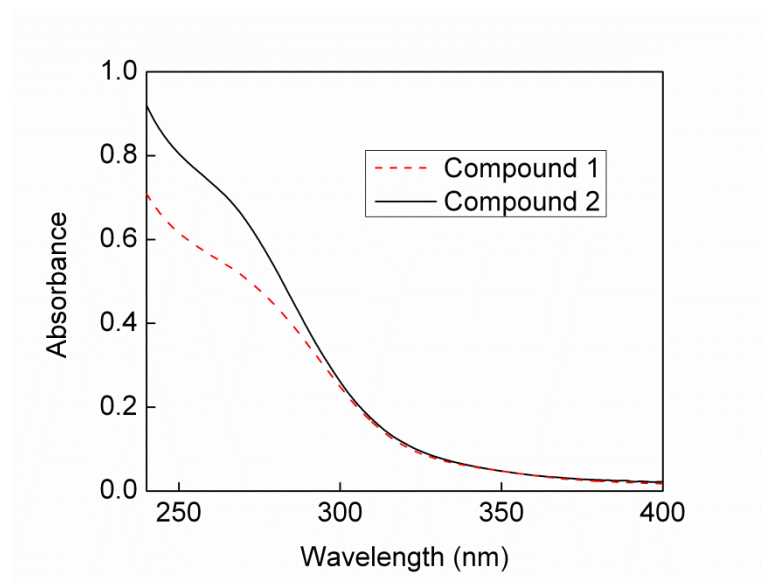


Figure S5. Figure showing compound **1** and the Co₉ keggin trimer characterised by Weakley.⁶ Top: cobalt core of the Dawson (this paper, left) and Weakley Keggin (right) and bottom, the full structures (Dawson on the left and Keggin on the right).

Electronic absorption spectra compounds 1 and 2#

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Figure S6. Comparison of the electronic spectra of compounds **1** (red dashed line) and **2** (black solid line) in the range 240-400 nm. The concentration of both samples was 5×10^{-5} M in de-ionised water.

Comparison of the UV-vis spectra for compound 1 after 0 and 24 hours in aqueous solution#

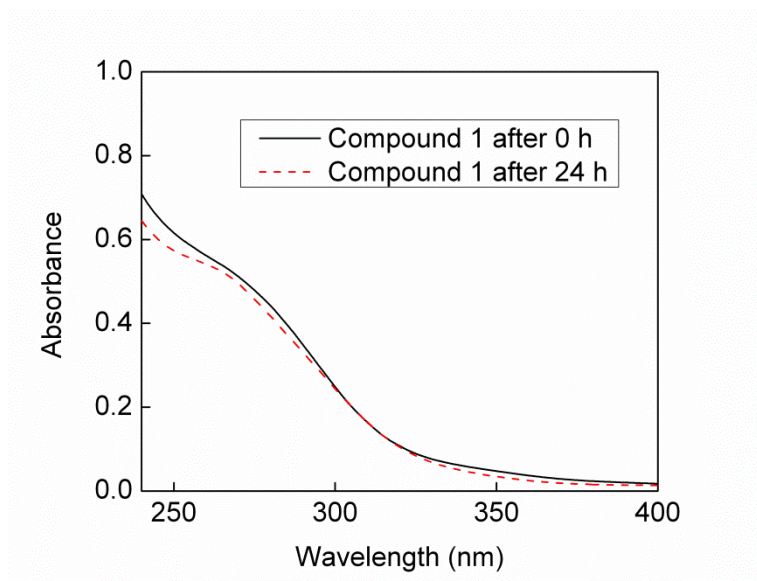


Figure S7. Comparison of the electronic absorption spectra of compound 1 after 0 (black solid line) and 24 hours (red dashed line) in the range 240-400 nm. The concentration of both samples was 5×10^{-5} M in de-ionised water.

Comparison of the UV-vis spectra for compound 2 after 0 and 24 hours in aqueous solution

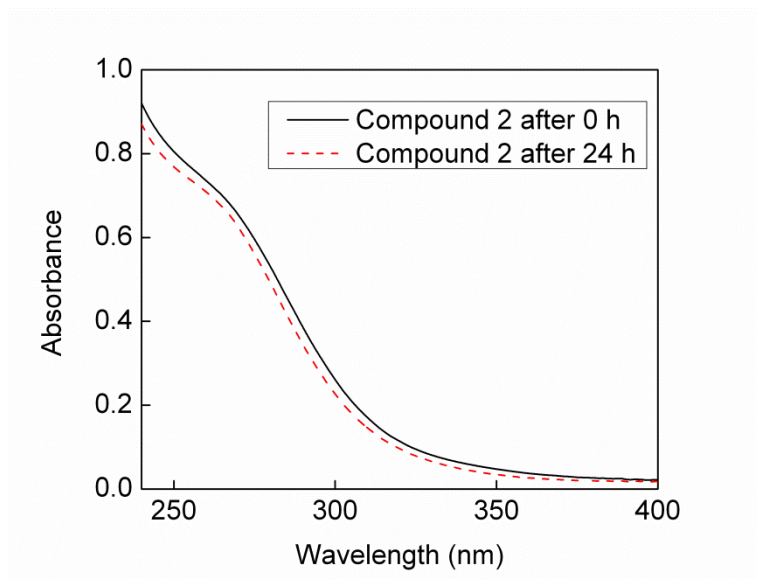


Figure S8. Comparison of the electronic absorption spectra of compound 2 after 0 (black solid line) and 24 hours (red dashed line) in the range 240–400 nm. The concentration of both samples was 5×10^{-5} M in de-ionised water.

References

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