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## An unprecedented Co<sup>II</sup> cuboctahedron as the secondary building unit in a Co-based metal–organic framework<sup>†</sup>

Rebecca J. Holmberg, Marika Kay, Ilia Korobkov, Eugene Kadantsev, Peter G. Boyd, Tomoko Aharen, Serge Desgreniers, Tom K. Woo and Muralee Murugesu\*

A cubic metal-organic framework with an unprecedented octanuclear secondary building unit (SBU) was isolated. The obtained SBU is composed of 8 Co<sup>II</sup> ions at each vertex, 6  $\mu_4$ -OH groups at each face, and 12 cpt<sup>-</sup> ligands framing the metal core. The cuboctahedra arrange in a ubt framework topology, eliciting a highly symmetrical MOF structure. Magnetic measurements as well as DFT calculations on this crystalline MOF reveal intramolecular antiferromagnetic coupling between Co<sup>II</sup> ions in the octanuclear SBU.

Metal–organic frameworks (MOFs) continue to fascinate the scientific community with their ubiquitous potential application within: catalysis,<sup>1</sup> gas storage,<sup>2</sup> chemical sensing,<sup>3</sup> separation methods and drug delivery.<sup>4</sup> Due to the inherent demand for the development of such sought-after materials, new MOFs are continuously synthesised and reported with a plethora of different metal ions and organic linkers. Often rigid organic linkers are utilized in synthetic tuning of the structural topology and pore sizes to suit particular applications. However, even with attempted structural tuning, metal secondary building units (SBUs) are often serendipitously isolated with low metal nuclearities.<sup>5</sup> Higher nuclearity SBUs are rare, this is mainly due to the difficulty in controlling large cluster formation as well as the challenge of nucleating single crystals of suitable quality for X-ray diffraction.<sup>6</sup>

We recently reported two unique cobalt-based MOFs: Co-MOF1 and Co-MOF2,<sup>7</sup> through the use of an asymmetric ligand, 4-(4'carboxyphenyl)-1,2,4-triazole (Hcpt). We observed a 2D structure as well as a distinct 3D structure, with the latter containing a triangular SBU (Scheme 1, Co-MOF1) as often seen in wellestablished MIL series MOFs.<sup>5a,8</sup> With the aim of isolating MOFs with novel, high nuclearity SBUs we have focused our attention on



**Scheme 1** Synthetic scheme highlighting the subtle difference in synthetic conditions, leading to a significant change in the SBU.

tweaking the reaction conditions to promote structural changes while retaining the same rigid Hcpt ligand and metal source.

We present a novel cubic octanuclear  $\text{Co}^{\text{II}}$  MOF structure,  $[\text{Co}^{\text{II}}_{8}(\text{OH})_{6}(\text{cpt})_{6}][\text{CoCl}_{4}]_{2}\cdot 2\text{H}_{2}\text{O}$ , hereafter termed Co-MOF3. This compound was obtained through subtle modification of solvo-thermal synthetic methods, predicating the use of a Teflon bomb as the reaction takes place at 150 °C. This is followed by a gradual cooling procedure found to be essential for the isolation of X-ray quality single crystals. The crystallization was further optimized by varying the ratio of DMF, ethanol and water within the solvent mixture, as was previously reported.<sup>7</sup> The crystalline quality was particularly dependent upon the amount of water present within the solvent mixture, as well as a low pH environment to induce crystal growth. This low pH mother liquor was achieved through the

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, ON, Canada K1N 6N5. E-mail: m.murugesu@uottawa.ca;

Tel: +1 (613) 562 5800 ext. 2733

<sup>†</sup> Electronic supplementary information (ESI) available: Crystallographic information for Co-MOF3, experimental details, IR and Raman, TGA, SQUID magnetic measurements, details of DFT calculations, and supplementary figures. CCDC 944829. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc46396f



**Fig. 1** (a) Molecular core structure of  $[Co^{II}_8(OH)_6(cpt)_{12}]^{2-}$  secondary building unit. (b) An isosurface plot of the spin density difference of the calculated *S* = 0 spin ground state.

addition of concentrated HCl, the chloride ions from which led to the formation of  $[CoCl_4]^{2-}$  counter ions. These molecules not only provide the necessary charges, but also serve to stabilize the lattice framework. Octahedron-shaped dark purple-blue crystals with triangular faces (Fig. S1 and S2, ESI<sup>†</sup>) were isolated and studied using single crystal X-ray.<sup>‡</sup>

The Co-MOF3 crystallizes with the formation of a MOF structure in the cubic space group, *F*23, with cell constants *a*, *b*, *c* = 23.3565(6) Å, and  $\alpha$ ,  $\beta$ ,  $\gamma = 90^{\circ}$ . The cubic system of the MOF structure elicits a highly symmetrical framework. Further crystallographic information can be found in Tables S1 and S2 (ESI<sup>†</sup>). Most notably within the molecular structure of the Co-MOF3, shown in Fig. 1, is the core: an octanuclear Co<sup>II</sup> cube. This high nuclearity constituent represents a new SBU in the rapidly expanding field of MOFs.

The unprecedented octanuclear cubane SBU consists of Co–Co bonds of 2.999(1) Å and Co···Co··Co corner angles of 90.00(6)°. The faces are capped by  $\mu_4$ -hydroxide groups, with Co–OH–Co angles of 86.19(8)°. Each Co<sup>II</sup> ion displays an octahedral coordination environment: one O atom (O2/O3) from the carboxylate group of a cpt<sup>-</sup> ligand, two N atoms (N2/N3) from the triazole rings of the other cpt<sup>-</sup> ligands, and three  $\mu_4$ -O (O1) atoms of the cubane core. In the crystal lattice, two tetrahedral [CoCl<sub>4</sub>]<sup>2–</sup> guest molecules, per cubane SBU, can be seen. They serve to stabilize the lattice, and prevent the presence of disordered solvents, while simultaneously acting as counter anions to balance the overall charges. The structure contains voids which are accessible to solvent molecules, made evident through several partially occupied water molecules which were localized and modelled during refinement.



Fig. 2 The octanuclear complex connected to twelve neighboring complexes to form a cuboctahedron.

Each edge of the cubic SBU is capped by a disordered cpt<sup>-</sup> ligand, thus linking the core to 12 neighbouring cubic SBUs and forming a cuboctahedron, as is shown in Fig. 2. The observed 3-D network is reminiscent of a ubt framework topology, which is a face-centered cubic (fcc) style packing of cuboctahedra within 3D space.<sup>5b,9</sup> Thus, we can elucidate that this is a high surface area MOF structure with a highly symmetric arrangement.<sup>9a,10</sup>

The Co<sup>II</sup> ions from each cube, and those which are arranged within the lattice framework, are well separated (Fig. 2), with the nearest distances being:  $Co_8-Co_8$  (Co1-Co1) 12.275(1) Å,  $Co_8-CoCl_4$  (Co1-Co3) 7.5169(7) Å, and  $CoCl_4-CoCl_4$  (Co3-Co4) 11.6783(3) Å. Thus, these intermolecular distances preclude any intercluster interactions (*vide infra*).

Raman and Infrared spectroscopic analyses of Co-MOF3 serve as fingerprints of the structure, confirming its stability upon filtration and drying (Fig. S3 and S4, ESI<sup>†</sup>).<sup>11</sup> In order to ascertain the bulk sample purity X-ray Powder Diffraction (XRPD) experiments were also performed, and were found to be in good agreement with the generated pattern from single crystal XRD (Fig. S5, ESI<sup>†</sup>). According to thermo-gravimetric analysis (TGA) measurements (Fig. S6, ESI<sup>†</sup>) the Co-MOF3 structure is stable up to 200 °C. Significant weight changes in the material were observed around 200 and 275 °C, where presumably the ligand is undergoing decomposition. Slight losses in weight were also observed prior to 200 °C, which can be attributed to solvent losses (2H<sub>2</sub>O molecules, 6.4 wt%).

Direct current (dc) susceptibility measurements were performed in order to elucidate the magnetic behaviour of the Co-MOF3, specifically the Co<sub>8</sub> SBU. The Co<sub>8</sub> core was determined to be well isolated according to the crystal structure, with the shortest non-core Co–Co distance being (Co1–Co3) 7.5169(7) Å. Thus, any magnetic interactions observed between Co<sup>II</sup> ions most-likely originate from within the octanuclear SBU. The temperature dependence of the dc magnetic susceptibility (1.8–300 K) was measured at 1000 Oe. Plots of the temperature dependence of  $\chi$  and  $\chi^{-1}$  (Fig. S7 and S8, ESI†) were fit in order to obtain the Weiss constant,  $\theta$ , as well as the Curie constant, *C*, which were calculated to be -32.07 K and

8.34 cm<sup>3</sup> K mol<sup>-1</sup>, respectively. The negative value of  $\theta$  indicates the presence of non-negligible antiferromagnetic interaction between  $Co^{II}$  ions. The  $\chi T \nu s. T$  plot (Fig. S9, ESI<sup>†</sup>) suggests the presence of a predominant antiferromagnetic interaction between Co<sup>II</sup> ions, which is developed at higher temperatures than room temperature since the plot does not show saturation of  $\gamma T$  in the measured range. The room temperature  $\chi T$  value decreases monotonically from 14.76 cm<sup>3</sup> K mol<sup>-1</sup> to 2.88 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K. This behaviour further indicates the presence of strong antiferromagnetic interaction between Co<sup>II</sup> ions even at higher temperature, as the theoretical spin-only value for a single non-interacting Co<sup>II</sup> ion is 1.88 cm<sup>3</sup> K mol<sup>-1</sup> ( ${}^{4}F_{9/2}$ , S = 3/2, L = 3, g = 2), and is thus 18.8 cm<sup>3</sup> K mol<sup>-1</sup> per molecular formula. The decrease to a  $\chi T$ product of 2.88 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K indicates the presence of an S = 0 spin ground state for the Co<sub>8</sub> cluster, attributed to strong antiferromagnetic interactions, and 2 isolated Co<sup>II</sup> counter ions  $(3.76 \text{ cm}^3 \text{ K mol}^{-1})$ . This type of antiferromagnetic coupling leading to an S = 0 spin ground state was observed in a similar Ni<sub>8</sub> molecular species,<sup>12</sup> as well as in other cluster-based Co<sup>II</sup> organic frameworks.5c

The isotherm magnetisation (*M*) measurements (Fig. S10, ESI<sup>†</sup>) show no saturation, suggesting the presence of non-negligible anisotropy within the system as well as population of excited states even at 1.8 K. This behaviour is most likely arising from Co<sup>II</sup> counter ions within the structure, as the molecular cluster has a singlet ground state, however, population of the excited states for the Co<sub>8</sub> cluster cannot be ruled out. This is further confirmed in Fig. S11 (ESI<sup>†</sup>), where there is no superposition of isothermal lines in the reduced magnetisation plots at indicated temperatures. Thus, from these measurements, and based on the previously studied Ni<sub>8</sub> analogue, we can conclude that at low temperatures the observed magnetism is primarily due to two isolated [CoCl<sub>4</sub>]<sup>2-</sup> counter ions.

In order to further investigate the observed magnetic behaviour of the SBU in Co-MOF3, periodic density functional theory calculations were performed (the full details of which are provided in the ESI<sup>†</sup>). For calculation purposes, a simulation cell was used that contains a single Co cubane core. The fully ferromagnetic and various anti-ferromagnetic arrangements of magnetic moments on the Co atoms were calculated. For the anti-ferromagnetic configuration (4 spin 'up' and 4 spin 'down') there are a total of 35 possible arrangements (8!/4!4!2) of the magnetic moments, some of which are related by symmetry. Shown in Fig. S12 (ESI<sup>+</sup>) is the energy spectrum of these anti-ferromagnetic states relative to the ferromagnetic state. Consistent with the measured magnetic susceptibility data, we find an anti-ferromagnetic ground state that is 4.5 kcal  $mol^{-1}$  lower in energy than the ferromagnetic solution. Interestingly, we find that the lowest energy anti-ferromagnetic S = 0state corresponds to the parallel arrangement of magnetic moments on two faces of the octanuclear cluster. This is shown by the calculated spin density of the ground state given in Fig. 1b.

Gas adsorption isotherms for  $N_2$  and  $CO_2$  can be observed in Fig. S13 (ESI<sup>†</sup>), where it is apparent that the  $N_2$  uptake (77 K) was much higher than that of  $CO_2$  (298 K). In contrast, it was found that the uptake for  $N_2$  (298 K) is almost negligible. The uptake values at 1.0 bar were found to be ~14, 6 and 0.2 mmol g<sup>-1</sup> for  $N_2$  (77 K),  $CO_2$  (298 K) and  $N_2$  (298 K), respectively. Void volume

(0.18 cm  $^3$  g<sup>-1</sup>), and surface area (1201 m  $^2$  g<sup>-1</sup>) calculations were also performed on Co-MOF3.

In summary, we have successfully synthesized a unique, highly symmetrical cubic MOF structure with an octanuclear  $\text{Co}^{\text{II}}$  cubane core as SBU. The cuboctahedral arrangement of the  $\text{Co}_8$  SBU elicits a ubt framework topology. This structure has been shown to be thermally stable up to 200 °C, and displays antiferromagnetic interactions within the  $\text{Co}_8$  core leading to an S = 0 ground state. This unprecedented high nuclearity SBU provides a highly symmetrical building block on which up to 12 rigid pillars can link to form highly symmetrical MOF structures. Subsequently, these MOFs can be further altered through systematic spacer length (ligand) tuning to create MOFs with large surface area. Overall, this new MOF with cuboctahedral arrangement has the potential to be a customizable, highly functional material based on a unique SBU.

## Notes and references

‡ Data for  $[Co_{8}^{T}(OH)_{6}(cpt)_{6}][CoCl_{4}]_{2}$ ·2H<sub>2</sub>O (Co-MOF3), FW: 2146.06 g mol<sup>-1</sup>: cubic, *a*, *b*, *c* = 23.3565(6) Å,  $\alpha$ ,  $\beta$ ,  $\gamma$  = 90.00(6)°, *V* = 12.741.58(57) Å<sup>3</sup>, s.u.<sub>mean</sub> = 0.000, s.u.<sub>max</sub> = 0.002, *T* = 200(2) K, *F23*, *Z* = 16, a total of 55.588 reflections collected in the range 2.47° <  $\theta$  < 30.49°, of which 3203 were unique, *R*<sub>int</sub> = 0.0294, *R*<sub>1</sub> = 0.0512 [*I* > 2 $\sigma$ (*I*)], w*R*<sub>2</sub> = 0.1182 (for all data), largest diff. peak and hole = 0.489 and -0.693 e Å<sup>-3</sup>. Absorption coefficient = 1.487 mm<sup>-1</sup>, GOF = 1.046, *F*(000) = 4488.

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