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Two microporous metal-organic frameworks constructed from trinuclear cobalt(II) and cadmium(II) cluster subunits

Xingjun Li,‡ Feilong Jiang, Lian Chen, Mingyan Wu, Shan Lu,‡ Jiandong Pang,‡ Kang Zhou,‡ Xueyuan Chen‡ and Maochun Hong‡

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Metal–organic frameworks (MOFs) have recently emerged as a new type of nanoporous materials with tailorable structures and have been attracting intense research interest due to their broad range of possible applications such as gas storage and separation, molecular magnetism, drug delivery, explosive detection, proton conduction, catalysis and nonlinear optics.1–8 Among the various tetracarboxylate ligands, H4TCPBDA and Co(ClO4)2•6H2O in solvothermal reaction between a tetracarboxylate ligand and Co2+ SBUs. Their structures and properties in magnetism and photoluminescence were obtained by a solvothermal reaction between a tetracarboxylate ligand H4TCPBDA and Co(ClO4)2•6H2O in N,N’-dimethylformamide (DMF) with an additional HAc at 100 °C for 2 days (see ESI† for details). The phase purity of above prism product has been confirmed by powder X-ray diffraction (PXRD) (Fig. S8, ESI†). X-Ray crystallography reveals that complex 1 crystallizes in the monoclinic system with space group C2/c. The asymmetrical unit of complex 1 contains one-and-a-half independent Co2+ ions, one fully deprotonated TCPBDA4− ligand and one MeNH3+ cation as counterion (Fig. 1a). In this structure, we assume that the distorted MeNH3+ cations lie inside the accessible void which is the byproduct of in situ decomposition of the DMF solvent, thus leading to the charge equilibrium.16 The central

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crystallizes in the monoclinic space group P21/c. Its asymmetric unit consists of three Cd$^{2+}$ cations, two TCPBDA$^{4-}$ ligands and two MeNH$_3^+$ cations (Fig. 2a). Similarly, complex 2 contains a linear trimetallic unit. However, the three Cd$^{2+}$ atoms adopt different coordinated geometries from each other (Fig. 2b). The independent Cd1 center has a distorted octahedral geometry coordinated by six carboxylate oxygen atoms from four fully deprotonated TCPBDA$^{4-}$ ligands. The Cd1-O bond distances are in the range of 2.218(5)-2.311(5) Å. Whereas, the Cd3 center is linked by seven oxygen atoms from four TCPBDA$^{4-}$ ligands, generating a distorted pentagonal bipyramidal [CdO$_7$] coordination geometry. The Cd3-O bonds range from 2.364(7) Å to 2.511(6) Å. Every TCPBDA$^{4-}$ ligand links to seven Cd$^{2+}$ centers through three pairs of μ2-bidentate COO$^-$ groups and one μ1-bridging monodentate COO$^-$ group (Fig. S5, ESI†). The trinuclear [Cd$_3$(COO)$_3$] SBU’s are bridged by the carboxylate groups of TCPBDA$^{4-}$ to form a three-dimensional (3D) microporous framework with 1D rhombic channels along the a-axis (Fig. 2c). Topologically, if the [Cd$_3$(COO)$_3$] SBUs are viewed as 8-connected nodes and the TCPBDA$^{4-}$ ligands as two 2-connected nodes. As a result, the over-all structure of complex 1 can be simplified to a 3, 3, 8-c 2-nodal topological network with a point symbol of {4.6}$_2$ {4.6}$^{12}$.8$11$.10}$_2$ {6}$^1$_2 (Fig. 1d). In the literature, as we know, much effort has been paid to the exploration of high nuclear cobalt based coordination polymers and their applications. However, there is still limited research focused on the linear trinuclear cobalt based complexes, which might exhibit unique magnetic properties.

Single crystals of complex 2 were produced by a solvothermal reaction with H$_3$TCPBDA and CdCl$_2$$\cdot$2.5H$_2$O in DMF with an additional HAc at 120 °C for 3 days (see ESI† for details). The phase purity of the block crystals has been confirmed by powder X-ray diffraction (PXRD) (Fig. S8, ESI†). Complex 2 crystallizes in the monoclinic space group P21/c. Its asymmetric unit consists of three Cd$^{2+}$ cations, two TCPBDA$^{4-}$ ligands and two MeNH$_3^+$ cations (Fig. 2a). Similarly, complex 2 contains a linear trimetallic unit. However, the three Cd$^{2+}$ atoms adopt different coordinated geometries from each other (Fig. 2b). The independent Cd1 center has a distorted octahedral geometry coordinated by six carboxylate oxygen atoms from four fully deprotonated TCPBDA$^{4-}$ ligands. The Cd1-O bond distances are in the range of 2.218(5)-2.311(5) Å. Whereas, the Cd3 center is linked by seven oxygen atoms from four TCPBDA$^{4-}$ ligands, generating a distorted pentagonal bipyramidal [CdO$_7$] coordination geometry. The Cd3-O bonds range from 2.364(7) Å to 2.511(6) Å. Every TCPBDA$^{4-}$ ligand links to seven Cd$^{2+}$ centers through three pairs of μ2-bidentate COO$^-$ groups and one μ1-bridging monodentate COO$^-$ group (Fig. S5, ESI†). The trinuclear [Cd$_3$(COO)$_3$] SBUs are bridged by the carboxylate groups of TCPBDA$^{4-}$ to form a three-dimensional (3D) microporous framework with 1D rhombic channels along the a-axis (Fig. 2c). Topologically, if the [Cd$_3$(COO)$_3$] SBUs are viewed as 8-connected nodes and the TCPBDA$^{4-}$ ligands are regarded as two 2-connected nodes, the overall motif of complex 2 will be a 3, 8-c 2-nodal network with a point symbol of {4.6}$^1$_4 {4.6}$^{12}$.8$11$.9$2$.10}$_2$ (Fig. 2d).

Fig. 1 Description of complex 1: (a) The coordination environment of cobalt(II) atoms in complex 1; symmetry code: A 1.5 - x, 1.5 - y, 1 - z; B x, 1 - y, 0.5 + z; C 0.5 + x, 0.5 + y, z; D 0.5 + x, 0.5 + y, z. (b) The 1D cylindrical channels viewed along the c-axis. (c) The 3D framework of complex 1. (d) The (3,3,8)-c 3-nodal topology of complex 1.

The temperature-dependent magnetic susceptibility was measured on crystalline samples of complex 1 at 1000 Oe in the range of 2-300 K. The $g$$\times$T and $g$$\times$ T versus T plots of complex 1 are shown in Fig. 3. At room temperature, the $g$$\times$T value is 7.15...
cm$^3$ mol$^{-1}$ K for complex 1, which is higher than the spin-only value (5.625 cm$^3$ mol$^{-1}$ K) for three isolated HS Co$^{2+}$ metal ions, indicating spin-orbital couplings present. As the temperature decreases to 10.4 K, the $g \cdot T$ value slightly decreases to a minimum of 6.18 cm$^3$ mol$^{-1}$ K, suggesting an appreciable antiferromagnetic coupling between the neighbouring Co$^{2+}$ ions, and then increases to 6.83 cm$^3$ mol$^{-1}$ K at 2 K. The magnetic susceptibility between 2-300 K conforms to the Curie-Weiss law, giving the Curie constant $C = 7.23$ emu mol$^{-1}$ K and the Weiss temperature $\theta = -2.16$ K (Fig. 3 and Fig. S11, ESI†). The negative Weiss temperature shows that the neighbouring magnetic Co$^{2+}$ ions are coupled with an antiferromagnetic interaction exchanges. 19

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Notes and references
Crystal data for complex 1 (CCDC 1433242): Cu$_2$O$_8$H$_8$N$_4$Co$_3$, $M = 1498.01$, monoclinic, space group C2/c, $a = 40.267(1)$, $b = 12.903(5)$, $c = 25.995(9)$ Å, $\beta = 104.20^\circ$, $V = 14108(8)$ Å$^3$, $Z = 4$, $D_	ext{c} = 0.705$ g/cm$^3$, $F_{000} = 3060$, CuK$\alpha$ radiation, $\lambda = 1.54184$ Å, $T = 100(2)$ K, $2\theta_{\text{max}} = 70.5^\circ$, 28579 reflections collected, 14179 unique ($R_{int} = 0.034$). Final Goof/$F = 1.023$, $R_1 = 0.0393$, $wR_2 = 0.0887$, $R$ indices based on 8471 reflections with I $> 2\sigma$(I) (refinement on $F^2$). Crystal data for complex 2 (CCDC 1435244): Cu$_8$O$_{16}$H$_{16}$N$_4$Cd$_3$, $M = 1658.42$, monoclinic, space group $P2_1/c$, $a = 26.936(7)$, $b = 22.123(4)$, $c = 26.046(8)$ Å, $\beta = 109.74^\circ$, $V = 14609(6)$ Å$^3$, $Z = 4$, $D_	ext{c} = 0.754$ g/cm$^3$, $F_{000} = 3312$, CuK$\alpha$ radiation, $\lambda = 1.54184$ Å, $T = 100(2)$ K, $2\theta_{\text{max}} = 73.3^\circ$, 27969 reflections collected, 14244 unique ($R_{int} = 0.051$). Final Goof/$F = 1.057$, $R_1 = 0.0826$, $wR_2 = 0.2709$, $R$ indices based on 15755 reflections with I $> 2\sigma$(I) (refinement on $F^2$). The diffraction data for complexes 1 and 2 were treated by the “SQUEEZE” method as implemented in PLATON to remove diffuse electron density associated with the badly disordered solvent molecules. The final formula of 1 and 2 were determined by combining with thermogravimetric analysis (TGA) and elemental analyses.


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