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Crystallographic report

A two-dimensional layer structure containing calcium: $[Ca_3(1,3,5\text{-benzenetricarboxylate})_2(H_2O)_{12}]_n$

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In the crystal structure, an eight-coordinated calcium center is connected to adjacent seven-coordinated calcium ions by a pair of μ-aqua bridging ligands, leading to the formation of a chain, which is linked via benzenetricarboxylate ligands to neighboring chains to furnish a two-dimensional layer structure. Layers are connected into a three-dimensional structure facilitated by hydrogen bonding interactions.

KEYWORDS: 1,3,5-benzenetricarboxylic acid; calcium; coordination polymer; crystal structure

COMMENT

Construction of inorganic–organic hybrid coordination polymers with multidentate carboxylic acids is of current interest due to their potential application as functional materials.[1–3] Most documented 1,3,5-benzenetricarboxylic-acid-based (H_3btc) coordination polymers have been constructed using transition metals.[4,5] Herein, we report the crystal structure of a two-dimensional calcium-btc coordination polymer, $[Ca_3(btc)_2(H_2O)_{12}]_n$ (**1**). In the crystal structure, there are two types of calcium ion center; Fig. 1. The Ca1 atom is seven-coordinated by two carboxylate oxygen atoms and five water molecules, and the Ca2 atom, which sits on a center of inversion, is eight-coordinated by four carboxylate oxygen atoms and four water molecules. Two Ca1 atoms are linked to a Ca2 atom via a pair of μ-aqua bridges, forming a linear trinuclear metal aggregate, that is further linked by six btc ligands at two mutually plumb directions to furnish a two-dimensional layer; Fig. 2. All btc ligands link three trinuclear Ca aggregates employing all three carboxylate groups. Finally, all coordinating water molecules, as well as the carboxylic groups, engage in hydrogen bonding interactions that serve to connect the coordination layers into a three-dimensional network structure.

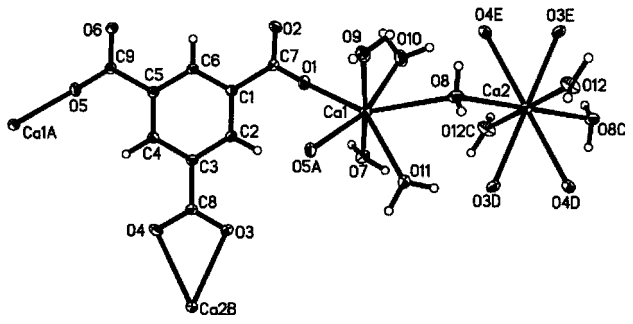

Figure 1. ORTEP plot showing the coordinating environment of Ca atoms and btc ligand. Selected geometric parameters: Ca1–O1 2.308(1), Ca1–O7 2.422(1), Ca1–O8 2.730(1), Ca1–O9 2.457(1), Ca1–O10 2.407(1), Ca1–O11 2.349(1), Ca1–O5A 2.380(1), Ca2–O8 2.508(1), Ca2–O12 2.367(1), Ca2–O3D 2.528(1), Ca2–O4D 2.583(1) Å. All O–Ca–O angles are in the range of 49.88(3) to 180°. Symmetry codes: A = $-x$, $-y$, $-z$; B = x, $y-1$, z; C = $-x+1/2$, $-y+3/2$, $-z$; D = x, $y+1$, z; E = $-x+1/2$, $-y+1/2$, $-z$.

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EXPERIMENTAL

A mixture of H_3btc (20 mg) and triethylamine (50 mg) was dissolved in isopropanol (5 ml), layered on a 5 ml aqua solution of $CaAc_2$ (20 mg) in a long tube that was sealed with a wooden stopper. Colorless block crystals deposited after 1 month. Intensity data were collected at 298 K on a Bruker AXS SMART CCD diffractometer using a colorless crystal of size 0.22 × 0.23 × 0.25 mm^3. $C_{18}H_{30}Ca_3O_{24}$, $M = 750.66$, monoclinic, $C2/c$, $a = 19.337(4)$, $b = 11.491(2)$, $c =$

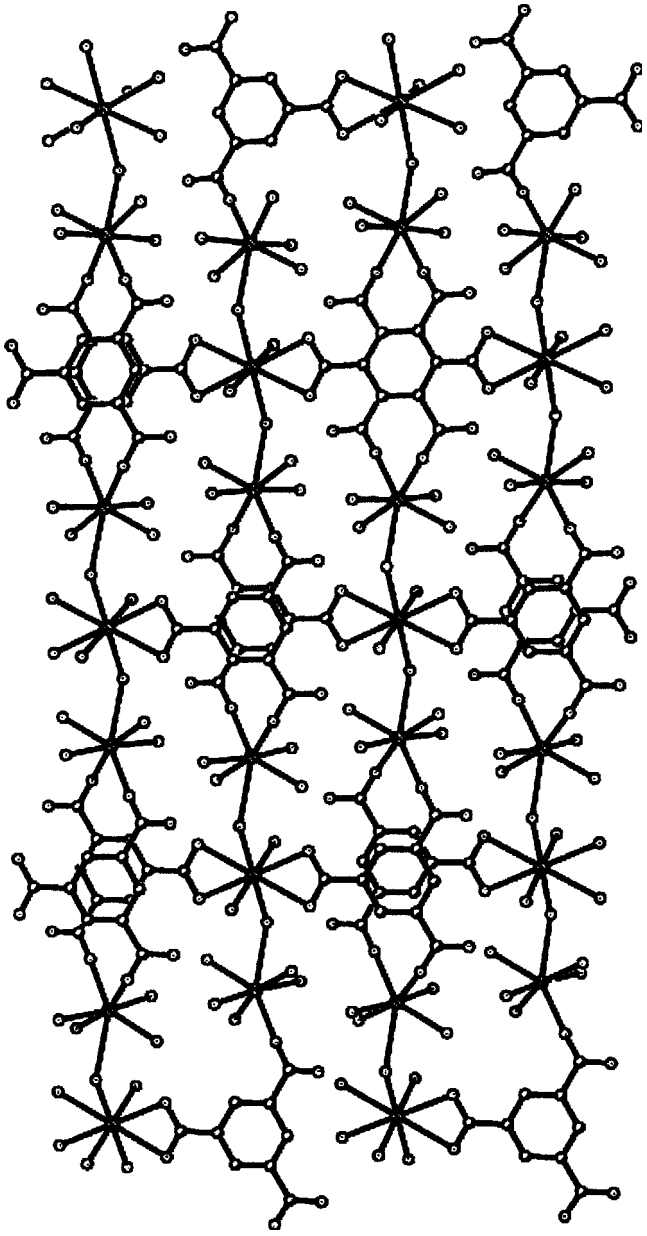

Figure 2. Perspective diagram of the three-dimensional network in **1**; hydrogen bonding interactions are not shown.

13.042(3) Å, $\beta = 106.397(3)°$, $V = 2780.3(1)$ Å^3, $Z = 4$, $R_1 = 0.025$ for 2690 reflections with $I > 2\sigma(I)$, $wR_2 = 0.074$ for 3094 unique data, $\rho_{max} = 0.31$ e$^-$ Å^{-3}. Programs used: SHELXS-97, SHELXL-97. CCDC reference number: CCDC216409.

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