

Construction of a new open-framework solid from 1,3,5-cyclohexanetricarboxylate and zinc(II) building blocks

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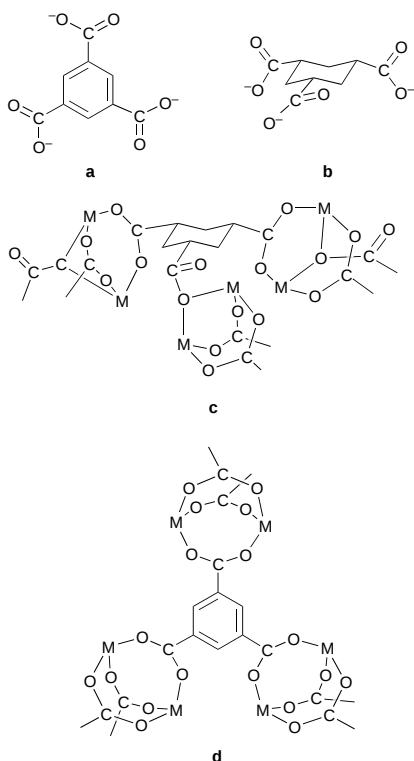
Addition copolymerization of *cis,cis*-1,3,5-cyclohexanetricarboxylate (CTC) with zinc(II) at 25 °C yielded the extended co-ordination solid, $\text{Zn}_3[(\text{CTC})(\text{C}_5\text{H}_5\text{N})]_2 \cdot 2(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$, which has one-dimensional channels with an aperture of nearly 6 Å as found by an X-ray crystallographic study.

Highly symmetric molecular organic building blocks have been copolymerized with transition-metal ions to yield a wide array of intricate porous architectures¹ having unusual inclusion behavior^{2,3} that is as yet unobserved in the well established chemistry of porous zeolitic oxides. The versatility of organic functional groups and the diversity of metal co-ordination geometries coupled with the ability to exploit weak intermolecular forces such as π - π interactions and hydrogen bonding have allowed access to porous co-ordination solids that are capable of size-, shape- and electronic-selective binding. Specifically, this has been illustrated through the systematic study of the principles governing the assembly of metal(II) ions and 1,3,5-benzenetricarboxylate (BTC), **a**, into one-, two- and three-dimensional porous networks.³ In our continuing efforts to uncover the parameters regulating the supramolecular assembly of co-ordination porous solids, we chose to focus on *cis,cis*-1,3,5-cyclohexanetricarboxylate (CTC), **b**, as a building block. The specific choice of **b** was motivated by its structural similarity to BTC, its virtually unexplored assembly reactions into extended co-ordination networks, and the utility of derivatives in designing molecular recognition host systems.⁴ This

report shows how CTC can be copolymerized with zinc(II) to yield an extended co-ordination solid, formulated as $\text{Zn}_3[(\text{CTC})(\text{C}_5\text{H}_5\text{N})]_2 \cdot 2(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$, which possesses channels having a pore diameter of nearly 6 Å.

A dimethylformamide (dmf) solution (10 cm³) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (450 mg, 1.51 mmol) and 1,3,5-cyclohexanetricarboxylic acid (95% *cis*) (216 mg, 1.01 mmol) was placed in a vial (20 cm³), which was placed in a vial (70 cm³) containing pyridine (3 cm³). The larger vial was left closed at room temperature for at least 6 d. The resulting colorless crystals were collected by filtration and washed with acetone to give 0.20 g (43% yield based on Zn). This material is soluble in water and insoluble in common organic solvents such as acetone, methanol, ethanol, chloroform, tetrahydrofuran, acetonitrile and dimethylformamide. The crystals were formulated by elemental microanalysis (Found: C, 43.37; H, 4.54; N, 5.86; Zn, 20.62. Calc. for $\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_{14}\text{Zn}_3$: C, 44.06; H, 4.57; N, 6.04; Zn, 21.16%) and structurally characterized by a single-crystal X-ray diffraction study.[†] The principal building unit in its structure is shown in Fig. 1, where three zinc(II) centers [Zn(1), Zn(2) and Zn(2B)] are bridged by a total of six carboxylate functionalities. Four carboxylate units [O(3), C(8), O(4); O(1B), C(7B), O(2B); O(3D), C(8D), O(4D); and O(1E), C(7E), O(2E)] bind the zinc centers through both of their oxygens, while the remaining two [O(6D) and O(6C)] bind through only one oxygen. Pyridine [N(1) and N(1B)] and dmf [O(7) and O(7B)] ligands occupy the remaining co-ordination sites on Zn(2) and Zn(2B). This arrangement results in an almost perfect octahedral Zn(1) [O(6C)-Zn(1)-O(6D) 180.0, O(6C)-Zn(1)-O(3D) 93.0(2), O(6C)-Zn(1)-O(1E) 87.8(2) and O(6D)-Zn(1)-O(1E) 92.2(2)°], and a distorted trigonal bipyramidal Zn(2) [O(4)-Zn(2)-O(7) 176.4(2), O(4)-Zn(2)-O(6D) 94.7(2), O(2B)-Zn(2)-O(7) = 83.7(2), N(1)-Zn(2)-O(7) 86.8(2) and N(1)-Zn(2)-O(6D) 137.4(2)°] geometries. This building unit is linked through the other CTC carboxylates to form a layer three zinc centers thick that is nearly perpendicular to the crystallographic *a* axis. Each CTC is thus bound to a total of six zinc centers. The pyridine ligands extend along the *a* axis and form long connections [3.917(7) Å] to other pyridines of adjacent layers.

Close examination of the structure revealed that the Zn-O (carboxylate) and Zn-N (pyridine) bond lengths are



[†] Single crystal of $\text{Zn}_3[(\text{CTC})(\text{C}_5\text{H}_5\text{N})]_2 \cdot 2(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ was analyzed at 20 ± 1 °C: $M = 926.90$, colourless parallel piped plate of size $0.25 \times 0.20 \times 0.07$ mm, monoclinic, space group $P2_1/c$ with $a = 13.958(3)$, $b = 8.814(2)$, $c = 16.215(3)$ Å, $\beta = 104.21(3)^\circ$, $U = 1933.8(7)$ Å³, $Z = 2$, $D_c = 1.592$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.916$ mm⁻¹, $F(000) = 952$. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and full 1.60° wide ω scans to a maximum of $2\theta = 50^\circ$, giving 3427 unique reflections. The structure was solved by direct methods (SHELXTL PLUS⁵) and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index $R = 0.0617$ and $R' = 0.1025$ for 3424 reflections with $F > 4\sigma(F)$. Anisotropic thermal parameters were refined for all non-hydrogen atoms and fixed thermal parameters were used for included hydrogens. The magnitude of R and R' is attributable to some difficulty in performing accurate absorption corrections due to the irregular shaped edges of the examined crystal ($R_{\text{int}} = 0.0677$). CCDC reference number 186/567.

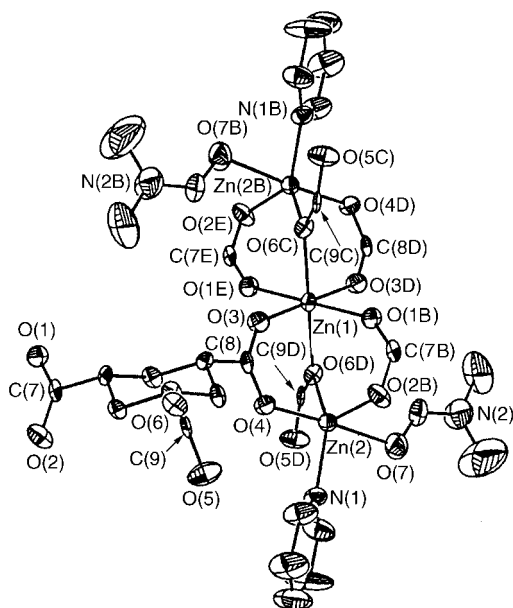


Fig. 1 The building unit in the solid-state structure of the layered compound, $\text{Zn}_3[(\text{CTC})(\text{C}_5\text{H}_5\text{N})]_2 \cdot 2(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$, with the atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms have been omitted for clarity. Only one full CTC unit is shown along with only one carboxyl group of each of the remaining CTC units. Atoms labelled with additional letters A–D are related by symmetry to atoms without such designation

unexceptional, however, the Zn–O (dmf) bond lengths are longer [Zn(2)–O(7) 2.322(7) Å] than those generally observed (1.9–2.1 Å) for analogous interactions.⁶ Furthermore, the dmf ligands point into extended one-dimensional channels of approximately 6 Å cross-section internuclear distance, which run along the *a* axis of the crystal, as shown in Fig. 2. This observation prompted us to examine the mobility of the dmf molecules and their possible removal from the pores. Thermal gravimetric analysis performed on a 35.3 mg sample showed a clean weight loss of 6.90 mg (19.5%) at nearly 140 °C, which is equivalent to the loss of 2 dmf and 0.40 pyridine molecules per formula unit (19.2%). The loss of pyridine continues until 390 °C, where the Zn–CTC framework begins to collapse as evidenced by the observed weight loss due to CTC decomposition products. The concomitant loss of pyridine was confirmed by heating a sample of the original solid to 115 °C under a vacuum of 0.1 mmHg (≈ 13.3 Pa) to give a material that was formulated as $\text{Zn}_3(\text{CTC})_2(\text{C}_5\text{H}_5\text{N})_{1.5} \cdot 0.5\text{dmf}$ (Found: C, 41.90; H, 3.76; N, 3.36. Calc. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_{12.5}\text{Zn}_3$: C, 41.70; H, 3.78; N, 3.60%). Preliminary experiments showed that the X-ray powder diffraction (XRPD) lines of this solid are significantly broadened from that of the original solid, presumably due to loss of long range order resulting from the partial removal of pyridine. However, these lines sharpen and become more intense upon exposure of the partially evacuated solid with pyridine vapor for 10 h, which indicates the commencement of framework restoration. The fragile nature of the partially evacuated framework is most likely due to its layered structure and to the presence of a reactive open co-ordination site on zinc resulting from dmf removal. Such open sites have been observed in the three-dimensional framework of $\text{Zn}_2(\text{BTC}) \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})_5$ and implicated in highly selective inclusion processes due to their specific steric and electronic requirements for guest binding.^{3a}

It is worth noting that the metal carboxylate co-ordination pattern observed in the two-dimensional structure of **c**, is not dissimilar to that found in the aforementioned three-dimensional Zn–BTC framework **d**. However, the three-dimensional structure of the latter is achieved only when bases with weaker ligating ability, such as triethylamine, are employed to deprotonate the carboxylates. In fact, using pyridine for this

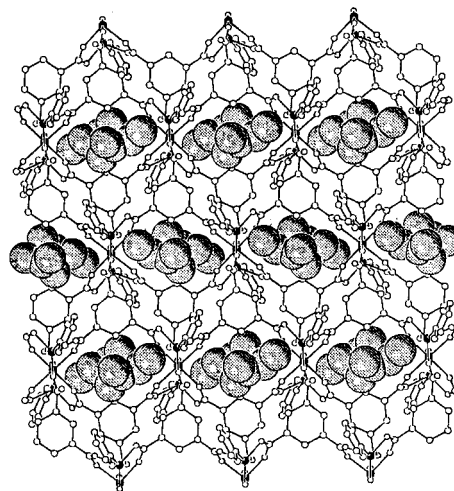


Fig. 2 The solid-state structure of $\text{Zn}_3[(\text{CTC})(\text{C}_5\text{H}_5\text{N})]_2 \cdot 2(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ shown along the *a* axis, where the one-dimensional channels are occupied by dmf (drawn in space-filling style). The hydrogen atoms are omitted and only the zinc atoms are shown as dark spheres with all remaining framework atoms drawn as open spheres

purpose yields $\text{M}(\text{HBTC})(\text{NC}_5\text{H}_5)_2 \cdot 0.67\text{NC}_5\text{H}_5$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} or Zn^{II}),^{3c} which has a two-dimensional framework similar to that reported here.

The close analogy between the reaction and structural chemistry of CTC and BTC may indicate that using a weaker ligating base in reactions involving *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (CTCA) will also yield a three-dimensional Zn–CTC porous network. It also points to the crucial balance that must be achieved between the intrinsic co-ordination chemistry of the metal centers and the lability of the bound ligands in order to construct rigid porous networks.

Acknowledgements

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