

Hydrothermal synthesis of a thermally stable porous supramolecular π - π framework: $[\{Co_2(C_{12}H_8N_2)_4(\mu-C_4O_4)(OH_2)_2\}C_4O_4] \cdot 8H_2O^\dagger$

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The title compound was synthesized by hydrothermal methods and characterized by single-crystal X-ray diffraction, which reveals an open-framework structure containing dumbbell-shaped windows with hydrophilic and hydrophobic characteristics.

Crystalline porous materials such as aluminosilicates (zeolites), aluminophosphates, pillared clays, and other layers are widely used in catalyst and separation applications.^{1,2} Recently, coordination polymers and organic networks sustained by coordinated covalent bonds and directional noncovalent interactions have become a rapidly expanding field. However, a major challenge in the highly porous coordination materials is their fragility. Unlike zeolites, which are held together with rugged covalent bonds, their solid molecules are glued with relatively weak intermolecular forces. To date the number of coordination networks with new structural aspects is increasing,^{3–16} but to our knowledge thermally stable network structures sustained by π - π interactions are still rare or lacking.

Using polyfunctional squarates as molecular building blocks, we and other groups have prepared compounds that exist as supramolecular networks in the solid state.^{13–15} We have recently focused our attention on introducing noncovalent interactions for constructing new classes of zeolite analogues possessing hydrophilic and hydrophobic void characteristics. In this present work, we report a supramolecular complex,

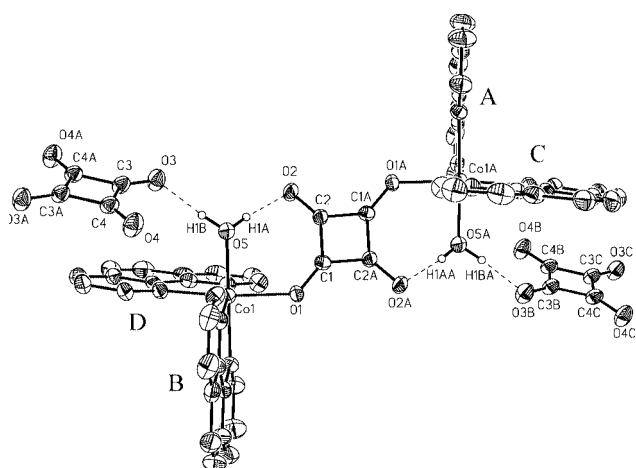


Fig. 1 ORTEP drawing of the building block units relating to the discrete μ -squarate-bridged cobalt(II) cations and squarate anions in **1** with thermal ellipsoids at 50% probability. A and B phen molecules induce the pair of in-planar-sheet π - π interactions while C and D induce the pair of out-of-planar-sheet π - π interactions. Selected bond distances (\AA): Co(1)–O(5) 2.076(3), Co(1)–O(1) 2.118(2), C(1)–O(1) 1.256(4), C(2)–O(2) 1.252(4), C(3)–O(3) 1.261(4), C(4)–O(4) 1.257(4), O(5)–O(2) 2.649(3), O(5)–O(3) 2.634(3).

[†] Electronic supplementary information (ESI) available: TGA curve for **1** and X-ray powder diffraction patterns. See <http://www.rsc.org/suppdata/cc/b1/b100921o/>

$[\{Co_2(C_{12}H_8N_2)_4(\mu-C_4O_4)(OH_2)_2\}C_4O_4] \cdot 8H_2O$ **1**, that adopts a neutral open-framework structure with one-dimensional channels containing disordered water molecules.

Hydrothermal reaction of Co_3O_4 , squaric acid, and 1,10-phenanthroline (phen) in molar ratios at 1:3:2 at 200 °C for 96 h in water produced crystals of **1**.[‡] The X-ray structure analysis of **1** reveals an extended structure composed of the building-block units (Fig. 1).[§] The discrete dinuclear cations, two octahedrally coordinated cobalt(II) centers bridged by a squarate ligand, are alternately connected squarate anions *via* hydrogen bonds to form infinite chains, $[\cdots C_4O_4 \cdots \{Co(OH_2)-C_4O_4-Co(OH_2)\} \cdots]_n$, incorporating phen ligands (Fig. 2 arrows). The interatomic O \cdots O distances between the ligated waters and the oxygen atoms of squarates are in the range 2.63–2.65 \AA indicative of strong hydrogen bonds. The strength of the interionic hydrogen bonds of *ca.* 40–190 kJ mol^{-1} makes for the construction of more robust framework structures.¹⁷ The infinite chains are further held together by the natural tendency of π overlap in phen molecules yielding a planar sheet [Fig. 2(a)]. A significant feature is that the planar sheets are stacked in three dimensions to give ‘sinuous’ channels with a dimension (phen to phen distances) of nearly $12 \times 7 \text{\AA}$, in which free water molecules fill the dumbbell-shaped voids [Fig. 2(b)]. Thermogravimetric analysis (TGA) reveals that the guest water molecules are liberated below 100 °C, a weight loss of 8.73% consistent with the loss of eight water molecules in the

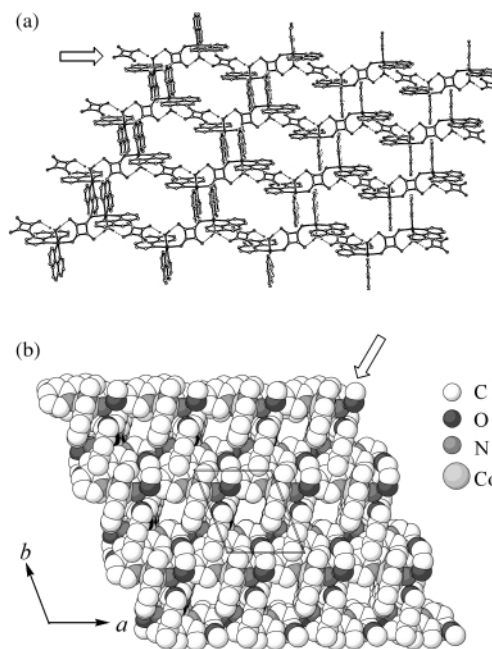


Fig. 2 (a) Ball-and-stick representation of the sheetlike network in **1**, showing the dumbbell-shaped windows ($12 \times 7 \text{\AA}$) with hydrophilic and hydrophobic characteristics; (b) perspective view of the open-framework structure containing one-dimensional channels along the crystallographic *c* axis. The arrows show the infinite hydrogen-bonding chains. Lattice water molecules are omitted for clarity.

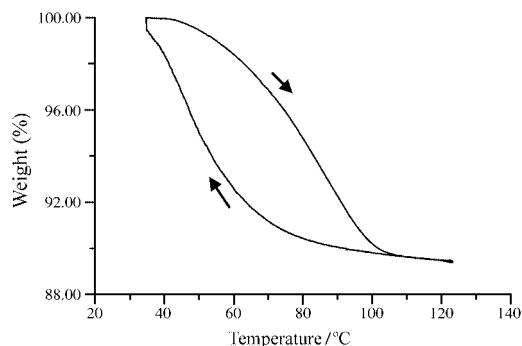


Fig. 3 TGA profile of a reversible N_2 adsorption–desorption cycle on **1**. The sample was initially heated at 120 °C for 0.5 h, cooled to 40 °C, maintained at 40 °C for 0.5 h, and then heated again to 120 °C.

channels. No weight loss was observed the temperature range 100–200 °C. The powder X-ray diffraction pattern of a sample heated to 200 °C for 2 h shows that the positions of the most intense lines remain unchanged relative to the simulated pattern based upon the single-crystal data. In order to examine the porous functionality of **1**, an N_2 adsorption–desorption study was conducted. Fig. 3 reveals a reversible N_2 adsorption–desorption cycle, which was confirmed by TGA with purified N_2 as the purging gas (2 atm). Besides demonstrating that the channel structure is retained throughout this process, this study also indicates that the cooperative π – π interactions are robust enough to sustain such an open space in crystals. Moreover, the most intriguing feature of the dumbbell-shaped windows is the presence of hydrophilic (the pendant C=O groups of squarates protrude into windows) and hydrophobic (phen groups) void characteristics that have a natural affinity for organic molecules. Further experiments to explore whether this nanoporous material can be filled by organic guests are in progress.¹⁸

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Notes and references

‡ *Synthesis of 1*: a mixture of Co_2O_4 (0.1204 g, 0.51 mmol), squaric acid (0.1743 g, 1.53 mmol), phen (0.2018 g, 1.02 mmol), CsOH (0.3 mL, w/w

50%) and H_2O was sealed in a Teflon-lined stainless autoclave (23 mL), heated at 200 °C for four days, and cooled to 80 °C at 6 °C h^{-1} . Needle-shaped orange–yellow crystals of **1** and unidentified black materials were filtered off. Additionally, allowing the deep-orange filtrate to stand at room temperature for one week also gave crystals of **1** (yield: 10%). Elemental analysis (%): calc. C 54.13, N 9.01, H 4.18, O 23.17; found: C 53.20, N 8.52, H 4.17, O 22.72.

§ *Crystal data for $C_{56}H_{52}Co_2N_8O_{18}$, 1*: $M = 1242.92$, triclinic, space group $P\bar{1}$, $a = 9.918(3)$, $b = 11.292$, $c = 13.276(4)$ Å, $\alpha = 93.33(2)$, $\beta = 101.21(3)$, $\gamma = 110.44(2)^\circ$, $V = 1353.8(7)$ Å³, $Z = 1$, $D_c = 1.525$ g cm^{-3} , $\mu(Mo-K\alpha, \lambda = 0.71069$ Å) = 6.97 cm^{-1} , $2\theta_{max} = 50^\circ$. Of the 4982 reflections collected 4757 unique reflections ($R_{int} = 0.028$) were used in all calculations after Lorentz polarization and empirical absorption corrections; $R_1 = 0.041$ for 2802 reflections with $I > 2.0\sigma(I)$; $wR_2(F^2)$ 0.121 (all data), GOF = 0.925, residual electron density between -0.32 and 0.35 e Å⁻³.

CCDC 144421. See <http://www.rsc.org/suppdata/cc/b1/b100921o/> for crystallographic data in .cif or other electronic format.

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- 18 This material also reveals thermo-chromic as well as vapor-chromic data that will be published elsewhere.