

12-21-2001

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Publication Info

Chemical Communications, 2001, pages 74-75.

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<http://pubs.rsc.org/>

DOI: 10.1039/b108219a

[Cu(pyrazine-2-carboxylate)₂]₂Cd₄I₈: unprecedented 1-D serpentine inorganic chains and regular 2-D metal–organic square grids in a 3-D framework

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Received (in Columbia, MO, USA) 12th September 2001, Accepted 15th November 2001

First published as an Advance Article on the web 21st December 2001

A novel three-dimensional coordination polymer containing an unprecedented one-dimensional serpentine motif conjoined with a two-dimensional square grid motif is presented.

Intriguing physical properties and tremendous structural variety has caused the design and synthesis of new hybrid organic–inorganic materials to become a prolific domain in the field of coordination chemistry. An impressive library of one-, two- and three-dimensional frameworks with various structural motifs has been reported to date. However, few of these frameworks feature assemblages of two different motifs within the same crystal structure. Some mixed-motif interpenetrating networks have been reported,^{1–5} the constituents of which are usually one-dimensional chains or ribbons or two-dimensional square or rectangular grids.^{6–8} In these examples, purely covalent networks interpenetrate with either organic, non-covalent sublattices or else with other covalent arrays.^{9–12} Non-interpenetrating examples are also known: Zubieta and coworkers¹³ have reported the synthesis of anionic 1-D oxide chains covalently bound to a cationic 2-D metal–organic net in the same crystal. A reasonable approach to the design of such mixed-motif compounds is to employ two different metals. Manifestation of the unique coordination preferences of two dissimilar metals (like Cu and Cd), could lead to the formation of different structural sub-components, and create new composite frameworks containing each metal in its own structural motif. Additionally, the simultaneous presence of two different metal centers should increase the diversity and complexity of the polymeric structures. Herein we present the synthesis and structural characterisation of a new mixed-metal, mixed-motif coordination polymer, [Cu(pyzca)₂]₂Cd₄I₈ (**1**; pyzca = pyrazine-2-carboxylate, C₅H₃N₂O₂), whose remarkable three-dimensional structure consists of two topologically and chemically very different covalent networks: regular square grid metal–organic layers and serpentine one-dimensional inorganic chains.

Hydrothermal reaction of CdI₂ and Cu(pyrazine-2-carboxylate)₂ in a 2:1 ratio at 130 °C for 24 h yielded small green rectangular crystals in low yield (<10%). Single crystal X-ray analysis† of the invariably twinned samples revealed, as expected, that the individual coordination preferences of the two metals caused them to segregate into their own structural motifs. The really unexpected and incredible aspect of **1** is how structurally divergent the two motifs are topologically, while still joined together. The metal–organic part of the structure consists of two-dimensional square grid layers of composition [Cu(pyzca)₂]_n assembled from two symmetry-independent but chemically identical Cu(pyzca)₂ moieties (Fig. 1). The square grids lie parallel to the crystallographic *ac* plane. The nodes of the square net consists of two crystallographically different coppers (Cu1 and Cu2) disposed such that each Cu1 (or Cu2) atom is surrounded by four Cu2 (or Cu1) atoms. Each Cu atom resides on an inversion center in a 4 + 2 pseudo-octahedral coordination sphere, with the equatorial sites occupied by two symmetry-equivalent chelating pyzca ligands (Cu1–N1 = 1.939(11) (×2), Cu1–O1 = 1.982(7) (×2); Cu2–N3 = 2.009(10) (×2), Cu2–O3 = 1.973(8) Å (×2)). The axial sites

are occupied by the *para* nitrogen atom from the other symmetry-independent Cu(pyzca)₂ moiety (Cu1–N4 = 2.466(12) (×2), Cu2–N4 = 2.575(12) Å (×2)). The cavities in these two-dimensional layers are almost perfect squares (Cu to Cu dimension = 7.24 × 7.24 Å²) with N–Cu1–N angles of 89.78 and 90.22° and N–Cu2–N angles of 89.45 and 90.55°. The pyzca oxygen atoms O2 and O4 do not participate in linking the metal–organic square grids, but instead donate to the remarkable Cd–O–I inorganic chains described next, thereby creating the full 3-D structure of **1**.

The inorganic part of this three-dimensional material consists of chains of infinite one-dimensional vertex-sharing cadmium-centered tetrahedra. As illustrated in Fig. 2, two different tetrahedra alternate in the chains, namely CdO₂I₂ (T1) and CdI₄ (T2). There are two crystallographically different T1 and T2 tetrahedra, yielding a total of four inequivalent cadmium centers: Cd1 and Cd3 (in T1) and Cd2 and Cd4 (in T2). The coordination environment around the T1 cadmium atoms is comprised of two iodines and the two carboxylic oxygen atoms O2 and O4, donated by the organic ligands in the [Cu(pyzca)₂]_n layers (Cd–O = 2.230(8), 2.216(9) Å; Cd–I = 2.667(2), 2.683(2), 2.749(2), 2.750(2) Å). In T2, all coordination sites around the cadmium centers are occupied by iodine atoms, with Cd–I bond lengths ranging between 2.690(2) and 2.938(3) Å. The Cd–O and Cd–I bond lengths in **1** are consistent with those in previous Cd-based polymeric chains.¹⁴ The chains run along the crystallographic *a* axis and adopt a spectacular ‘serpentine’ conformation. As shown in Fig. 2, the repeat distance in the chains is 1448 pm and contains eight tetrahedra ((T1)₄(T2)₄). Hence, the connection between the metal–organic part and the inorganic part is *via* coordinative cadmium–oxygen bonds involving only one of the two kinds of Cd-centered tetrahedra

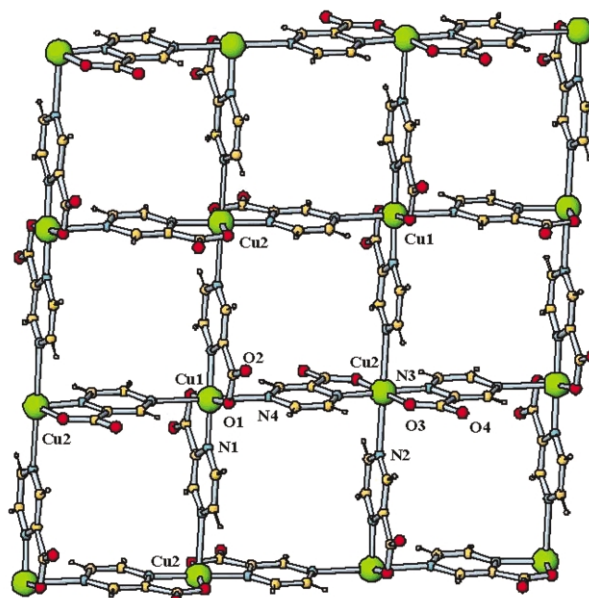


Fig. 1 View of a Cu(pyzca)₂ square grid layer (slightly rotated from true perpendicular).

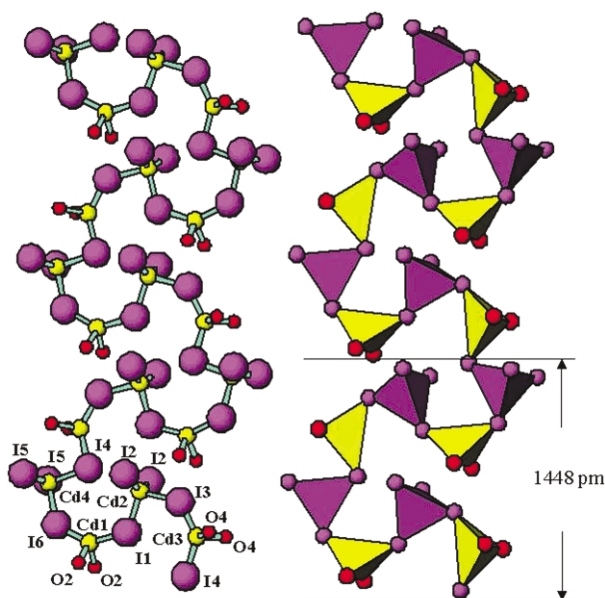


Fig. 2 View of two adjacent one-dimensional chains represented as ball and sticks (left) and vertex-sharing tetrahedra (right). T1 is shown in yellow and T2 in purple.

(T2). The beautiful 3-D structure of alternating layers of square grids and serpentine chains is shown in Fig. 3.

The serpentine shape of the chains resembles the structures of the inosilicates (chain metasilicates), and while inosilicate repeating units of 1–7, 9 or 12 tetrahedra are known,¹⁵ to the

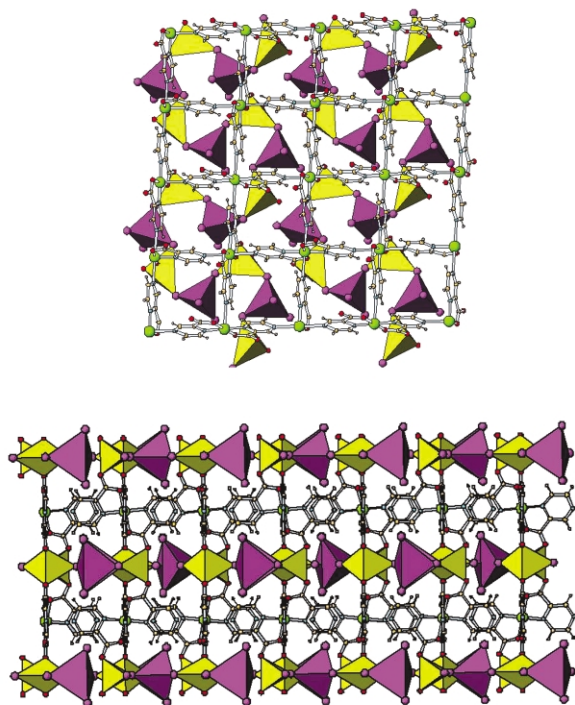


Fig. 3 View of the three-dimensional network, showing one square grid layer connected to two adjacent chains (top, view perpendicular to the layers) and the stacking of alternating layers of square grids and serpentine chains (bottom, view parallel to the layers).

best of our knowledge the chain repeating unit in **1** of 8 tetrahedra has not been previously observed. Also, because of the tortuous course taken by the cadmium–iodide chains (the bond angle at the bridging atom, Cd–I–Cd, ranges between 99.00(6) and 133.21(8)°), the repeat distance in **1** is considerably smaller (1448 pm) than found in inosilicates with a repeat distance of 7 tetrahedra (1740 pm).

Financial support was provided in part by the National Science Foundation through Grant DMR: 9873570 and in part by the South Carolina Commission for Higher Education through Grant CHE: R00-U25. The Bruker CCD Single Crystal Diffractometer was purchased using funds provided by the NSF Instrumentation for Materials Research Program through Grant DMR: 9975623.

Notes and references

† *Crystal data* for **1**: $M = 2084.26$. Green plate, $0.18 \times 0.14 \times 0.08$ mm³. Orthorhombic, space group $Pnma$, $a = 14.4875(14)$, $b = 19.9430(20)$, $c = 14.4911(15)$ Å, $V = 4186.7(7)$ Å³, $Z = 4$, $D_{\text{calc}} = 3.307$ g cm⁻³, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 8.94$ mm⁻¹, $R1 = 0.0664$, $wR2 = 0.1753$, for 4207 reflections with $I > 2\sigma(I)$. Intensity data covering a hemisphere of reciprocal space measured (ω scan mode) to $2\theta_{\text{max}} = 56.6^\circ$ with a Bruker SMART APEX CCD diffractometer (MoK α radiation, $\lambda = 0.71073$ Å). 32472 reflections collected; 5547 independent, 4207 with $I > 2\sigma(I)$. Lp and absorption corrections applied (SADABS). Structure solved with direct methods; refined against F^2 using all data with SHELXTL v. 5.1.¹⁶ Though metrically consistent with the tetragonal crystal system, the internal symmetry of **1** is incompatible with a four-fold axis of rotation. Additionally, all crystals sampled were pseudo-tetragonal orthorhombic twins (twin law by rows = 0 0 1 / 0 -1 0 / 1 0 0).

CCDC reference number 174413. See <http://www.rsc.org/suppdata/cc/b1/b108219a/> for crystallographic data in CIF or other electronic format.

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