

A new supramolecular isomer of $[\text{Zn}(\text{nicotinate})_2]_n$: a novel $4^2.8^4$ network that is the result of self-assembly of 4-connected nodes[†]

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Self-assembly of $\text{Zn}(\text{NO}_3)_2$ with *m*-pyridinecarboxylate (nicotinate) under mild conditions affords several products including a novel three-dimensional network $[\text{Zn}(\text{nicotinate})_2]_n$ that has connectivity defined by the circuit symbol $4^2.8^4$.

Structural diversity in coordination polymers can occur through the existence of phenomena such as interpenetration^{1–3} or supramolecular isomerism^{4,5} and it is thereby possible to generate a wide range of structures from even simple ligands and known chromophores. In such a context, pyridinecarboxylates represent readily available ligands that have already been shown to be capable of generating coordination polymer networks that exhibit properties such as polarity,^{6–8} porosity^{9,10} or magnetism.¹¹

$\text{Zn}(\text{II})$ chromophores generally exhibit tetrahedral coordination¹² and can in appropriate circumstances serve as pseudo square planar nodes. Therefore, coordination of an angular bifunctional ligand, *e.g.* nicotinate, to a tetrahedral $\text{Zn}(\text{II})$ ion can result in a 4^4 (square grid) network. Indeed, $[\text{Zn}(\text{nicotinate})_2]_n$, **1a**, exhibits such topology.^{6,8} However, there are other possible topologies that are based solely upon square planar nodes: the 3D networks NbO ($6^4.8^2$)¹² and CdSO_4 ($6^5.8$).¹³ PtS exhibits ($4^2.8^4$)¹⁴ topology but it is sustained by both square planar and tetrahedral nodes in a 1:1 ratio. It should also be noted that a hydrogen bonded network with $4^2.8^4$ topology has been reported.¹⁵

We report herein a new supramolecular isomer of $[\text{Zn}(\text{nicotinate})_2]$ which represents what is to our knowledge the first example of a three-dimensional coordination polymer that possesses a $4^2.8^4$ topology based solely upon square planar nodes, $\{[\text{Zn}(\text{nicotinate})_2] \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}\}_n$, **2**, and two new forms of **1a**— $\{[\text{Zn}(\text{nicotinate})_2] \cdot \text{naphthalene}\}_n$, **1b**, and $\{[\text{Zn}(\text{nicotinate})_2] \cdot 2 \text{ nitrobenzene}\}_n$, **1c**—both of which exhibit the same 4^4 topology as **1a**.[‡]

The crystal structure of **2** is illustrated in Fig. 1(a).[§] The chromophore is the same as that in **1a–c**. However, when one examines the connectivity of the Zn centers, adjacent square planar nodes are twisted at an angle of *ca.* 25°, resulting in a 3D network [Fig. 1(b)] instead of a 2D square grid. The circuit symbol of this network is $4^2.8^4$. PtS¹⁴ is defined by the same circuit symbol; however, the two nets are fundamentally different and the projections down [100] are non-superimposable (Fig. 2). The nodes are eclipsed along the *z*-axis with a vertical distance between two Zn atoms of 6.92 Å and there are edge-to-face interactions between the pyridyl rings of nicotinate ligands with a shortest distance $d(\text{C–C}) = 3.8$ Å.

2 possesses cavities of effective dimensions 4.35×4.35 Å that form infinite channels parallel to the *z*-axis, (Fig. 1, left). These channels contain columns of disordered solvent molecules. The density of **2** is 1.56 g cm^{-3} (1.30 g cm^{-3} without solvent). Thermogravimetric analysis of **2** revealed a weight loss of *ca.* 16% between 100 and 250 °C, which is consistent

with the removal of solvent molecules (calculated loss of 18% for two molecules of H_2O and one molecule of MeOH).[†]

In order to systematically determine the effect of templates on the formation of **1a** or **2**, the same reaction was conducted in the presence of several aromatic guests: benzene, nitrobenzene, naphthalene, chlorobenzene, *o*- and *p*-xylenes, *p*-nitroaniline and anisole, as well as in the absence of template. Analysis of simulated and calculated XPD patterns indicated that most reactions resulted in the formation of **1a** whereas nitrobenzene affords **2** or **1c** and naphthalene affords **1b**.[‡]

1b and **1c** contain 2D square grid networks (4^4) [Fig. 3(a)].[§] **1b** crystallizes in the centrosymmetric space group $C2/c$, the parallel infinite layers of square grids are eclipsed and the $d(\text{Zn–Zn})$ separations are 7.68 Å, resulting in the formation of parallel channels perpendicular to the planes of the square grids. Each cavity has effective dimensions of 4.45×4.45 Å, and is filled by one molecule of naphthalene that interacts with the aromatic rings of the surrounding nicotinate ligands by face-to-face π – π stacking with distances between the centroids in a range of 3.4–3.7 Å. The density of **1b** is 1.56 g cm^{-3} (1.10 g cm^{-3} without guest). Structure **1c** contains a larger amount of guest (density without guest = 0.86 g cm^{-3}) and exhibits much larger interlayer separations than either **1a** or **1b** [$d(\text{Zn–Zn}) = 10.05$ Å]. It should be noted in **1a** that adjacent grids are staggered whereas in **1b** and **1c** they are almost eclipsed.

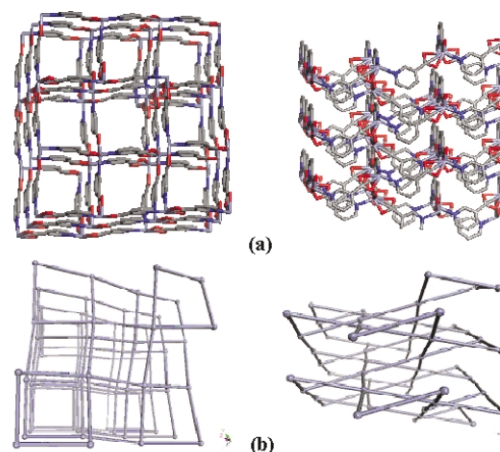


Fig. 1 (a) Crystal structure of the 3D $4^2.8^4$ network $[\text{Zn}(\text{nicotinate})_2]_n$, **2**. Guest molecules are omitted for clarity. (b) Schematic representations of the connectivity of the Zn centres in **2**.

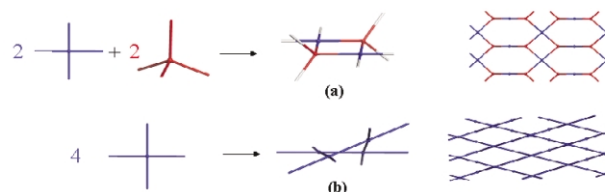


Fig. 2 Connectivity of two tetrahedral and two square planar nodes to form the $4^2.8^4$ network of PtS (a) and connectivity of four square planar nodes to form **2** (b) and projections of the two networks down [100].

[†] Electronic supplementary information (ESI) available: experimental details, TGA and XRPD of all compounds. See <http://www.rsc.org/suppdata/cc/b1/b111280p/>

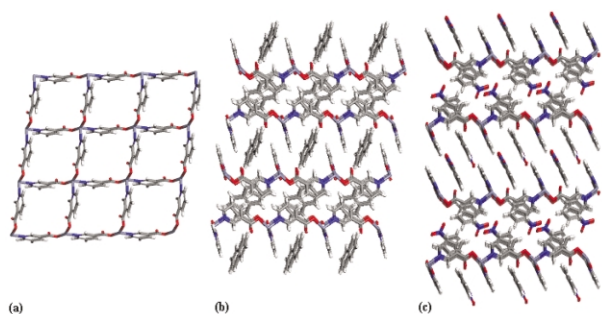


Fig. 3 Crystal structure of the 2D square grid in **1b** and **1c** (a) and the vertical stacking between parallel infinite layers showing the intercalation of naphthalene (b) and nitrobenzene (c) molecules.

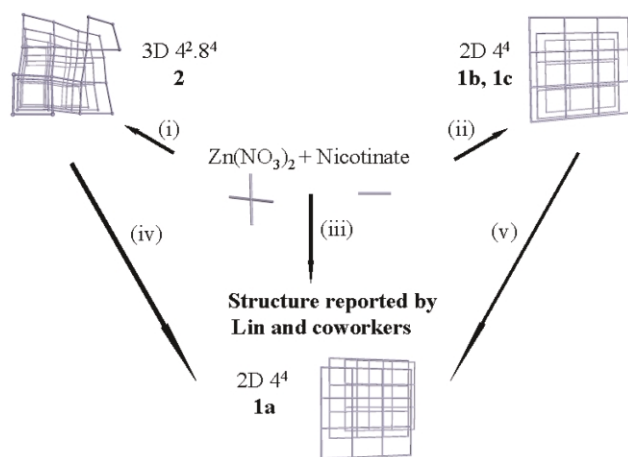


Fig. 4 The relationship between **1a–c** and **2**. *Reagents and conditions:* (i) PhCH_3 or PhNO_2 in MeOH, diffusion; (ii) C_{10}H_8 or PhNO_2 in MeOH, slow diffusion; (iii) MeOH or PhH or PhCl or *o*-, *p*- $\text{Ph}(\text{CH}_3)_2$ or *p*- H_2NPhNO_2 or PhOCH_3 in MeOH, precipitation; (iv) and (v) 220–250 °C, 1 h.

1a–c and **2** are sustained by the same chromophore. Only a subtle difference of the conditions during crystallization influences which phase is generated. A summary of the relationships between the structural supramolecular isomers is shown in Fig. 4. The characterization of components, achieved by powder diffraction and thermogravimetric analysis,[§] reveals that heating above 220 °C results in conversion of **1b**, **1c** and **2** into **1a**. **1a** was formed *via* hydrothermal conditions and it should therefore be unsurprising that it appears to be the thermodynamically favored product.

In conclusion, a novel $4^2.8^4$ network based upon square planar nodes has been generated and it can be rationalized on the basis of the connectivity and the geometry of the molecular building blocks. The ability of guests to intercalate in the square grid form of $[\text{Zn}(\text{nicotinate})_2]$ is perhaps unsurprising^{16,17} but to our knowledge such a wide range of separations has not yet been seen in laminated coordination polymers. This study further confirms how supramolecular isomerism can afford superstructural diversity from even the most simple chemical building blocks.

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Notes and references

‡ **1b**, **1c** and **2** were prepared as the result of attempts to synthesize the dimetal tetracarboxylate cluster, $\text{Zn}_2(\mu_2\text{-nicotinate-O,O'})_4$, a methanolic solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (149 mg, 0.5 mmol) was carefully layered onto

a methanolic solution of nicotinic acid (123 mg, 1 mmol), pyridine (79 mg, 1 mmol) and toluene (3 ml, 28 mmol), **2**, or naphthalene, (640 mg, 5 mmol), **1b**, or nitrobenzene, (3 ml, 29 mmol), **1c**, under ambient conditions. The solutions were left undisturbed for 48 h and colorless crystals of **2** (112 mg, 60.5%) formed at the interlayer boundary in addition to a white precipitate (60 mg, 33%) that was characterized by XPD to be the square grid **1a** synthesized by Lin *et al.* in 1998.⁶ After 1 and 9 months, colorless crystals of **1b** (15 mg, 7%) and **1c** (119 mg, 43%) were collected from the mother liquor by physical separation.

§ *Crystallographic data:* intensity data for **1b**, **1c** and **2** were collected at 200 K on a Bruker SMART-APEX diffractometer using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS¹⁸ program. Structures were solved using direct methods and refined by full-matrix, least-squares on $|F|^2$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. The two molecules of solvent in the asymmetric unit of **2** were disordered, the methanol molecule was two-fold disordered and refined over two equally occupied positions of the O atoms. All crystallographic calculations were conducted with the SHELXTL 5.1 program package.

Crystal data: for **2**: tetragonal, $I4_2d$, $a = b = 21.351(3)$, $c = 6.9183(15) \text{ \AA}$, $V = 3153.9(10) \text{ \AA}^3$, $Z = 8$, $D_c = 1.559 \text{ g cm}^{-3}$, $\mu = 1.593 \text{ mm}^{-1}$, $F(000) = 1492$, $2\theta_{\text{max}} = 56.50^\circ$ ($-8 \leq h \leq 27$, $-25 \leq k \leq 12$, $-8 \leq l \leq 8$). Final residuals (for 102 parameters) were $R1 = 0.0477$ for 1767 reflections with $I > 2\sigma(I)$, and $R1 = 0.0576$, $wR2 = 0.1213$, $\text{GOF} = 1.130$ for all 4472 data. Absolute structure parameter was 0.10(3). Residual electron density was 0.662 and $-0.359 \text{ e \AA}^{-3}$.

For **1b**: monoclinic, $C2/c$, $a = 10.899(2)$, $b = 11.292(2)$, $c = 15.358(3) \text{ \AA}$, $\beta = 100.47(3)^\circ$, $V = 1858.6(7) \text{ \AA}^3$, $Z = 4$, $D_c = 1.564 \text{ g cm}^{-3}$, $\mu = 1.354 \text{ mm}^{-1}$, $F(000) = 896$, $2\theta_{\text{max}} = 56.52^\circ$ ($-13 \leq h \leq 5$, $-15 \leq k \leq 14$, $-9 \leq l \leq 20$). Final residuals (for 132 parameters) were $R1 = 0.0424$ for 1692 reflections with $I > 2\sigma(I)$, and $R1 = 0.0571$, $wR2 = 0.0888$, $\text{GOF} = 0.855$ for all 2739 data. Residual electron density was 0.556 and $-0.335 \text{ e \AA}^{-3}$.

For **1c**: monoclinic, $C2/c$, $a = 11.922(3)$, $b = 9.990(9)$, $c = 20.107(5) \text{ \AA}$, $\beta = 93.708(4)^\circ$, $V = 2389.9(9) \text{ \AA}^3$, $Z = 4$, $D_c = 1.545 \text{ g cm}^{-3}$, $\mu = 1.086 \text{ mm}^{-1}$, $F(000) = 1136$, $2\theta_{\text{max}} = 50.00^\circ$ ($-14 \leq h \leq 11$, $-11 \leq k \leq 8$, $-23 \leq l \leq 23$). Final residuals (for 168 parameters) were $R1 = 0.0463$ for 2099 reflections with $I > 2\sigma(I)$, and $R1 = 0.0696$, $wR2 = 0.0977$, $\text{GOF} = 1.035$ for all 5878 data. Residual electron density was 0.371 and $-0.280 \text{ e \AA}^{-3}$.

CCDC reference numbers 175888–175890. See <http://www.rsc.org/suppdata/cc/b1/b111280p/> for crystallographic data in CIF or other electronic format.

- S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461.
- S. R. Batten, *CrystEngComm*, 2001, **18**.
- J. Y. Lu and A. M. Babb, *Chem. Commun.*, 2001, 821.
- B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972.
- W. Lin, O. R. Evans, R. G. Xiong and Z. Y. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13 272.
- O. R. Evans and W. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 3949.
- O. R. Evans and W. Lin, *Chem. Mater.*, 2001, **13**, 3009.
- O. R. Evans, Z. Y. Wang, R. G. Xiong, B. M. Foxman and W. Lin, *Inorg. Chem.*, 1999, **38**, 2969.
- P. Ayyappan, O. R. Evans and W. Lin, *Inorg. Chem.*, 2001, **40**, 4627.
- W. Lin, O. R. Evans and G. T. Yee, *J. Solid State Chem.*, 2000, **152**, 152.
- A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 1984.
- J. M. Bregeault and P. Herpin, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1970, **93**, 37.
- A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, 1977.
- S. C. Hawkins, R. Bishop, I. G. Dance, T. Lipari, D. C. Craig and M. L. Scudder, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1729.
- M. J. Zaworotko, *Chem. Commun.*, 2001, 1.
- V. A. Russell, C. C. Evans, W. J. Li and M. D. Ward, *Science*, 1997, **276**, 575.
- SADABS, Siemens Industrial Automation, Inc., Madison, WI, 1996.