A unique example of a 3^6 tessellated 2-D net based on a tri-nuclear zinc(II)-1,4-benzenedicarboxylate framework†

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Reaction of Zn(NO$_3$)$_2$ and 1,4-benzenedicarboxylic acid (1,4-H$_2$BDC) at 100 °C for 24 hours in a pressure tube yielded on cooling {[Zn$_3$(1,4-BDC)$_3$(DEF)$_2$]·DEF}$_\infty$ (DEF = diethylformamide) incorporating planar six-connected centres to give a unique 3^6 tessellated 2-D framework polymer.

In a recent article,[1] we simplified the analysis and interpretation of the architectures of complex metal–organic frameworks by considering their construction as being derived from combinations of linked 2-D sheets or sub-tectons. The simplest 2-D sheets are those which comprise just one kind of regular polygon and are known as regular tilings or regular tessellations[2] based upon hexagons, squares and triangles. Since three hexagons, four squares and six triangles meet at a node in a 2-D network with angles of 120°, 90° and 60°, respectively, the corresponding Schläfli topology symbols are 6^3, 4^4 and 3^6, respectively [Fig. 1(a)–(c)].[2] To form regular hexagons, squares and triangles, the nodes necessarily have 3-, 4- and 6-fold rotational symmetry, respectively. Loss of this symmetry results in alternative 2-D networks. For example, 3-connected nodes with angles of 180, 90 and 90° result in brickwall or herringbone architectures, which retain 6^3 topologies [Fig. 2(a), (b)], while those with angles of 90, 135 and 135° give rise to networks of 4^18^2 topology [Fig. 2(c)]. Similarly, 4-connected nodes with angles of 120, 60, 120 and 60° give rise to networks of 3^26^2 topology, the so-called Kagomé lattices [Fig. 2(d)] as well as rhombic grids of 4^4 topology, while 5-connected nodes with angles of 90, 60, 60, 90 and 60° form two different networks both of which comprise 3^34^2 topologies [Fig. 2(e), (f)]. In all these cases, the networks are uninodal and the edges of the polygons in any one network are of identical length. Loss of these constraints leads to networks of more complex topology.

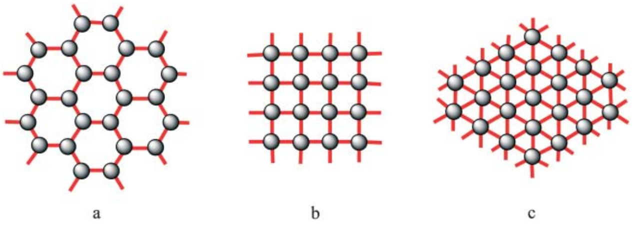
a b c

Fig. 1 2-D Nets, regular ‘tilings’ or ‘tessellations’ with (a) 6^3 (typified by {[Cu(L^1)$_{1.5}$]$^{2+}$}$_\infty$, L^1 = pyrazine[3]), (b) 4^4 (typified by [Co(OH$_2$)$_2$(L^2)$_2$]$_\infty$, L^2 = 4,4′-bipyridine,[4] [Cd(ONO$_2$)$_2$(L^2)$_2$]$_\infty$,[5] [La(O$_2$NO)$_3$(L^3)$_2$]$_\infty$, L^3 = 4,4′-bipyridine-*N*,*N*′-dioxide[6]) and (c) 3^6 topologies (illustrated by the present example).

In our earlier article,[1] we noted that although there were many examples of uninodal regularly tiled 2-D metal–organic frameworks comprising linked squares or hexagons, there were no examples comprising triangles. Few metal ions would appear capable of generating such an isolated 3^6 net, the challenge being to generate a six-connected planar metal-centred node. The uranyl [UO$_2$]$^{2+}$ and analogous cations do have six co-ordination sites located in an equatorial plane, but metal–organic frameworks containing such cations have yet to be reported. We, therefore, approached this problem by seeking to use polynuclear metal centres as potential nodes of high connectivity. We report herein

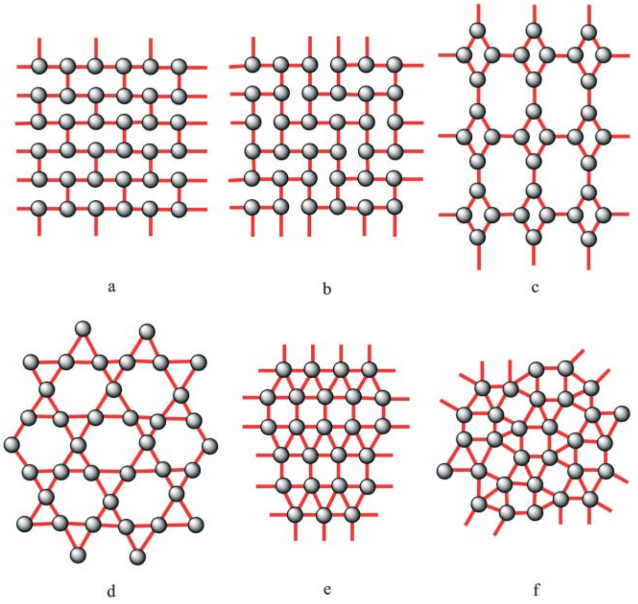
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Fig. 2 2-D Nets based on (a–c) 3-connectivity nodes with (a) brickwall 6^3 (typified by [Cd(O$_2$NO)$_2$(L^4)$_{1.5}$]$_\infty$, L^4 = 1,4-bis(pyridine-4-yl)methyl-2,3,5,6-tetrafluorobenzene),[7] (b) herringbone 6^3 (typified by [Co(O$_2$NO)$_2$(L^5)$_{1.5}$]$_\infty$, L^5 = 4,4′-azobis(pyridine)),[8] or (c) 4^18^2 topologies (typified by [Ln(O$_2$NO)$_3$(L^3)$_{1.5}$]$_\infty$, Ln = Er or Tb),[9] on (d) a 4-connectivity node with 3^26^2 topology (a so-called Kagomé lattice, typified by {[In(L^6)$_2$]$^-$}$_\infty$, L^6 = 2,5-pyridine dicarboxylate)[10] and on (e, f) 5-connectivity nodes with 3^34^2 topology of which (e) is illustrated by [La(NCS)$_3$(L^7)$_{2.5}$]$_\infty$ (L^7 = *meso*-1,2-bis(ethylsulfinyl)ethane)[11] and (f) has no reported examples.

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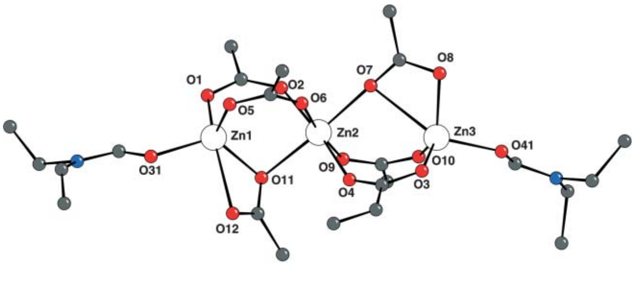
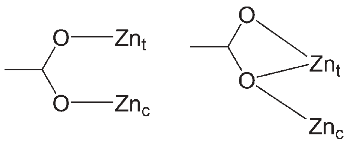


Fig. 3 Molecular structure of the trinuclear building block of **1** showing the terminal DEF molecules and the bridging carboxylate moieties. The remainder of the carboxylate anions are omitted to aid clarity (zinc, large open circles; oxygen, intermediate red circles; carbon, intermediate grey circles; nitrogen, intermediate blue circles).

the formation of $\{[Zn_3(1,4\text{-}BDC)_3(DEF)_2]\cdot DEF\}_\infty$ (1,4-BDC = 1,4-benzene dicarboxylate; DEF = diethylformamide) which shows a 3^6 tessellated structure.

Slow cooling of a reaction mixture comprising a 2 : 1 molar ratio of hydrated zinc nitrate and 1,4-benzene dicarboxylic acid dissolved in diethylformamide (DEF), previously heated to 100 °C for 24 hours in a pressure tube, yielded the hitherto unreported $\{[Zn_3(1,4\text{-}BDC)_3(DEF)_2]\cdot DEF\}_\infty$, **1**. Despite extreme susceptibility to decomposition when removed from mother liquor, the complex could be identified unambiguously by single crystal X-ray diffraction. The structure of **1** comprises stacked 3^6 tessellated, 2-D nets based on tri-nuclear zinc(II) building blocks bridged by 1,4-benzenedicarboxylate, with space within the 2-D sheets occupied by disordered solvent molecules. The structure of the tri-nuclear zinc(II) building block is shown in Fig. 3, and involves two five-co-ordinate, crystallographically independent, terminal zinc(II) centres, each of which has a co-ordinated DEF molecule, and a six-co-ordinate central zinc(II) centre. Three carboxylate moieties of separate anions link each pair of zinc centres adopting monodentate co-ordination to the central zinc(II) centre and either monodentate [Fig. 4(a)] or asymmetric chelating bidentate [Fig. 4(b)] co-ordination to the terminal zinc(II) centres to give a building block of stoichiometry $Zn_3(carboxylate)_6(DEF)_2$. The asymmetry of the chelating bidentate carboxylates is quite pronounced with one Zn–O contact in the range 1.97–2.03 Å and the other in the range 2.51–2.53 Å. The disposition of the ligands around the tri-nuclear building block is reminiscent of that in the molecular cluster of $[Zn_3(cro)_6(quin)_2]$ (Hcro = crotonic acid, quin = quinoline).[12] Similar hexagonal parallel packed sheets have been reported very recently for the anionic cadmium(II) 1,3-benzenedicarboxylate framework of $\{(Me_2NH_2)_2[Cd(1,3\text{-}BDC)_4]\}_\infty$.[13] The overall architecture of this latter species, however, differs from that of **1** in that the cadmium(II) centres form polynuclear chains which link the sheets into a 3-D matrix.



(a) (b)

Fig. 4 Co-ordination modes of the zinc(II)···carboxylate interactions (Zn_c and Zn_t represent the central and terminal zinc(II) centres, respectiively).

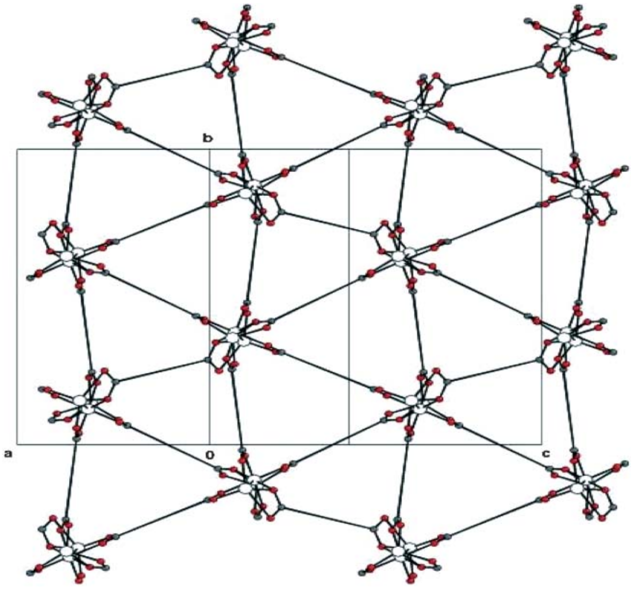


Fig. 5 Projection of the structure of **1** onto the (1 0 0) plane showing the architecture of the 3^6 tessellated 2-D sheet.

In **1**, each of the six 1,4-benzenedicarboxylate anions associated with a building block links to six separate building blocks to give the 3^6 tessellated 2-D net (Fig. 5), which lies parallel to the (1 0 0) plane. The inter building-block separations, which are best quantified by the Zn···Zn distances between central zinc(II) centres range from 9.648(2) to 11.337(2) Å and average 10.4(4) Å. The nets stack along the *a* axis with each arranged such that the co-ordinated diethylformamide molecules on the terminal zinc(II) centres of the building-blocks interdigitate with the triangular cavities of the adjacent sheets. The remaining space in the structure is occupied by disordered diethylformamide molecules.

The carboxylate moieties bound to five-co-ordinate zinc(II) are more closely held than those bound to six-co-ordinate zinc(II). For example, for carboxylates co-ordinated according to Fig. 4(a), the five-co-ordinate Zn–O contacts, which range in length from 1.917(3) to 1.962(3) Å [average 1.94(2) Å] are much shorter than those for the six-co-ordinate Zn–O interactions which range in length from 2.040(2) to 2.103(3) Å [average 2.06(3) Å]. The reason may be traced to the difference in the efficacy of the overlap of the lone pairs of the carboxylate moieties with the zinc(II) centres, which is most effective when the zinc(II) centre is in the plane of the carboxylate moiety (*i.e.*, the Zn–O–C–X torsion angle is zero) and the Zn–O–C angle is 120° (*i.e.*, the sp^2 hybridised angle predicted for the carboxylate oxygen). Thus, while the Zn–O–C–X torsion angles for the five-co-ordinate zinc(II) centre are all less than 2.69° [average 2.0(8)°] those for the six-co-ordinate zinc(II) centre differ widely ranging up to 41.31°. Similarly, while the Zn–O–C angles for the five-co-ordinate zinc(II) centre average 125(8)° those for the six-co-ordinate zinc(II) centre are considerably greater with an average of 140(5)°.

Metal–organic frameworks based on zinc(II)–carboxylate interactions are rich and varied.[14–19] Zinc(II) clusters have been observed with monocarboxylates,[12,20] while compounds containing tri-nuclear zinc(II) clusters include $\{[Zn_3(1,4\text{-}BDC)_3(MeOH)_4]\cdot 2MeOH\}_\infty$,[15] which forms a 3-D porous material, $\{[Zn_3(PTC)_3(MeOH)_4]\cdot 2MeOH\}_\infty$ (H_3PTC = *trans*-1,2,3-propenetricarboxylic acid),[7] which forms a 6^3 tessellated 2-D sheet structure, $\{(Et_3NH)_2[Zn_3O(BTC)_2(OH_2)_2(DMF)\}_\infty$ (H_3BTC = 1,3,5-benzenetricarboxylic acid)[17] and $\{[Zn_3O(HBTB)_2(OH_2)\cdot DMF\}_\infty$ (H_3BTB = benzene-1,3,5-tris(4-benzenecarboxylic acid)),[17] and $[Zn_3(cro)_6(quin)_2]$,[12] which has six carboxylates disposed around the tri-nuclear zinc(II)-containing cluster in a hexagonal planar arrangement.[17]

Although 3^6 tessellation is common in face- and hexagonal-close packed structures of many elements, it is very unusual in co-ordination polymers owing to the requirement for a six-connecting planar node with a 60° inter-contact angle. Since multi-nuclear metal-containing building blocks have led not only to this unusual 3^6 tessellated 2-D structure, but also to 2-D sheets of 4^4 topology {the $[Zn_2(DBC)_{4/2}]$ paddle wheel}[21] and 3-D matrices of $4^{12}6^3$ topology {the $[Zn_4O(DBC)_{6/2}]$ cluster},[14] we are now extending our studies to identify new multinuclear building blocks for the construction of novel frameworks with unusual architectures.†‡

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Notes and references

‡ *Crystallographic data for* **1**. $C_{39}H_{45}N_3O_{15}Zn_3$, M = 991.89, monoclinic, $C2/c$, a = 25.143(3), b = 20.821(2), c = 17.748(2) Å, β = 114.174(2), U = 8476.6(17) $Å^3$, T = 150(2) K, Z = 8, μ (Mo-$K\alpha$) = 1.75 mm^{-1}, 37735 data collected, 9656 independent reflections (R_{int} = 0.053). Final R_1 [$I > 2\sigma(I)$] = 0.0479, wR_2 [all data] = 0.1330. CCDC 278855. See http://dx.doi.org/10.1039/b509929c for crystallographic data in CIF or other electronic format.

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