

An unusual three-dimensional chiral threefold polycatenating network self-assembled from inclined two-dimensional (4,4) layer motifs

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Received 1 March 2010

Accepted 1 April 2010

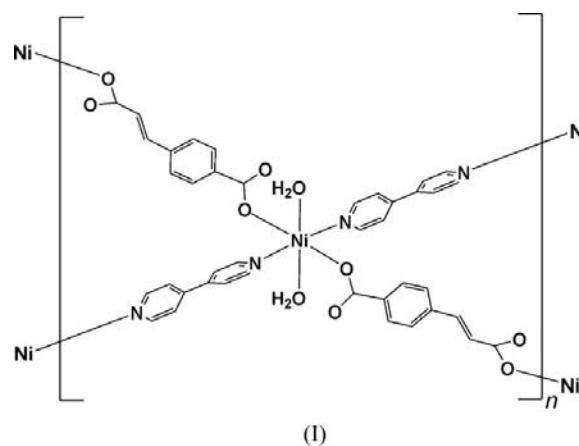
Online 29 April 2010

In the coordination compound poly[diaqua(μ_2 -4,4'-bipyridine)(μ_2 -4-carboxylatocinnamato)nickel(II)], $[\text{Ni}(\text{C}_{10}\text{H}_6\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]_n$, both the 4-carboxylatocinnamate and 4,4'-bipyridine (4,4'-bpy) ligands act as bidentate bridges, connecting the Ni^{II} centres in an octahedral coordination geometry into a two-dimensional (4,4) layer. Each layer polycatenates two other identical layers, thus giving a rare 2D \rightarrow 3D polycatenating network (2D and 3D are two- and three-dimensional, respectively), with a mutually parallel arrangement of the layers. The chiral 4,4'-bpy ligands link the Ni^{II} centres into chiral chains, thus introducing chirality into the layer and the resulting 3D network.

Comment

The construction of metal-organic assemblies has attracted increasing attention in recent years, not only for their potential applications but also due to their fascinating architectures and topologies (Ferey *et al.*, 2005; Murray *et al.*, 2009). Examples of some of the interesting networks of entanglement systems include polycatenation, polythreading, polyknotting and Borromean links (Batten & Robson, 1998; Batten, 2001; Carlucci, Ciani & Proserpio, 2003). Of particular interest to us is the fact that the entanglement of lower-dimensional polymeric structures can generate a structure of overall higher dimensionality, which has been classified as polycatenation. That is, the whole catenated array has a higher dimensionality than the component motifs, such as 1D \rightarrow 2D, 1D \rightarrow 3D and 2D \rightarrow 3D (1D, 2D and 3D are one-, two- and three-dimensional, respectively). A dimensionality increase from 2D layers to an overall 3D entanglement can occur for systems interpenetrating in a parallel or inclined fashion. Although the first 2D \rightarrow 3D parallel interpenetration was reported over ten years ago (Liu & Tilley, 1997), such compounds are still relatively rare (Blatov *et al.*, 2004; Baburin *et al.*, 2005; Guo *et al.*, 2009).

The (4,4) and (6,3) nets are the most common 2D topologies, which are inclined to interpenetrate when large four- or six-membered rings are formed, or when the network shows undulating features, or both. For the former case, three possible arrangements of interpenetrating sheets have been observed in the examples reported to date, *viz.* parallel-parallel (p-p), parallel-diagonal (p-d) and diagonal-diagonal (d-d), depending on how the networks orient and penetrate through each other (Zaworotko, 2001; Herbstein, 2001; Biradha *et al.*, 2000). The majority of them, however, consist of two identical sets of 2D parallel layers, spanning two different stacking directions. Only a limited number of networks have been found that contain more than two sets of differently oriented layers (Kondo *et al.*, 2000; Carlucci, Ciani, Proserpio & Rizzato, 2003; Chen *et al.*, 2006; Zhuang *et al.*, 2007) since this possibility was first predicted (Batten & Robson, 1998).



Meanwhile, chiral units and homochiral interactions between them would be crucial to the synthesis of chiral interpenetrating structures through spontaneous resolution upon crystallization without any chiral auxiliary (Gao *et al.*, 2004; Bai *et al.*, 2005). 4,4'-Bipyridine (4,4'-bpy), which only possesses the ideal achiral geometry of D_{2h} symmetry without any twist between the two pyridyl rings, would easily become chiral if there were any twist in the molecule. This kind of ligand is a potential source of chiral units which may be induced into a chiral configuration by coordination bonds or hydrogen bonds (Cotton *et al.*, 2003; Mukherjee *et al.*, 2004). We report here the title coordination compound, $[\text{Ni}(\text{acc})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_2]_n$ (H_2acc is 4-carboxycinnamic acid), (I), which features an unusual chiral 3D threefold polycatenating network self-assembled from inclined interpenetration of 2D (4,4) layer motifs.

Compound (I) crystallizes in the noncentrosymmetric hexagonal space group $P3_2$, and the asymmetric unit is composed of one Ni^{II} centre, one acc dianion, one 4,4'-bpy molecule and two coordinated water molecules (Fig. 1). The Ni^{II} centre adopts an octahedral coordination geometry, with two carboxylate O atoms from different acc dianions and two N atoms from two 4,4'-bpy ligands in the equatorial plane, and two aqua O atoms occupying the axial positions. The acc dianion is significantly disordered (see below) and adopts a bis(monodentate) bridging mode, linking two Ni^{II} centres. The

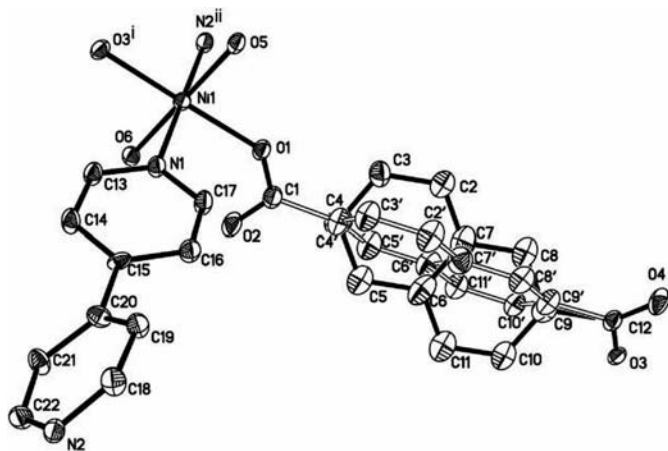


Figure 1
The local coordination environment for the Ni^{II} centre in (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity. The disordered orientations of the acc ligand are shown as primed and unprimed atoms and with open and filled bonds, respectively. [Symmetry codes: (i) $x, y, z + 1$; (ii) $x + 1, y, z$.]

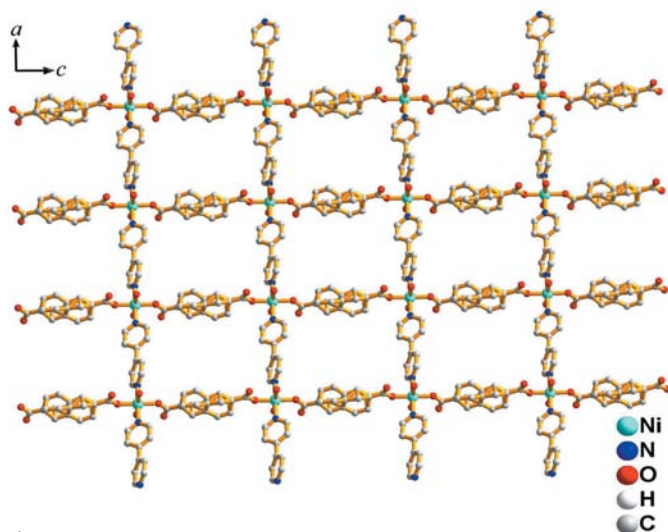
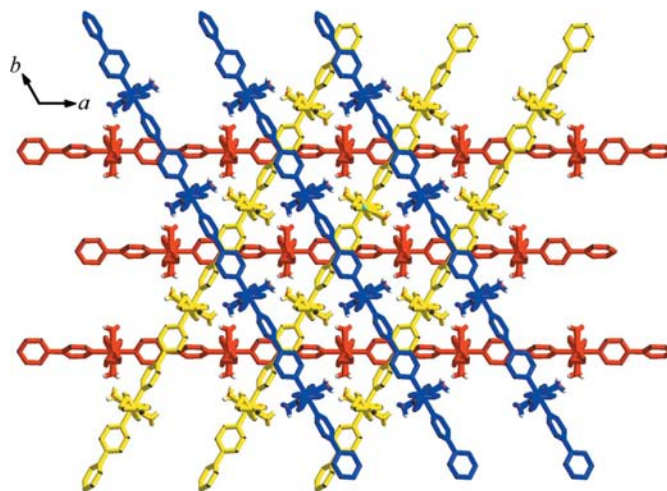


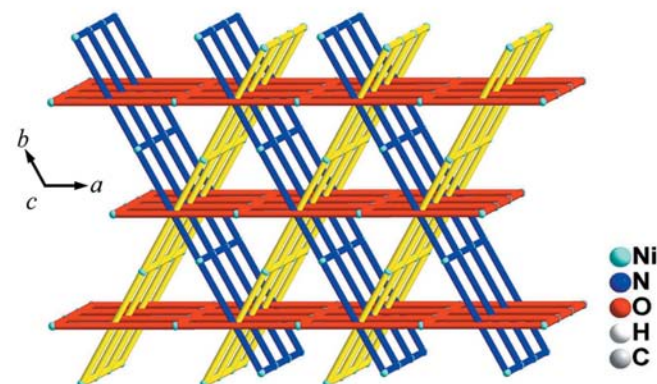
Figure 2
The 2D grid of (I) in the ac plane, constructed from acc dianions and with 4,4'-bpy ligands connecting the Ni^{II} ions.

Ni^{II} centres are linked by acc dianions and 4,4'-bpy ligands into a 2D grid in the ac plane (Fig. 2), with dimensions of $13.495(6) \times 11.261(2)$ Å based on the separation of the metal ions.

As expected, the large dimensions of these 2D grids allow them to interpenetrate in an extensive and unusual fashion (Fig. 3a). Each 2D grid interpenetrates two adjacent grids, and these three different sets are parallel to the crystallographic c axis, displaying relative rotations about this axis of 120° as required by symmetry. This network is highly unusual in that the three stacking sheets occur along three coplanar directions, and the interlocking mode can be described as parallel-parallel-parallel (p-p-p) with the same 'density of catenation' (2/2/2) (Carlucci, Ciani, Proserpio & Rizzato, 2003). Each grid is surrounded by four other grids to form triangular interstices



(a)

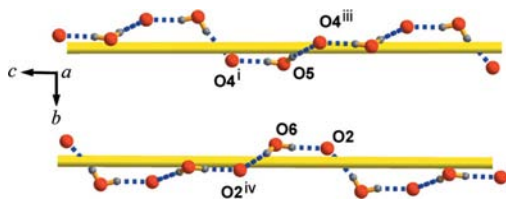


(b)

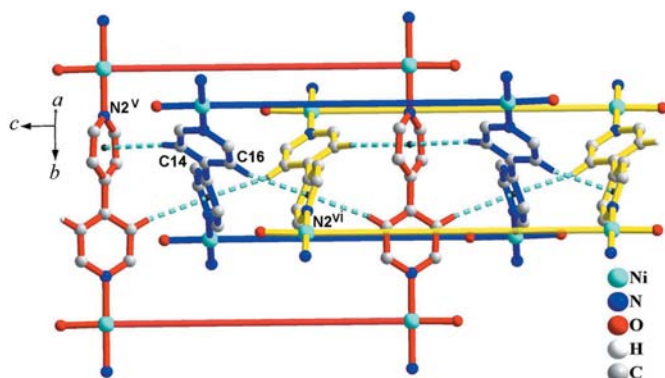
Figure 3
(a) A view of the 3D structure of (I) along the c axis. (b) A schematic representation of the modes of inclined interpenetration by complementary (4,4) networks.

(Fig. 3b), in which the coordinated water molecules (O5 and O6) form O—H...O hydrogen bonds with the uncoordinated carboxylate O atoms (O4 and O2, respectively), resulting in a right-handed helical chain (Fig. 4 and Table 2). These weak interactions may play a role in directing the interpenetration.

To the best of our knowledge, only a few compounds are known to contain three sets of (4,4) nets. The first two, *viz.* [Pt(HL)₂L₂] \cdot 2H₂O (HL is isonicotinic acid) and [Fe(bpb)₂(NCS)₂] \cdot 0.5MeOH [bpb is 1,4-bis(4-pyridyl)butadiyne], are both 3D networks containing three sets of (4,4) layers stacked in three 'perpendicular' directions (Aakeroy *et al.*, 1999; Moliner *et al.*, 2000). Structures with three sets in coplanar directions, however, were only reported very recently, namely [Ni(cpoa)(4,4'-bpy)(H₂O)₂] [H₂cpoa is (4-carboxyphenoxy)acetic acid; Chen *et al.*, 2006], [Ni(L)(4,4'-bpy)(H₂O)₂] (H₂L is *trans,trans*-muconic acid; Zhuang *et al.*, 2007) and [Ni₆(bpe)₁₀(H₂O)₁₆](SO₄)₆ \cdot x H₂O [bpe is bis(4-pyridyl)ethane; Carlucci, Ciani, Proserpio & Rizzato, 2003]. The first two examples are very similar to (I), with the same three sets


Figure 4

The left-handed hydrogen-bonded helical chains formed between the coordinated water molecules and the uncoordinated carboxylate O atoms within the triangular interstices. The helical axes are represented by the long bars. [Symmetry codes: (i) $x, y, z + 1$; (iii) $-y + 1, x - y, z + \frac{2}{3}$; (iv) $-x + y + 1, -x + 2, z + \frac{1}{3}$.]


Figure 5

Weak C—H... π interactions between adjacent two-dimensional layers. For clarity, the acc dianions are simplified into long rods connecting the metal centres. The centroids (C_g) of the pyridyl rings of 4,4'-bpy are represented by black dots. [Symmetry codes: (v) $-x + y, -x + 1, z + \frac{1}{3}$; (vi) $-y + 1, x - y + 1, z - \frac{1}{3}$.]

interpenetrating each other, while the third is different in that one rectangular net and two sets of square nets interpenetrate in inclined mode with a density of catenation of (2/4/4). The compound we report thus represents one of the very few examples of a 2D \rightarrow 3D polycatenating framework generated by inclined (4,4) nets.

Another fascinating feature of the title compound is the introduction of chirality into the structure by spontaneous resolution upon crystallization. The two pyridine rings of 4,4'-bpy are twisted with a dihedral angle of 44.6 (5) $^\circ$, nearly twice the twist seen in similar structures (Chen *et al.*, 2006). The 4,4'-bpy ligand thus introduces chirality into the Ni^{II}-4,4'-bpy chains, the 2D homochiral sheets and finally the 3D framework. Interactions between the 4,4'-bpy molecules of the different nets contribute to reinforcement of the 3D framework. Two C—H groups (C14—H14 and C16—H16) in one pyridyl ring of the 4,4'-bpy in a given sheet have C—H... π interactions with the centroid C_g of the other pyridyl ring of a neighbouring sheet containing atom N2 (Fig. 5). The C... C_g distances and the C—H... C_g angle are in the ranges 3.76 (1)–3.77 (1) Å and 164.2 (7)–166.2 (7) $^\circ$, respectively.

Experimental

A mixture of NiCl₂·6H₂O (0.025 g, 0.1 mmol), H₂acc (0.020 g, 0.1 mmol), 4,4'-bpy (0.017 g, 0.1 mmol), dimethylformamide (5 ml)

and H₂O (5 ml) was placed in a Teflon reactor and heated at 393 K for 24 h. After cooling to room temperature, green crystals of (I) were obtained in 45% yield based on H₂acc. Elemental analysis for C₂₀H₁₈N₂NiO₆: C 35.09, H 2.63, N 4.09%; found: C 35.18, H 2.70, N 4.02%. FT-IR (KBr pellet, cm⁻¹): 3407 (s), 1630 (s), 1577 (s), 1386 (w), 1298 (w), 1218 (w), 1113 (w), 1050 (w), 1004 (w), 931 (w), 898 (w), 704 (w), 638 (w), 544 (w), 516 (w).

Crystal data

[Ni(C₁₀H₆O₄)(C₁₀H₈N₂)(H₂O)₂]
 $M_r = 441.07$
 Hexagonal, $P3_2$
 $a = 11.261$ (2) Å
 $c = 13.495$ (6) Å
 $V = 1482.0$ (8) Å³

$Z = 3$
 Mo $K\alpha$ radiation
 $\mu = 1.02$ mm⁻¹
 $T = 298$ K
 $0.32 \times 0.30 \times 0.26$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.736$, $T_{\max} = 0.777$

7628 measured reflections
 3429 independent reflections
 2458 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.211$
 $S = 1.06$
 3429 reflections
 324 parameters
 937 restraints

H-atom parameters constrained
 $\Delta\rho_{\max} = 1.02$ e Å⁻³
 $\Delta\rho_{\min} = -0.65$ e Å⁻³
 Absolute structure: Flack (1983), with 1740 Friedel pairs
 Flack parameter: 0.01 (4)

Table 1

Selected geometric parameters (Å, $^\circ$).

Ni1—O3 ⁱ	2.009 (10)	Ni1—O6	2.096 (6)
Ni1—O1	2.011 (9)	Ni1—N2 ⁱⁱ	2.103 (7)
Ni1—O5	2.091 (6)	Ni1—N1	2.107 (7)
O3 ⁱ —Ni1—O5	92.5 (3)	O5—Ni1—N2 ⁱⁱ	90.1 (3)
O1—Ni1—O5	87.4 (3)	O6—Ni1—N2 ⁱⁱ	89.9 (3)
O3 ⁱ —Ni1—O6	87.6 (2)	O3 ⁱ —Ni1—N1	91.1 (3)
O1—Ni1—O6	92.5 (3)	O1—Ni1—N1	90.9 (3)
O5—Ni1—O6	179.9 (4)	O5—Ni1—N1	90.1 (3)
O1—Ni1—N2 ⁱⁱ	89.0 (3)		

Symmetry codes: (i) $x, y, z + 1$; (ii) $x + 1, y, z$.

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5C...O4 ⁱ	0.85	1.84	2.681 (10)	168
O5—H5D...O4 ⁱⁱⁱ	0.85	2.04	2.873 (9)	169
O6—H6D...O2 ^{iv}	0.85	2.03	2.871 (9)	168
O6—H6C...O2	0.85	1.84	2.679 (10)	168

Symmetry codes: (i) $x, y, z + 1$; (iii) $-y + 1, x - y, z + \frac{2}{3}$; (iv) $-x + y + 1, -x + 2, z + \frac{1}{3}$.

All C-bound H atoms were placed geometrically and treated as riding on their parent atoms, with C—H = 0.93 (pyridine and arene) or 0.97 Å (methylene) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Water H atoms were located in a Fourier map and constrained to ride on their parent atoms, with O—H = 0.85 Å, H—O—H = 109 $^\circ$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

The acc dianionic ligand is disordered both rotationally, about the axis that includes the carboxylate C—C bonds, and lengthwise, having the arene ring connected to either atom C1 or C12. That is, when the arene ring is connected to atom C1, the bond between atoms C8 and C9 represents the vinyl group, while when the arene ring is connected to atom C12, the vinyl group should be assigned to the bond between atoms C4 and C5. The disordered arene rings and C=C bonds were refined using a rigid group model, where the atoms were fitted to two orientations of an ideal naphthalene moiety which were allowed to translate and rotate (AFIX 116 instruction in *SHELXL97*; Sheldrick, 2008). The first group, including atoms C4–C9, possesses the same occupancy factors, which were all distributed over two positions (unprimed and primed) with refined site occupancies of 0.56 (1) and 0.44 (1) related to the rotational disorder about the carboxylate C—C bonds. Atoms C2, C3, C10 and C11 assigned to the second group were also distributed over two positions, and they were refined with site occupancies of 0.279 (6) and 0.221 (6) due to the lengthwise disorder that flips the entire ligand. H atoms were assigned site occupancies consistent with the parent C atoms. Similarity restraints (SIMU in *SHELXL97*) were applied to the displacement parameters of the atoms in the disordered region. The disorder model still leaves several residual electron-density peaks in this region of the structure, but further attempts to model the disorder were unfruitful.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Version 3.0; Brandenburg, 2004); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge the National Natural Science Foundation of China (grant No. 20801025) and the Taishan Scholar Fund for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3241). Services for accessing these data are described at the back of the journal.

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