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Poly[bis(2,2′-bipyridine-κ^2N,N')-bis(μ_6-2,4,6-trimethylbenzene-1,3,5-tricarboxylato)tricadmium(II)], a two-dimensional ‘Kagomé dual’ (kgd) sheet structure

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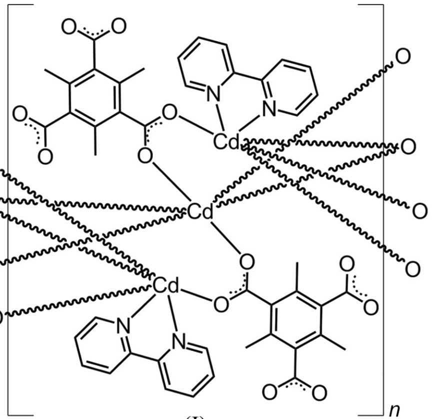
The title metal–organic framework, $[\mathrm{Cd_3(C_{12}H_9O_6)_2(C_{10}H_8N_2)_2}]_n$, has been synthesized by a solvothermal reaction. The $\mathrm{Cd^{II}}$ ions are located in $\mathrm{CdO_4N_2}$ and $\mathrm{CdO_6}$ six-coordinated environments, with the latter $\mathrm{Cd^{II}}$ ion lying on an inversion centre. The 2,4,6-trimethylbenzene-1,3,5-tricarboxylate ligand (TMBTC) connects the $\mathrm{Cd^{II}}$ ions to form a two-dimensional sheet incorporating hourglass-like $[\mathrm{Cd_3(COO)_6}]$ secondary building units (SBUs). Topologically, taking the TMBTC ligand and the $[\mathrm{Cd_3(COO)_6}]$ SBU as 3- and 6-connected nodes, respectively, the overall two-dimensional sheet can be simplified to a rare (3,6)-connected 2-nodal kgd (Kagomé dual) net with a short Schläfli vertex notation of $\{4^3\}_2\{4^6.6^6.8^3\}$, which further stacks into a three-dimensional supramolecular framework through π–π stacking interactions.

Comment

Recently, the design and synthesis of metal–organic frameworks (MOFs) have attracted much attention due to their interesting topologies and potential applications in fields such as gas adsorption, nonlinear optics, magnetism, molecular recognition (Evans & Lin, 2002; Chen *et al.*, 2010; Leong & Vittal, 2011; Sun *et al.*, 2011). The construction of novel carboxylate-based MOFs with desired topologies is still a huge challenge since many factors, such as the geometries of the ligand, metal ion and solvent, influence the structure of the resulting MOF (Sun *et al.*, 2010). The widely used carboxylic acids, including aliphatic and aromatic carboxylic acids, often participate in coordination with transition metals, rare earth metal ions or mixed metal ions, exhibiting diverse coordination modes such as monodentate bridging, bidentate chelating or bridging (Ma *et al.*, 2008; Zhang *et al.*, 2008). In these carboxylate-based MOFs, the carboxyl groups and central benzene rings are frequently almost coplanar, which is one of the most important factors in determining the topology of the final structure. Despite the fact that MOFs constructed from 1,3,5-benzenetricarboxylic acid ($\mathrm{H_3BTC}$) have been widely reported, to the best of our knowledge only one MOF based on $\mathrm{H_3TMBTC}$ (2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid) has been documented to date (He *et al.*, 2010). The introduction of methyl groups on the C atoms between the carboxyl groups may generate novel MOFs different from those constructed from the unsubstituted BTC ligand. Based on the above-mentioned points and our previous work (Sun *et al.*, 2009; Dai *et al.*, 2008; Zhao *et al.*, 2009), we describe here the structure of the title compound, (I), obtained using 2,4,6-trimethylbenzene-1,3,5-tricarboxylate (TMBTC) and 2,2′-bipyridine (bpy) as mixed ligands, and $\mathrm{Cd^{II}}$ ions. The components build an infinite two-dimensional sheet incorporating hourglass-like $[\mathrm{Cd_3(COO)_6}]$ secondary building units (SBUs), which can be simplified to a (3,6)-connected 2-nodal net with the rare kgd (Kagomé dual) topology (O'Keeffe *et al.*, 2007).



(I)

The asymmetric unit of (I) contains two crystallographically independent $\mathrm{Cd^{II}}$ centres, one TMBTC ligand and one bpy ligand. As shown in Fig. 1, atom Cd1 is six-coordinated by two

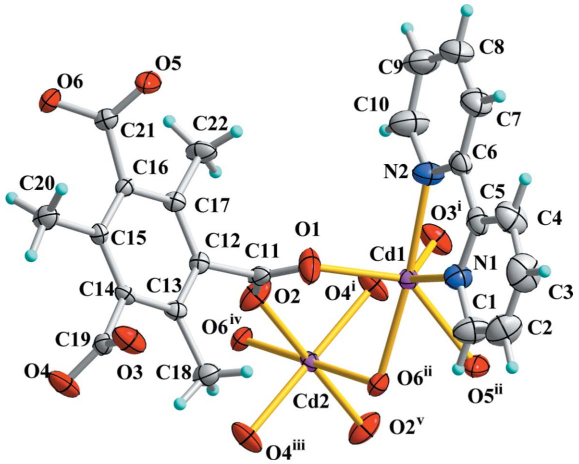


Figure 1
The structure of (I), showing the atom-numbering scheme and the coordination environment around the $\mathrm{Cd^{II}}$ centres. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x, y-1, z$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, -y+2, -z+1$; (v) $-x+1, -y+1, -z+1$.]

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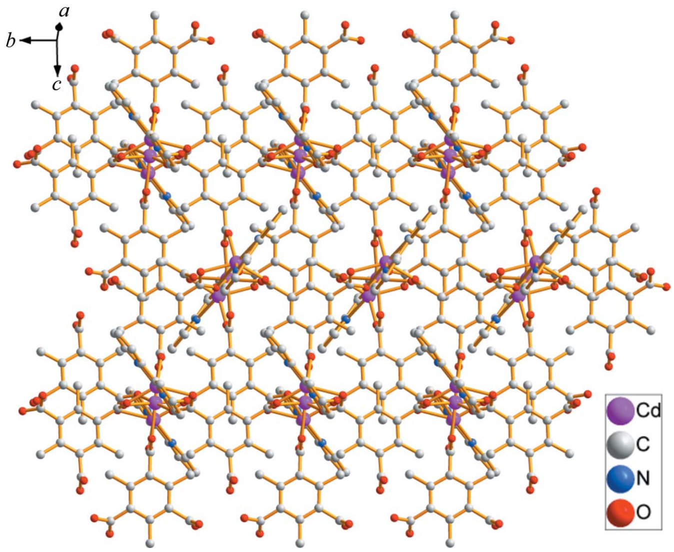

Figure 2
A ball-and-stick perspective view of the two-dimensional sheet of (I). H atoms have been omitted for clarity.

N atoms of the same bipy ligand and four carboxylate O atoms from three different TMBTC ligands, giving a distorted octahedral coordination geometry. Atom Cd2, located on a crystallographic inversion centre, has a CdO_6 octahedral environment surrounded by six carboxylate groups from six different TMBTC ligands. The Cd—N bond lengths are identical within experimental error and the average Cd—O distance is 2.281 (2) Å (Table 1), comparable with values reported for Cd-based MOFs (Liu *et al.*, 2008; Zhang *et al.*, 2003; Zhou *et al.*, 2003). Of the three carboxylate groups of the TMBTC ligand, one adopts a bidentate–chelating/bridging mode and the other two adopt bidentate-bridging modes. The three Cd^{II} ions are bridged by six carboxylate groups to form a trinuclear hourglass-like $[Cd_3(COO)_6]$ SBU with a $Cd\cdots Cd$ contact distance of 3.7205 (12) Å. Because of the steric hindrance between the methyl and carboxylate groups, the three carboxylate groups of the TMBTC ligand are not coplanar with the central benzene ring, with dihedral angles of 88.2 (4), 83.9 (2) and 63.1 (2)°, much larger than those found in MOFs constructed with BTC (Chui *et al.*, 1999).

The hourglass-like $[Cd_3(COO)_6]$ SBUs are joined by TMBTC ligands to form an infinite two-dimensional sheet (Fig. 2). The bpy ligand acts as a terminal group to occupy the remaining coordination sites, which prevents the structure from attaining higher dimensionalities. Adjacent two-dimensional sheets are interdigitated with each other to form a three-dimensional supramolecular framework (Fig. 3). This framework is reinforced by a weak intersheet π–π interaction (Janiak, 2000) between the bpy ligands, with a $Cg1\cdots Cg2^{vi}$ separation of 3.721 (3) Å [$Cg1$ and $Cg2$ are the centroids of the N1/C1–C5 and N2/C6–C10 rings, respectively; symmetry code: (vi) $-x + 2, -y + 1, -z + 1$], and by a $C—H\cdots\pi$ interaction [$C3—H3\cdots Cg3^{vii} = 143°$, $H3\cdots Cg3^{vii} = 2.63$ Å and $C3\cdots Cg3^{vii} = 3.418$ (5) Å; $Cg3$ is the centroid of the C12–C17 ring; symmetry code: (vii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$].

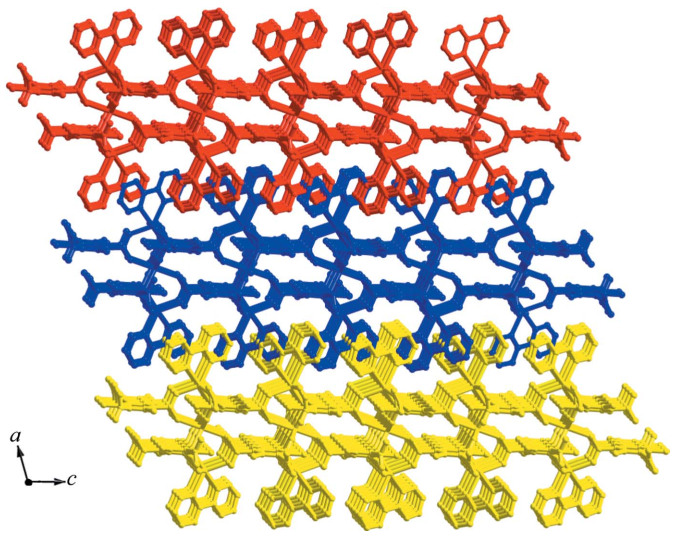

Figure 3
A perspective view of the three-dimensional supramolecular network of (I), constructed from the interdigitation of adjacent two-dimensional sheets, highlighted by different shading. H atoms have been omitted for clarity.

An appealing structural feature of (I) is that the two-dimensional sheet can be seen as a rare kgd network by simplifying the TMBTC ligand as a 3-connecting node and the trinuclear hourglass-like $[Cd_3(COO)_6]$ SBU as a 6-connecting

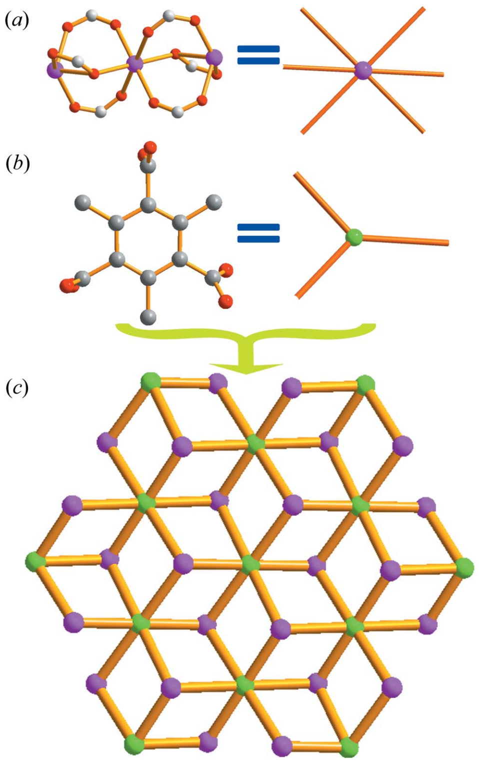

Figure 4
(*a*) The trinuclear hourglass-like $[Cd_3(COO)_6]$ SBU shown as a 6-connecting node. (*b*) The TMBTC ligand shown as a 3-connecting node. (*c*) A schematic representation of the formation of the two-dimensional kgd net of (I).

node (Fig. 4*a* and 4*b*). Therefore, the whole two-dimensional sheet can be represented as a (3,6)-connected 2-nodal net with a kgd topology (Fig. 4*c*). The ratio of 3-connecting nodes (vertex symbol 4^3) and 6-connecting nodes (vertex symbol $4^6.6^6.8^3$) in this net is 2:1. Therefore, the short Schläfli vertex notation of the net can be represented as $\{4^3\}_2\{4^6.6^6.8^3\}$, as indicated by the *TOPOS* software (Blatov, 2006). To the best of our knowledge, regular (4,4), (6,3) and (3,6) nets are the three most common topologies observed in two-dimensional coordination networks (Batten & Robson, 1998). The offset overlap of two common (6,3) nets connected together by Cd^{II} ions thus yields a kgd net. The TMBTC ligands in this kgd net are non-coplanar and are arranged alternately up and down to form a concavo–convex kgd net. Despite the fact that a kgd net can be constructed theoretically by employing a six-coordinate metal centre and a trigonal tridentate ligand, it is hard to achieve in practice due to the requirement for an approximately planar 6-connecting node, which illustrates why there are few cases known, even though there are various known coordination polymers based on trigonal ligands (Zheng *et al.*, 2008).

Experimental

2,4,6-Trimethylbenzene-1,3,5-tricarboxylic acid (H_3TMBTC) was synthesized according to the method of Zimmerman and co-workers with modifications (Kolotuchin *et al.*, 1999). The product was recrystallized from acetonitrile (yield 90%) as white needles. ^{1}H NMR (300 MHz, d_6-DMSO): δ 2.33 (*s*, 9H, CH_3), 13.51 (*s*, 3H, COOH). A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (20 mg, 0.06 mmol), H_3TMBTC (10 mg, 0.05 mmol) and bpy (10 mg, 0.06 mmol) was suspended in a mixed solvent of H_2O (8 ml) and EtOH (8 ml), and heated in a Teflon-lined steel bomb at 413 K for 3 d. Colourless crystals of (I) (14 mg) were collected, washed with water and dried in air (yield 51%, based on Cd)

Crystal data

$[Cd_3(C_{12}H_9O_6)_2(C_{10}H_8N_2)_2]$
$M_r = 1147.95$
Monoclinic, $P2_1/c$
$a = 14.178$ (4) Å
$b = 9.481$ (3) Å
$c = 15.901$ (4) Å
$\beta = 105.772$ (4)°
$V = 2056.9$ (10) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.61$ mm^{-1}
$T = 298$ K
0.10 × 0.08 × 0.06 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.856$, $T_{\max} = 0.910$
10768 measured reflections
4037 independent reflections
3371 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.068$
$S = 1.03$
4037 reflections
289 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

All H atoms were generated geometrically and allowed to ride on their parent atoms in the riding-model approximation, with aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) for aromatic H atoms and $1.5U_{\rm eq}$(C) otherwise.

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.184 (2)	Cd1—O6^{ii}	2.449 (2)
Cd1—O3^{i}	2.208 (2)	Cd2—O2	2.241 (2)
Cd1—O5^{ii}	2.343 (2)	Cd2—O4^{iii}	2.277 (2)
Cd1—N2	2.382 (3)	Cd2—O6^{iv}	2.304 (2)
Cd1—N1	2.383 (3)		
O1—Cd1—O3^{i}	116.07 (10)	O3^{i}—Cd1—O6^{ii}	96.77 (9)
O1—Cd1—O5^{ii}	135.11 (10)	O5^{ii}—Cd1—O6^{ii}	54.36 (8)
O3^{i}—Cd1—O5^{ii}	93.13 (10)	N2—Cd1—O6^{ii}	174.77 (9)
O1—Cd1—N2	88.34 (10)	N1—Cd1—O6^{ii}	115.40 (9)
O3^{i}—Cd1—N2	82.60 (10)	O2—Cd2—O4^{i}	95.41 (9)
O5^{ii}—Cd1—N2	130.81 (10)	O2^{v}—Cd2—O4^{i}	84.59 (9)
O1—Cd1—N1	100.40 (10)	O2^{v}—Cd2—O4^{iii}	95.41 (9)
O3^{i}—Cd1—N1	132.35 (10)	O2—Cd2—O6^{iv}	89.30 (8)
O5^{ii}—Cd1—N1	80.04 (9)	O2^{v}—Cd2—O6^{iv}	90.70 (8)
N2—Cd1—N1	68.25 (10)	O4^{i}—Cd2—O6^{iv}	85.31 (9)
O1—Cd1—O6^{ii}	87.28 (9)	O4^{iii}—Cd2—O6^{iv}	94.69 (9)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3421). Services for accessing these data are described at the back of the journal.

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