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A novel three-dimensional Cd^{II} metal–organic framework based on [Cd$_6$(malonate)$_6$] metallomacrocycles with zeolite SOD (sodalite) topology: poly[ammine-μ_3-malonato-cadmium(II)]

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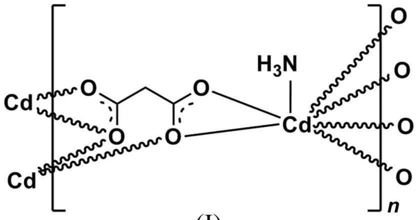
A novel Cd^{II} metal–organic framework, [Cd(C$_3$H$_2$O$_4$)(NH$_3$)]$_n$, was synthesized by liquid diffusion conducted in the presence of ammonia. The Cd^{II} atom has seven-coordinate O$_6$N pentagonal–bipyramidal geometry. Six Cd^{II} centers are joined by six malonate ligands to form an S_6-symmetric [Cd$_6$(malonate)$_6$] metallomacrocycle, which is further extended through a side-on chelating malonate ligand to form a three-dimensional network. Topologically, each Cd^{II} center is connected to four others to yield an infinite three-periodic four-coordinated SOD (sodalite) network with point symbol {$4^2 \cdot 6^4$}. The overall network structure in the crystal is maintained and stabilized by the presence of N—H···O hydrogen bonds.

Comment

Numerous functional crystalline solids based on coordination bonds, hydrogen bonding and other secondary interactions have been designed and synthesized in the field of crystal engineering (Evans & Lin, 2002; Chen *et al.*, 2010; Leong & Vittal, 2011; Sun *et al.*, 2011). There still remain many challenges to overcome in reaching the goal of tailor-made solid-state materials owing to the fact that structure prediction and synthetic control are often subverted by a host of factors, including weak noncovalent interactions, ligand geometry, the nature of the metal ion, pH value, temperature and solvent (Sun *et al.*, 2010). Malonate has been used widely in the preparation of transition metal and rare earth metal–organic frameworks (MOFs), exhibiting diverse coordination modes such as monodentate bridging or bidentate chelating or bridging (Li *et al.*, 1997; Ruiz-Pérez *et al.*, 2000; Shen *et al.*, 2000; Zhang *et al.*, 2000). Although diverse cadmium malonate MOFs with one and two aqua ligands have been documented (Post & Trotter, 1974; Chung *et al.*, 1995), cadmium malonate MOFs with NH$_3$ have not previously been observed, possibly because of the comparatively weak Cd—N coordination bond and the volatile nature of NH$_3$. Based on our previous work (Sun *et al.*, 2009; Dai *et al.*, 2008) on transition metal polycarboxylate MOFs with or without auxiliary ligands, we undertook a preparation with malonic acid and 1,3,5-tris(1*H*-imidazol-1-yl)benzene as mixed ligands and surprisingly obtained the title three-dimensional MOF based on an S_6-symmetric [Cd$_6$(malonate)$_6$] metallomacrocycle. The description of the three-dimensional network can be simplified to that of a four-connected uninodal net with a zeolite SOD (sodalite) topology.



(I)

The asymmetric unit of poly[ammine-μ_3-malonato-cadmium(II)], (I), contains one crystallographically independent Cd^{II} center, one malonate ligand and one coordinated NH$_3$ molecule. As shown in Fig. 1, the Cd1 atom is seven-coordinated by six O atoms of three different symmetry-related malonate ligands and one terminal NH$_3$ molecule, with pentagonal–bipyramidal geometry. The Cd1—N1(ammonia) bond length is 2.2577 (19) Å and the Cd1—O bond lengths vary from 2.2856 (14) for the axial O1^{i} atom to 2.5841 (14) Å for Cd1—O1, giving an average Cd—O bond length of

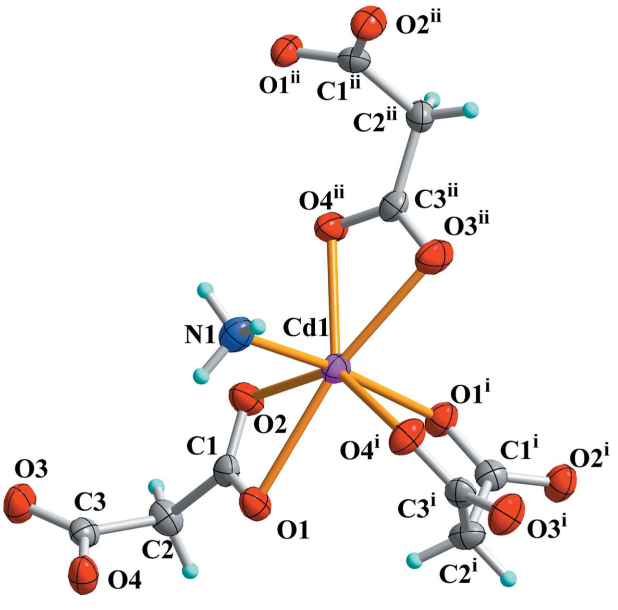
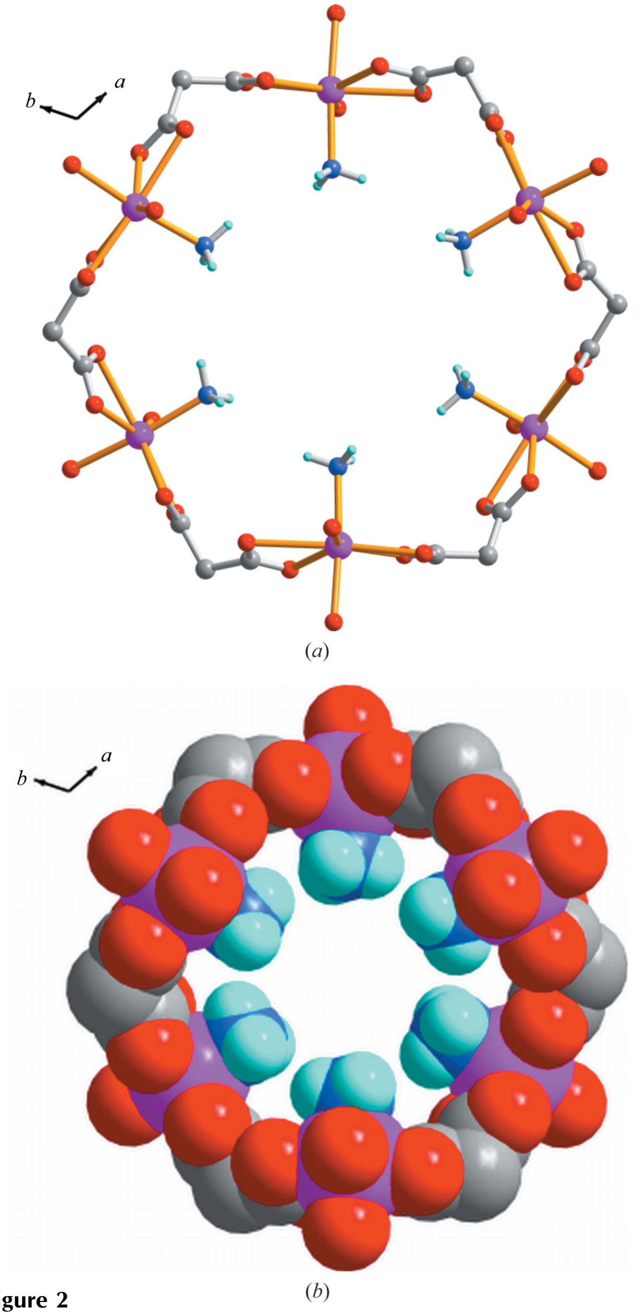


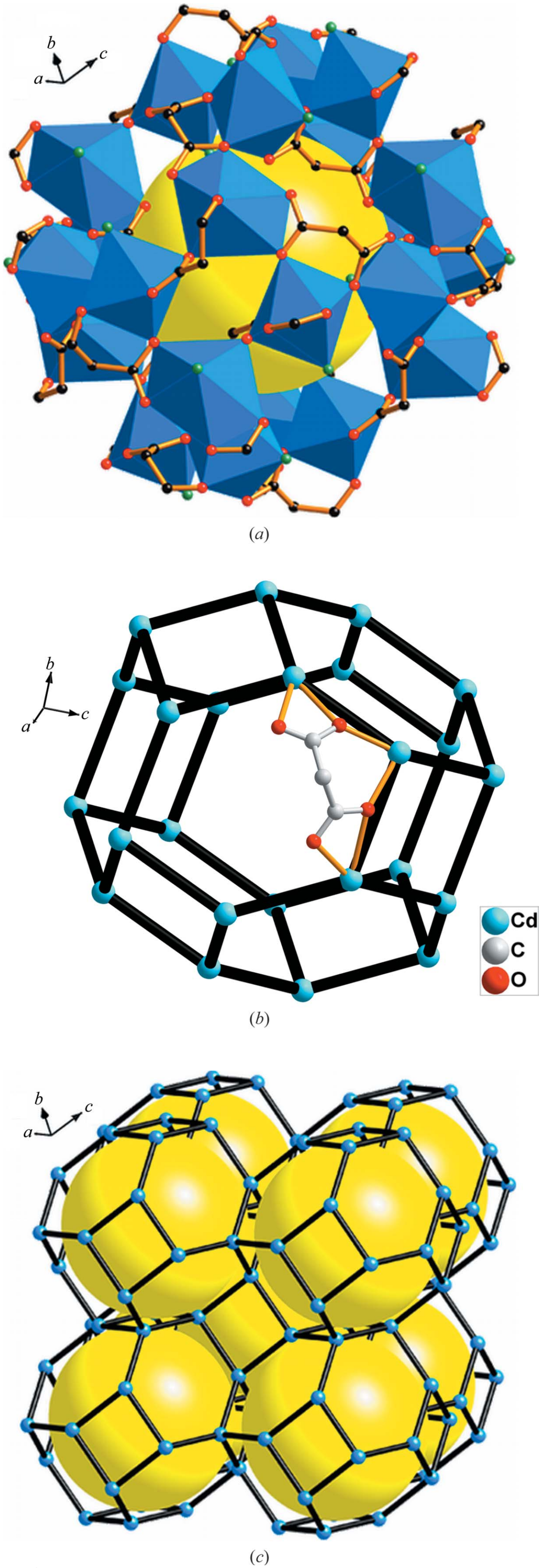
Figure 1
The coordination environment around the Cd^{II} center in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (ii) $x - y + 1, x, -z$.]



(*a*)

(*b*)

Figure 2
(*a*) Ball-and-stick and (*b*) space-filling views of the S_6-symmetric [Cd_6(malonate)$_6$] metallomacrocycle. (Color key in the electronic version of the paper: Cd purple, C gray, O red, N blue and H cyan.)



(*a*)

(*b*)

(*c*)

Figure 3
(*a*) A schematic representation of the truncated octahedron (CdO_6N polyhedra are shaded in blue in the electronic version of the paper), (*b*) a simplified truncated octahedron and (*c*) the topological SOD net.

2.3977 (14) Å [Table 1; symmetry code: (i) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$]. These are within the ranges found for similar Cd-based MOFs (Liu *et al.*, 2008). Each malonate ligand is involved in chelating three symmetry-related Cd^{II} ions, and each Cd^{II} ion is coordinated by three malonate ligands, two of which chelate two symmetry-related Cd^{II} ions through O1/O2 and O3/O4, forming four-membered rings with O—Cd1—O bite angles of 52.71 (5) and 53.12 (5)°, respectively. The third malonate unit ligates the Cd^{II} cation in a side-on fashion to form a distorted boat-like Cd1—O1^{i}—C1^{i}—C2^{i}—C3^{i}—O4^{i} six-membered ring with a larger bite angle of 81.83 (5)°. Interestingly, six Cd^{II} ions are linked by 12 chelating carboxylate groups of six malonate ligands to form a [Cd$_6$(malonate)$_6$] metallomacrocycle (Fig. 2*a*) located at a site of $\overline{3}$ symmetry. The distance between N1 and N1$^{\rm vi}$ [symmetry code: (vi) $-x+2, -y+2, -z$] within one metallomacrocycle is 8.612 (4) Å (Fig. 2*b*) and the void at the center of the metallomacrocycle is 78 Å^3 in volume. Six terminal NH$_3$ molecules point towards the center of the metallomacrocycle. The side-on chelating ligand plays an important role in joining the [Cd$_6$(malonate)$_6$] metallomacrocycles into the resulting three-dimensional network, which is reinforced by hydrogen bonds formed by terminal NH$_3$ molecules and the carboxylate groups of malonate ligands above and below the metallomacrocycle (Table 2).

Based on the deconstruction viewpoint (O'Keeffe & Yaghi, 2012), the secondary building units of the three-dimensional network are CdO$_6$N and the malonate ligand (Fig. 3*a*), from which truncated octahedral subunits are constructed when the malonate ligands are regarded as linkers between the metal centers (Fig. 3*b*). Each truncated octahedral cage has six square faces and eight hexagonal faces, which are all shared with neighboring cages. The overall network of (I) has the zeolite SOD topology (Baerlocher *et al.*, 2007; Fig. 3*c*) with point symbol {$4^2 \cdot 6^4$}, as indicated by the program *TOPOS* (Blatov, 2006), which means that there are two four-membered and four six-membered rings in the four-connected vertex (Delgado-Friedrichs & O'Keeffe, 2005). Although many zeolite-type MOFs, or so-called zeolitic imidazolate frameworks (ZIFs), have been constructed from simple and angular imidazole-based linkers with divalent and tetrahedral metal ions (Huang *et al.*, 2006; Hayashi *et al.*, 2007; Zhang & Chen, 2006; Yamamoto *et al.*, 2003), carboxylate-based zeolite-type MOFs are still rare, which may be due to the diverse coordination modes of carboxylate as compared to the monoanionic imidazolate.

Experimental

A mixture of Cd(NO$_3$)$_2$·4H$_2$O (31 mg, 0.1 mmol) and malonic acid (10 mg, 0.1 mmol) was dissolved in dimethylformamide–water (4 ml, 1:1 *v*/*v*) in the presence of ammonia (1 ml, 14 *M*) in a test tube. This solution was carefully layered with dimethylformamide (2 ml). Finally, a methanol solution (3 ml) of 1,3,5-tris(1*H*-imidazol-1-yl)benzene (28 mg, 0.1 mmol) was layered carefully on top of the dimethylformamide solvent. The mixture was capped and allowed to stand at room temperature. Colorless crystals of (I) formed at the solvent interface after one week at ambient temperature (*ca* 60% yield). Analysis calculated for C$_3$H$_5$CdNO$_4$: C 15.57, H 2.18, N 6.05%; found: C 15.69, H 2.41, N 5.78%. Although the 1,3,5-tris(1*H*-imidazol-1-yl)benzene is not present in the crystal, it plays an important role in the formation of (I). When it is not present in the upper solution, no crystalline product was formed.

Crystal data

[Cd(C$_3$H$_2$O$_4$)(NH$_3$)]
$M_r = 231.48$
Trigonal, $R\overline{3}$
$a = 17.3662$ (8) Å
$c = 11.4425$ (10) Å
$V = 2988.6$ (3) Å^3
$Z = 18$
Mo $K\alpha$ radiation
$\mu = 3.23$ mm^{-1}
$T = 298$ K
0.10 × 0.08 × 0.08 mm

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.2577 (19)	Cd1—O4$^{\rm ii}$	2.4258 (14)
Cd1—O1$^{\rm i}$	2.2856 (14)	Cd1—O3$^{\rm ii}$	2.4525 (16)
Cd1—O4$^{\rm i}$	2.3081 (14)	Cd1—O1	2.5841 (14)
Cd1—O2	2.3299 (15)		
N1—Cd1—O1$^{\rm i}$	170.71 (6)	O1$^{\rm i}$—Cd1—O3$^{\rm ii}$	84.22 (6)
N1—Cd1—O4$^{\rm i}$	89.62 (6)	O4$^{\rm i}$—Cd1—O3$^{\rm ii}$	83.15 (5)
O1$^{\rm i}$—Cd1—O4$^{\rm i}$	81.83 (5)	O2—Cd1—O3$^{\rm ii}$	135.40 (5)
N1—Cd1—O2	96.45 (6)	O4$^{\rm ii}$—Cd1—O3$^{\rm ii}$	53.12 (5)
O1$^{\rm i}$—Cd1—O2	87.71 (5)	N1—Cd1—O1	86.89 (6)
O4$^{\rm i}$—Cd1—O2	138.80 (5)	O1$^{\rm i}$—Cd1—O1	89.06 (7)
N1—Cd1—O4$^{\rm ii}$	88.67 (6)	O4$^{\rm i}$—Cd1—O1	87.22 (5)
O1$^{\rm i}$—Cd1—O4$^{\rm ii}$	99.96 (5)	O2—Cd1—O1	52.71 (5)
O4$^{\rm i}$—Cd1—O4$^{\rm ii}$	135.38 (5)	O4$^{\rm ii}$—Cd1—O1	137.14 (5)
O2—Cd1—O4$^{\rm ii}$	85.62 (5)	O3$^{\rm ii}$—Cd1—O1	168.94 (5)
N1—Cd1—O3$^{\rm ii}$	98.43 (7)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O3$^{\rm iii}$	0.87 (3)	2.19 (3)	3.043 (2)	166 (3)
N1—H1B···O2$^{\rm iv}$	0.88 (1)	2.17 (1)	3.033 (2)	167 (2)
N1—H1A···O3$^{\rm v}$	0.88 (2)	2.33 (2)	3.188 (3)	164 (2)

Symmetry codes: (iii) $-x+\frac{4}{3}, -y+\frac{5}{3}, -z-\frac{1}{3}$; (iv) $-x+y+\frac{2}{3}, -x+\frac{4}{3}, z+\frac{1}{3}$; (v) $-y+\frac{5}{3}, x-y+\frac{4}{3}, z+\frac{1}{3}$.

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.738$, $T_{\rm max} = 0.782$
5110 measured reflections
1317 independent reflections
1281 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.035$
$S = 1.13$
1317 reflections
92 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.53$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

The H atoms of malonate were placed geometrically and were allowed to ride on their parent atoms, with C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The positions of the ammine H atoms were located in difference maps and refined with the N—H distances restrained to 0.89 (2) Å, and the H···H distances restrained to be similar with an s.u. value of 0.04 Å and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N).

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: FA3269). Services for accessing these data are described at the back of the journal.

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