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Poly[μ_3-hydroxido-μ_6-sulfato-μ_3-(1,2,4-triazolato-κ^3N^1:N^2:N^4)-dicadmium(II)]: a cadmium–triazolate coordination polymer with a pseudo-cubane-like tetranuclear cluster

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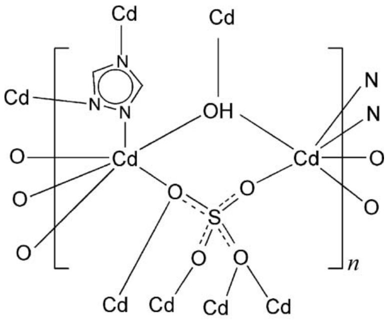
The title complex, $[Cd_2(C_2H_2N_3)(OH)(SO_4)]_n$, is a three-dimensional metal–organic framework consisting of pseudo-cubane-like tetranuclear cadmium clusters, which are formed by four Cd^{II} atoms, two sulfate groups and two hydroxide groups. The tetranuclear cadmium clusters are connected into a layered substructure by Cd—O bonds and adjacent layers are linked by triazolate ligands into a three-dimensional network. A photoluminescent study revealed that the complex exhibits a strong emission in the visible region which probably originates from a π–π* transition.

Comment

Metal–organic frameworks (MOFs) have been the focus of significant attention over past decades because of their increasingly wide range of applications (Nishikiori *et al.*, 2005; Qi *et al.*, 2008). Polyaza heterocyclic compounds have attracted considerable attention as useful ligands to produce coordination polymers with useful functional properties, such as gas storage (Zhang & Chen, 2008), magnetism (Ma *et al.*, 2010; Wang *et al.*, 2010) and catalysis (Wu *et al.*, 2005). Among these polyaza heterocyclic compounds, 1,2,4-triazole and its derivatives have been extensively applied as organic spacers in constructing MOFs because of their potential for $\mu_{1,2}$-, $\mu_{2,4}$- and $\mu_{1,2,4}$-bridging linkages (Lin *et al.*, 2008; Zhai *et al.*, 2007; Wei *et al.*, 2010). Generally, the $\mu_{1,2,4}$-bridging mode is preferred, if the ligand is deprotonated (trz). MOFs are primarily constructed from mononuclear metal centres and organic ligands, and this has resulted in a tremendous number of intriguing network topologies and a variety of packing motifs (Kitagawa *et al.*, 2004; Bradshaw *et al.*, 2005). Recently, more attention has been paid to expanding the classical Aufbau principles to include polynuclear coordination clusters as building units, with the intention of utilizing them as nodes in the design of coordination polymers (Marin *et al.*, 2004; Perry *et al.*, 2007). This represents an extension of the classical 'node-and-spacer' approach (Robson, 2000), giving rise to a family of cluster-based polymers with an enhanced variety of coordination geometries compared with single metal ions. In this report, we describe a new polymer, [Cd$_2$(trz)(OH)(SO$_4$)], (I), in which the basic building block is a pseudo-cubane-like tetranuclear cluster. To the best of our knowledge, compound (I) is the first example of a tetranuclear cluster as a unique node among the Cd^{II}–trz-based coordination polymers.



(I)

Complex (I) is a three-dimensional coordination polymer. There are two Cd^{II} atoms, one triazolate group, one sulfate group and one hydroxide group in the asymmetric unit (Fig. 1). The Cd1 atom adopts a distorted octahedral geometry, which is composed of three sulfate O atoms, two μ_3-hydroxide groups and one N atom from the μ_3-bridging triazolate ligand. Cd2 is also six coordinated, defined by three sulfate O atoms, two triazolate N-atom donors and a μ_3-hydroxide ligand. Detailed geometric parameters are given in Table 1. All the Cd—N or Cd—O bond lengths are comparable to those reported previously for Cd–triazolate complexes. The structure is based on $\{Cd_4(\mu_3\text{-}OH)_2(\mu_6\text{-}SO_4)_2\}$ clusters; four

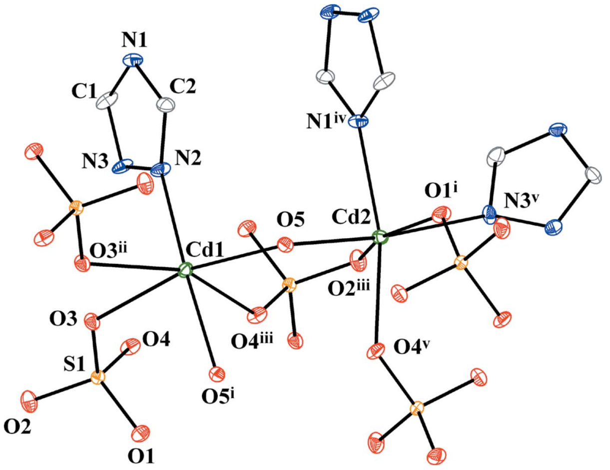


Figure 1
The structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x, -y, -z + 1$; (iii) $-x, -y + 1, -z + 1$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $x, -y + 1, z - \frac{1}{2}$.]

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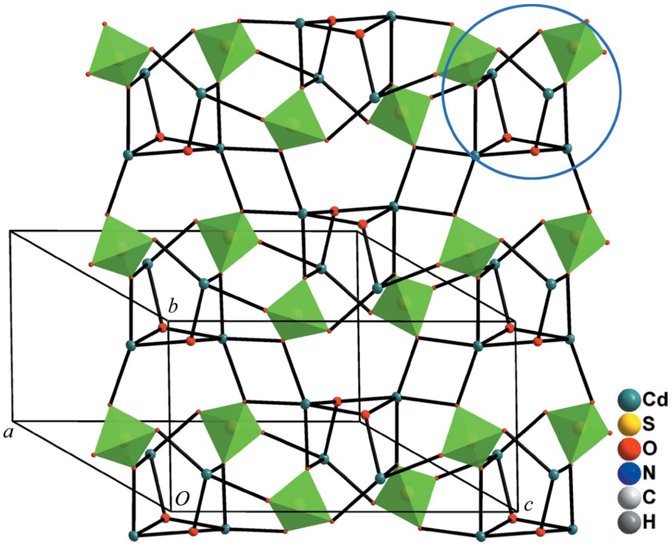

Figure 2
The layered substructure of (I), viewed in the *bc* plane. The tetranuclear cluster is circled and sulfate groups are represented by tetrahedra.

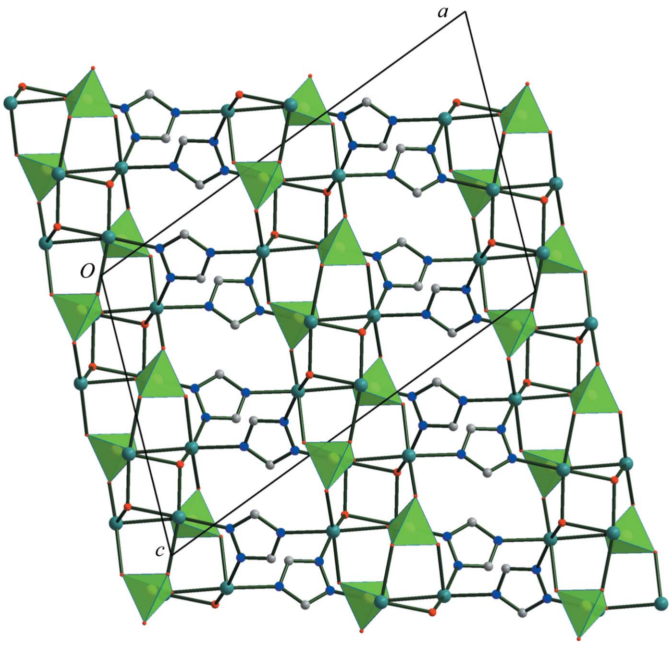

Figure 3
A view of the three-dimensional structure of (I) along the *b* axis.

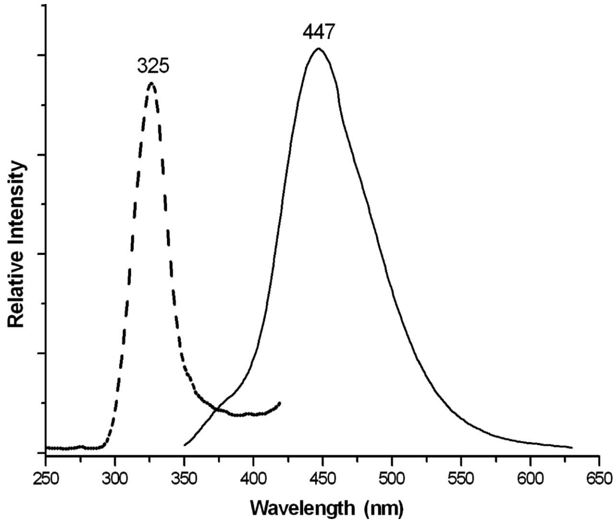

Figure 4
The solid-state fluorescence spectrum of (I) at room temperature. Key: solid line, emission spectrum; dashed line, excitation spectrum.

cadmium sites are bridged by two μ_3-hydroxide and two sulfate O atoms to produce the $\{Cd_4O_4\}$ core. This core resembles the cubane motif but is highly distorted, with the Cd—O distances (lengths of edges) ranging from 2.239 (3) to 3.155 (3) Å. The sulfate group connects to Cd1 and Cd2 sites of adjacent clusters forming a chain and connects to the Cd1 site of an adjacent chain to produce the layered substructure seen in Fig. 2. The sulfate group adopts a η^4,μ_6-coordination mode. The layered substructures are aligned by triazolates. Each triazolate ligand adopts the N^1:N^2:N^4-bridging mode, linking two Cd2 atoms of the layer and one Cd1 atom of the adjacent layer to connect the layered substructures into a network (Fig. 3).

Compared with the reported Zn analogue $[Zn_2(trz)(OH)(SO_4)]$ (Ouellette *et al.*, 2007), the differences in the radius and coordination number of the metal centres and the diverse coordination modes of the sulfate group lead to a different substructure. The building units of the title complex, (I), are tetranuclear clusters, and each sulfate adopts a η^4,μ_6-coordination mode. By contrast, in the $[Zn_2(trz)(OH)(SO_4)]$ complex, the building units are $\{Zn_3(\mu_3\text{-}OH)\}$ clusters, and each sulfate adopts a η^3,μ_5-coordination mode. Compared with another Cd/trz/sulfate complex $[Cd_8(trz)_4(OH)_2(SO_4)_5(H_2O)]$ (Ouellette *et al.*, 2007), the difference in the ratio of SO_4^{2-}/OH^- influences the substructure construction. The title complex, (I), consists of a layered cadmium/sulfate/hydroxide substructure, while the cadmium/sulfate/hydroxide substructure of $[Cd_8(trz)_4(OH)_2(SO_4)_5(H_2O)]$ is three-dimensional, which appears as cadmium sulfate layers stacking along the *a* axis and connected through sulfate linkages.

Luminescence properties have been explored at room temperature in the solid state (Fig. 4). The fluorescence spectrum shows that the title compound exhibits a broad and strong emission with a maximum wavelength of 447 nm upon excitation at 325 nm. The main chromosphere of this compound is the aromatic five-membered ring and its photoluminescence is assigned as originating from π–π* transitions.

Experimental

The title compound was prepared under mild hydrothermal conditions. $3CdSO_4\cdot 8H_2O$ (0.167 mmol, 128 mg), 1,2,4-triazole (1.0 mmol, 69 mg) and water (10 ml) were placed in a Teflon-lined autoclave (23 ml), the pH of the mixture was carefully adjusted to 6.0 by slow addition of NaOH (1.0 mol l^{-1}) solution. The mixture was heated to 423 K for 5 d, and then cooled to room temperature at a rate of 5 K h^{-1}. Colourless crystals suitable for X-ray analysis were obtained.

Crystal data

[$Cd_2(C_2H_2N_3)(OH)(SO_4)$]
M_r = 405.93
Monoclinic, $C2/c$
a = 19.098 (4) Å
b = 6.7985 (14) Å
c = 12.251 (3) Å
β = 111.85 (3)°
V = 1476.4 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 6.04 mm^{-1}
T = 298 K
0.22 × 0.08 × 0.07 mm

Data collection

Rigaku Saturn 724 CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
$T_{\rm min}$ = 0.566, $T_{\rm max}$ = 0.655
5862 measured reflections
1678 independent reflections
1650 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.051
S = 1.16
1678 reflections
123 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N2	2.236 (3)	Cd2—N1$^{\rm iv}$	2.297 (3)
Cd1—O5$^{\rm i}$	2.239 (3)	Cd2—O5	2.314 (3)
Cd1—O5	2.263 (3)	Cd2—O4$^{\rm v}$	2.318 (3)
Cd1—O3$^{\rm ii}$	2.349 (3)	Cd2—O2$^{\rm iii}$	2.326 (3)
Cd1—O4$^{\rm iii}$	2.388 (3)	Cd2—N3$^{\rm v}$	2.342 (3)
Cd1—O3	2.450 (3)	Cd2—O1$^{\rm i}$	2.365 (3)
N2—Cd1—O5$^{\rm i}$	172.64 (11)	O5—Cd2—O2$^{\rm iii}$	115.03 (9)
O5$^{\rm i}$—Cd1—O5	79.21 (11)	O4$^{\rm v}$—Cd2—O2$^{\rm iii}$	95.06 (10)
N2—Cd1—O3$^{\rm ii}$	89.36 (11)	N1$^{\rm iv}$—Cd2—N3$^{\rm v}$	87.39 (12)
O5$^{\rm i}$—Cd1—O3$^{\rm ii}$	96.93 (10)	O5—Cd2—N3$^{\rm v}$	163.85 (11)
N2—Cd1—O4$^{\rm iii}$	98.11 (11)	O2$^{\rm iii}$—Cd2—N3$^{\rm v}$	80.81 (11)
O5$^{\rm i}$—Cd1—O4$^{\rm iii}$	74.57 (10)	N1$^{\rm iv}$—Cd2—O1$^{\rm i}$	89.20 (11)
O3$^{\rm ii}$—Cd1—O3	70.57 (10)	O5—Cd2—O1$^{\rm i}$	84.59 (10)
O4$^{\rm iii}$—Cd1—O3	84.11 (9)	O4$^{\rm v}$—Cd2—O1$^{\rm i}$	87.25 (10)
N1$^{\rm iv}$—Cd2—O5	88.30 (11)	N3$^{\rm v}$—Cd2—O1$^{\rm i}$	79.79 (11)
N1$^{\rm iv}$—Cd2—O2$^{\rm iii}$	94.00 (11)		

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

H atoms bonded to C atoms were refined in idealized positions using the riding-model approximation, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The hydroxide H atom was located in a difference map and refined isotropically, with an O—H bond-length restraint of 0.86 (5) Å.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3070). Services for accessing these data are described at the back of the journal.

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