

A new two-dimensional cadmium coordination polymer with 1*H*-imidazole-4-carboxylate and oxalate

Xia Yin, Song-Liang Cai, Sheng-Run Zheng, Jun Fan and Wei-Guang Zhang*

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China

Correspondence e-mail: wgzhang@scnu.edu.cn

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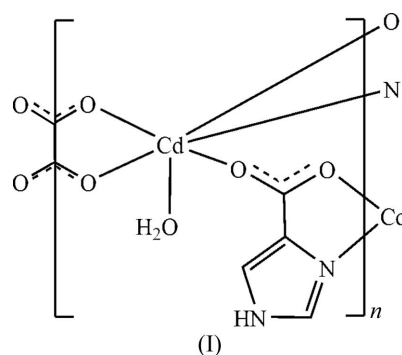
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The title compound, poly[aqua(μ_2 -1*H*-imidazole-4-carboxylato- $\kappa^3 N^3, O:O'$)hemi(μ_2 -oxalato- $\kappa^4 O^1, O^2:O^1, O^2'$)cadmium(II)], [Cd(C₄H₃N₂O₂)(C₂O₄)_{0.5}(H₂O)]_n, exhibits a two-dimensional network. The Cd^{II} cation is coordinated to one N atom and two carboxylate O atoms from two 1*H*-imidazole-4-carboxylate (Himc) ligands, two carboxylate O atoms from the bridging oxalate anion and one ligated water molecule; these six donor atoms form a distorted octahedral configuration. The oxalate anion lies on a centre of inversion. The Himc ligands connect the Cd^{II} cations to form –Cd–Himc–Cd–Himc–Cd– zigzag chains, with a Cd···Cd separation of 5.8206 (6) Å along the *b* direction, which are further linked by tetradentate oxalate anions to generate a two-dimensional herringbone architecture in the *ab* plane. These layers are extended to form a three-dimensional supramolecular framework *via* O–H···O and N–H···O hydrogen bonds and π – π stacking interactions. The solid-state photoluminescent behaviour of the title compound has been investigated at room temperature.

Comment

Coordination polymers with multicarboxylate imidazole ligands are of great current interest due to their intriguing architectures and topologies, as well as their many promising applications as functional materials, including optics, magnetism and porosity (Alkordi *et al.*, 2009; Gu *et al.*, 2011; Liu *et al.*, 2008). Many imidazole-based dicarboxylate ligands have been developed and widely applied in the construction of metal–organic frameworks (MOFs) over recent years (Li *et al.*, 2010; Wang *et al.*, 2011; Zheng *et al.*, 2011). However, the coordination chemistry of the simple imidazole-based ligand 1*H*-imidazole-4-carboxylic acid (H₂imc) has been less well explored. Similar to imidazole-based dicarboxylate ligands, H₂imc can be partially or fully deprotonated to generate Himc[–] or imc^{2–} anions at different pH values, and it can bind to metal ions through the N atoms of the imidazole ring and

the carboxylate O atoms. In addition, it may take part in the formation of noncovalent interactions, such as hydrogen bonds and π – π stacking interactions, thereby contributing greatly to the formation of a wide variety of supramolecular frameworks. To date, the few complexes with the H₂imc ligand or its derivatives reported in the literature exhibit mononuclear (Gryz *et al.*, 2006; Sun *et al.*, 2010; Yin *et al.*, 2009) or low-dimensional structures (Starosta & Leciejewicz, 2006; Sun & Yang, 2007). In our previous studies, we introduced different anions (such as acetate, NO₃[–], ClO₄[–], Cl[–], Br[–], I[–] and SO₄^{2–}) to investigate their effect (Cai *et al.*, 2012). Positive results indicated that the anions play crucial roles in the structure topologies and transformations. Herein, we selected oxalate for further study. The synthesis, structure and photoluminescence properties of the title novel two-dimensional cadmium coordination polymer, [Cd(Himc)(C₂O₄)_{0.5}(H₂O)]_n, (I), which was obtained by the hydrothermal reaction of cadmium oxalate trihydrate (CdC₂O₄·3H₂O) with H₂imc, are presented.



Compound (I) exhibits a two-dimensional network, in which the asymmetric unit consists of one Cd^{II} ion, one anionic Himc ligand, one half of an oxalate anion and one ligated water molecule, as shown in Fig. 1. The oxalate anion lies on a centre of inversion. In the structure, the six-coordinated Cd^{II} cation lies in a distorted octahedral environment, which is completed by one N atom [N1ⁱ; symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$] and two carboxylate O atoms (O1 and O2ⁱ) from two Himc ligands, two carboxylate O atoms from

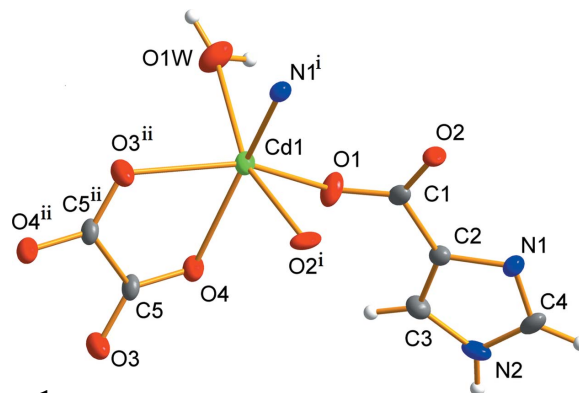


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 3, -z + 1$.]

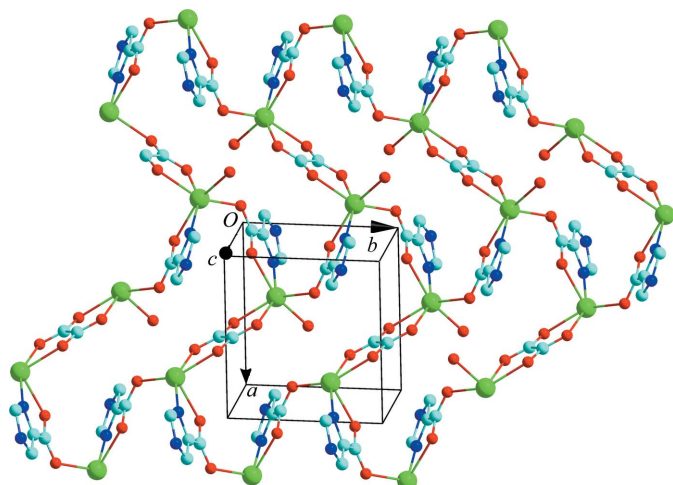


Figure 2
A packing diagram for (I), showing the two-dimensional herringbone-like network in the *ab* plane.

one bridging oxalate anion [O3ⁱⁱ and O4; symmetry code: (ii) $-x, -y + 3, -z + 1$], and the water O atom. The water molecule and atom O2ⁱ are disposed approximately *trans* to one another and the other donors are located in the plane perpendicular to this axis. Selected bond lengths for (I) are listed in Table 1. The Cd–O and Cd–N bond lengths are in the normal ranges (Cai *et al.*, 2012; Yin *et al.*, 2009).

In (I), the Himc and oxalate anions both act as μ_2 -bridges. The Himc ligands connect the Cd^{II} cations to form –Cd–Himc–Cd–Himc–Cd– zigzag chains, with a Cd···Cd separation of 5.8206 (6) Å along the *b* direction. These zigzag chains are further linked by tetradentate centrosymmetric oxalate anions to form a two-dimensional herringbone architecture in the *ab* plane (Fig. 2). Both surfaces of these layers are covered by protruding imidazole rings which interdigitate when adjacent layers come together. They form π – π stacking interactions and the centroid–centroid separations between pairs of adjacent imidazole rings are 3.484 (3) and 3.545 (3) Å. In addition, there are two types of hydrogen bond in the structure of (I). The first type is between the coordinated water molecule and the carboxylate O atoms of the oxalate anions (Table 2), and the second is between the N atom and one carboxylate O atom of the Himc anions. Thus, the action of both π – π stacks and hydrogen bonds results in the formation of a three-dimensional supramolecular network (Fig. 3).

As illustrated in Fig. 4, the powder X-ray diffraction (XRD) pattern of (I) is in agreement with that simulated based on the single-crystal structure. The diffraction peaks in the experimental and simulated patterns correspond well in their positions, suggesting that the crystal samples are pure.

In our previous work, three Cd^{II} coordination polymers with Himc anions exhibited a one-dimensional zigzag chain, a two-dimensional layer and a three-dimensional diamondoid network, respectively (Cai *et al.*, 2012). Although only a sulfate anion took part in the coordination of this last structure, positive results from many synthesis experiments revealed that the anions play crucial roles in the structure topologies of the resulting complexes. In this work, oxalate

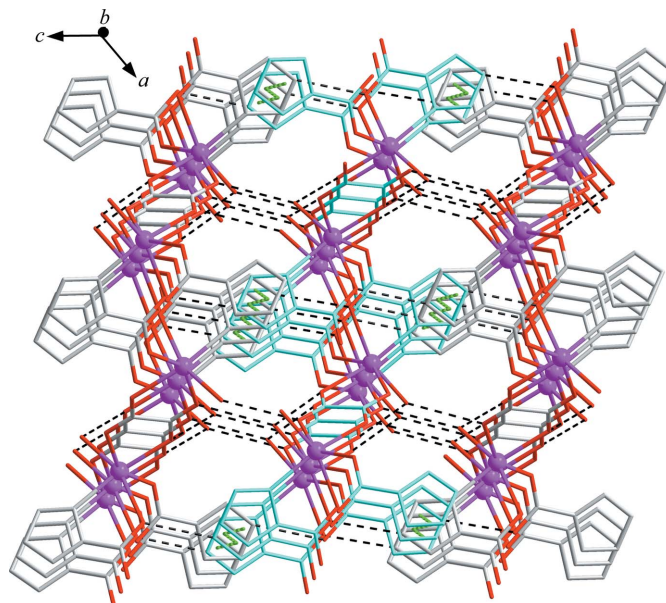


Figure 3
A packing diagram for (I), showing the three-dimensional supramolecular network driven by hydrogen bonds (dashed lines) and π – π stacking interactions.

was selected to construct a new Cd^{II} coordination polymer, because it is a commonly used bridging ligand and adopts various coordination modes. In the structure of (I), the oxalate anion adopts a bis-chelating bridging mode connecting two Cd^{II} cations. Finally, a two-dimensional network is formed through alternating connections between Himc ligands and oxalate anions, and this is quite different from that in [Cd₂(Himc)₂(SO₄)(H₂O)] (Cai *et al.*, 2012), which exhibits a two-dimensional structure with (3,4)-mixed connectivity. The results obtained from the crystal structures of (I) and three related complexes (Cai *et al.*, 2012) indicate that the anion plays a crucial role in the topologies. In addition, for complex

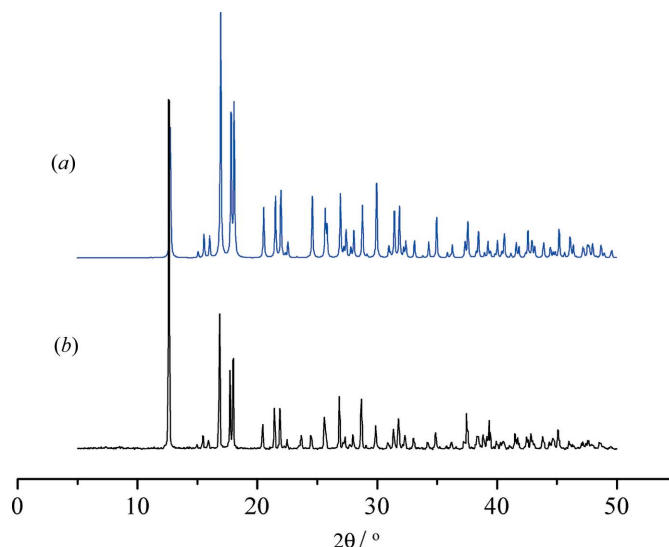


Figure 4
(a) The simulated powder X-ray diffraction (XRD) pattern and (b) the experimental powder XRD pattern of (I).

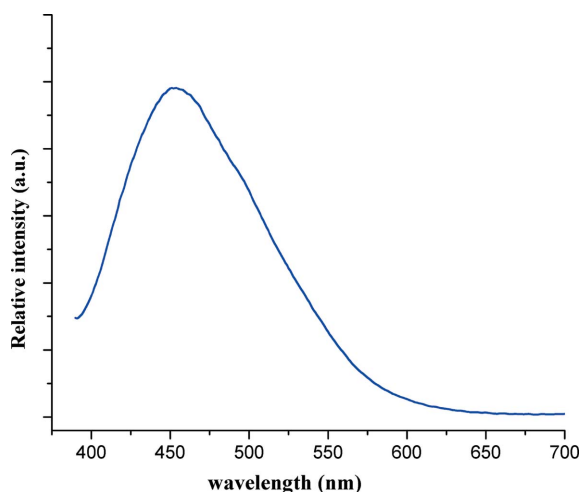


Figure 5
The solid-state photoluminescence of (I) at room temperature ($\lambda_{\text{ex}} = 369$ nm).

(I) and the sulfate structure, the coordination modes of H₂imc can be a key factor.

The solid-state photoluminescent behaviour of (I) was investigated at room temperature. As shown in Fig. 5, an intense broad emission band at 451 nm is observed after excitation at a wavelength of 369 nm. Compared with the free ligand H₂imc (emission at 463 nm with $\lambda_{\text{ex}} = 376$ nm), the blue-shifted emission for (I) may be attributed to intra-ligand transitions (Cai *et al.*, 2012).

In summary, the hydrothermal reaction of CdC₂O₄·3H₂O and H₂imc results in the formation of a two-dimensional herringbone-like cadmium coordination polymer. Combined with our previous work, it is clear that the anion plays a significant role in the assembly of the metal–anionic ligand system. That is to say, the choice of anion could promote different topological structures. In addition, (I) in the solid state exhibits characteristic emission at room temperature.

Experimental

CdC₂O₄·3H₂O (25.5 mg, 0.10 mmol) and H₂imc (22.4 mg, 0.20 mmol) were mixed in H₂O–C₂H₅OH (6 ml, 1:1 *v/v*) and the pH was adjusted to about 6 using aqueous NaOH (0.20 mol l^{−1}). The mixture was sealed in a 10 ml sample bottle reactor and heated at 373 K under autogenous pressure for 48 h. After the sample had been cooled slowly to room temperature at a rate of 2 K h^{−1}, colourless block-shaped crystals of (I) were obtained in a yield of 68%. Analysis calculated for C₅H₅CdN₂O₅: C 21.03, H 1.77, N 9.81%; found: C 20.97, H 1.82, N 9.88%. IR (KBr pellet, ν , cm^{−1}): 3341 (*s*), 3152 (*m*), 2977 (*w*), 1643 (*s*), 1589 (*s*), 1561 (*m*), 1514 (*w*), 1398 (*s*), 1313 (*s*), 1241 (*m*), 1083 (*w*), 997 (*m*), 930 (*w*), 809 (*s*), 793 (*m*), 652 (*m*), 613 (*w*), 564 (*w*), 501 (*w*).

Crystal data

[Cd(C ₄ H ₃ N ₂ O ₂)(C ₂ O ₄) _{0.5} (H ₂ O)]	$V = 766.07$ (14) Å ³
$M_r = 285.51$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.0259$ (12) Å	$\mu = 2.84$ mm ^{−1}
$b = 6.9271$ (8) Å	$T = 296$ K
$c = 13.9278$ (12) Å	$0.32 \times 0.25 \times 0.18$ mm
$\beta = 127.630$ (5)°	

Table 1
Selected bond lengths (Å).

Cd1–N1 ⁱ	2.220 (5)	Cd1–O3 ⁱⁱ	2.336 (4)
Cd1–O1	2.235 (4)	Cd1–O1W	2.351 (4)
Cd1–O4	2.298 (4)	Cd1–O2 ⁱ	2.422 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W–H1W \cdots O4 ⁱⁱⁱ	0.85	1.99	2.815 (6)	163
O1W–H2W \cdots O3 ^{iv}	0.85	2.14	2.972 (5)	167
N2–H2 \cdots O2 ^v	0.86	2.03	2.760 (6)	142

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

Data collection

Bruker APEXII CCD area-detector diffractometer	5542 measured reflections
Absorption correction: multi-scan (TWINABS; Sheldrick, 2008)	1393 independent reflections
$T_{\text{min}} = 0.395, T_{\text{max}} = 0.746$	1298 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	120 parameters
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.96$ e Å ^{−3}
1393 reflections	$\Delta\rho_{\text{min}} = -1.06$ e Å ^{−3}

The crystal under investigation was found to be nonmerohedrally twinned. The orientation matrices for the two components were identified using the program CELL_NOW (Sheldrick, 2008), with the two components being related by a 180° rotation around the real/reciprocal axis (1 −0.002 −0.999; −0.829 −0.001 1). The two components were integrated using SAINT (Bruker, 2007), resulting in a total of 8238 reflections. 3619 reflections (1506 unique) involved component 1 only (mean $I/\sigma = 13.2$), 3602 reflections (1500 unique) involved component 2 only (mean $I/\sigma = 10.2$) and 1017 reflections (519 unique) involved both components (mean $I/\sigma = 15.6$). The exact twin matrix identified by the integration program was found to be (−0.09207 0.00002 −0.90797; 0.00011 −1 0; −1.09202 −0.00026 0.09207).

The data were corrected for absorption using TWINABS (SHELXL97; Sheldrick, 2008) and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the HKLF 5 routine with all reflections of component 1 (including the overlapping reflections), resulting in a BASF value of 0.365 (2). The reflections involving component 2 only were omitted from the data set, as this component was somewhat weaker than component 1 and gave a slightly inferior R_{int} value.

The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS).

The H atoms of the water molecule were located in difference Fourier maps and the other H atoms were placed in calculated positions. They were refined as riding atoms, with C–H = 0.93 Å (imidazole C–H) and N–H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: APEX2 (Bruker, 2007); cell refinement: APEX2; data reduction: SAINT (Bruker, 2007); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3171). Services for accessing these data are described at the back of the journal.

References

- Alkordi, M. H., Brant, J. A., Wojtas, L., Kravtsov, V. C., Cairns, A. J. & Eddaoudi, M. (2009). *J. Am. Chem. Soc.* **131**, 17753–17755.
- Brucker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cai, S. L., Pan, M., Zheng, S. R., Tan, J. B., Fan, J. & Zhang, W. G. (2012). *CrystEngComm*, **14**, 2308–2315.
- Gryz, M., Starosta, W. & Leciejewicz, J. (2006). *J. Coord. Chem.* **60**, 539–546.
- Gu, Z. G., Fang, H. C., Yin, P. Y., Tong, L., Ying, Y., Hu, S. J., Li, W. S. & Cai, Y. P. (2011). *Cryst. Growth Des.* **11**, 2220–2227.
- Li, X., Wu, B. L., Wang, R. Y., Zhang, H. Y., Niu, C. Y., Niu, Y. Y. & Hou, H. W. (2010). *Inorg. Chem.* **49**, 2600–2613.
- Liu, Y. L., Kravtsov, V. C. & Eddaoudi, M. (2008). *Angew. Chem. Int. Ed.* **47**, 8446–8449.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Starosta, W. & Leciejewicz, J. (2006). *Acta Cryst.* **E62**, m2648–m2650.
- Sun, Y. G., Guo, M. Y., Xiong, G., Ding, F., Wang, L., Jiang, B., Zhu, M. C., Gao, E. J. & Verpoort, F. (2010). *J. Coord. Chem.* **63**, 4188–4200.
- Sun, Y. Q. & Yang, G. Y. (2007). *Dalton Trans.* pp. 3771–3781.
- Wang, W. Y., Yang, Z. L., Wang, C. J., Lu, H. J., Zang, S. Q. & Li, G. (2011). *CrystEngComm*, **13**, 4895–4902.
- Yin, W. P., Li, Y. G., Mei, X. L. & Yao, J. C. (2009). *Chin. J. Struct. Chem.* **28**, 1155–1159.
- Zheng, S. R., Cai, S. L., Pan, M., Fan, J., Xiao, T. T. & Zhang, W. G. (2011). *CrystEngComm*, **13**, 883–887.