

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND FLUORESCENCE OF A NEW 2D LAYERED
CADMIUM(II) MALATE COORDINATION POLYMER

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A new two-dimensional layered cadmium coordination polymer $[\text{Cd}(\text{D,L-mal})\text{H}_2\text{O}]_n$ ($\text{H}_2\text{mal} =$ malic acid) is solvothermally synthesized and characterized by elemental analysis, IR, TG and single crystal X-ray diffraction. Each Cd(II) centre is surrounded by seven oxygen atoms from three different malate ligands and one coordinated water molecular forming a pentagonal bipyramidal configuration. Furthermore, complex **1** exhibits blue intense photoluminescence property at room temperature.

Keywords: cadmium(II), crystal structure, malate ligand, coordination polymer, two-dimension, fluorescence.

INTRODUCTION

Crystal engineering of the coordination architecture of metal carboxylate complexes have received considerable current interest owing to their versatile framework topologies as well as their potential applications as functional materials in molecular magnetism, catalysis, gas sorption, fluorescent sensing, and optoelectronic devices [1—3]. Over the past decade, a significant number of efforts have been contributed to the building of these complexes with 1D, 2D, or 3D framework structures by the selection of a variety of dicarboxylate and tricarboxylate ligands [4, 5]. However, the rational design and synthesis of novel metal carboxylates by employing new synthetic tools, varying the nature of the reactants and synthetic conditions, are still currently under active investigation [6, 7].

Malic acid (H_2mal), as an α -hydroxycarboxylic acid, exhibiting a variety of coordination abilities and the tendency to form architectures with multidimensional frameworks, is an appealing ligand for building new chiral or achiral coordination compounds. Structurally characterized metal malate compounds include monomers [8], dimers [9, 10], tetramers [11], and polymeric chain compounds [12, 13] as well as 3D coordination polymers [14]. However, there are so far no reports of extended chiral or achiral networks of cadmium complexes malates except one [15]. Here we report the preparation, thermal and crystal structures of a new two-dimensional framework of $[\text{Cd}(\text{D,L-mal})\text{H}_2\text{O}]_n$ that exhibits a new coordination mode for this dicarboxylate ligand.

EXPERIMENTAL

Reagents and Apparatus. All commercially available starting materials were of analytical grade and used as received. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellet) were obtained on a FT-IR 170 SX (Nicolet) spectrometer. The photoluminescence (PL) spectra were taken on a Cary-Eclipse 500 spectrofluorometer (VARIAN) with a 60 W Xenon lamp as excitation source. Thermal stability (TG-DTA) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 700 °C.

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Table 1

Crystal data and structure refinement summary for 1

Empirical formula	C ₄ H ₆ CdO ₆
CCDC number	720901
F_w	262.50
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions (Å, deg.)	$a = 9.2322(18)$, $b = 11.802(2)$, $c = 12.311(3)$, $\alpha = 114.110(6)$
Volume, Å ³	1341.4(5)
Z	8
Density (calc.), g·cm ⁻³	2.600
μ , mm ⁻¹	3.235
$F(000)$	1008
Crystal size, mm	0.22 × 0.20 × 0.19
θ range, deg.	3.25 to 27.48
Range of h, k, l	-11/11, -15/15, -15/15
Reflections collected / unique	14265 / 1527
Max. and min. transmission	0.493 and 0.551
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1527 / 117 / 100
Goodness-of-fit on F^2	1.090
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1307$, $wR_2 = 0.3046$
R indices (all data)	$R_1 = 0.1311$, $wR_2 = 0.3047$
Largest diff. peak and hole, e/Å ³	4.722 and -4.711

The single crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. Intensities of reflections were measured using graphite-monochromatized MoK α -radiation ($\lambda = 0.71073$ Å) with ω scan mode in the range of $3.25 < \theta < 25.01^\circ$. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using SADABS program [16]. The structure was solved by the direct method [17], and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on F^2 by SHELXL-97 program package [18]. Water H atoms were located in a difference Fourier map; other hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. The summary of crystallographic data and structure analysis is given in Table 1. CCDC-720901 contains the supplementary crystallographic data for complex **1**. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Preparation of [Cd(D,L-mal)H₂O]_n 1. [Cd(D,L-mal)H₂O]_n synthesized by a solvothermal method from Cd(NO₃)₂·4H₂O (30.8 mg, 0.1 mmol), D,L-malic acid (53.6 mg, 0.4 mmol) and 2-ethylimidazole (38.4 mg, 0.4 mmol) and water/ethanol (6 mL, 60/40 vol.). The starting mixture was homogenised and transferred to a sealed Teflon-lined solvothermal bomb (bomb volume: 25 mL) and heated at 160 °C for three days under autogenous pressure. After cooling in a water bath, colorless crystals were obtained, washed and rinsed with distilled water and absolute ethyl alcohol (yield: 51.8% on the basis of)

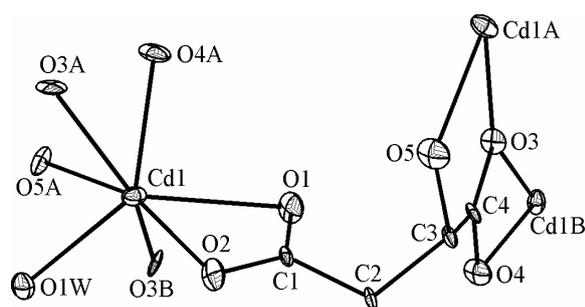


Fig. 1. Coordination and linkage modes of Cd(II) ions and DL-mal ligands in **1** (symmetry code A: $x-1/2, -y+1/2, -z+1$; B: $x, -y+1/2, z+1/2$) (hydrogen were omitted for clarity)

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Elemental analysis for $\text{C}_4\text{H}_6\text{CdO}_6$: found (calcd) (%): C 18.25 (18.30), H 2.29 (2.30). FT-IR (KBr, cm^{-1}): 3450s (broad), 2364w, 1590(vs), 1410s, 1090w, 684m, 579m.

RESULTS AND DISCUSSION

Syntheses and general methods. Reactions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with D,L-malic acid and 2-ethylimidazole in a 1:4:4 molar ratio at pH = 4–5 gave rise to an achiral 2D layered polymer of the formula $[\text{Cd}(\text{D,L-mal})\text{H}_2\text{O}]_n$ under solvothermal conditions, which is stable in air. The FT-infrared spectra of the title complex display characteristic features of the coordinated malato ligand. The absorptions for antisymmetric stretching carboxylate vibrations ν_{as} appear at 1590 cm^{-1} . The corresponding symmetric stretching vibrations ν_{s} appear at 1410 cm^{-1} . The separation of ν_{as} and ν_{s} ($\Delta\nu_{\text{a}} = 180 \text{ cm}^{-1}$) is much smaller than that observed with the corresponding acid (299 cm^{-1}) as expected for the observed coordination modes of the carboxylic groups [14b, 19].

Thermal analysis. Thermogravimetric (TG) analysis was carried out under air with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The TG curve of complex **1** is approximately divided into two stages (Fig. 1). The first weight loss is ca. 6.73 % (calculated value 6.86 %) in the temperature range 215–230 $^\circ\text{C}$, corresponding to the release of the coordinated water molecules. The whole weight loss is ca 43.14 % (calculated value 44.23 %) in the temperature range 233–500 $^\circ\text{C}$, matching to the decomposition of $[\text{Cd}(\text{D,L-mal})]_n$ into CdO. The compound does not lose weight at higher temperatures up to 500 $^\circ\text{C}$.

Description of the crystal structure. The coordination and linkage modes of Cd(II) ions and DL-mal ligands in **1** are shown in Fig. 1, and the selected bond lengths and angles are listed in Table 2. The asymmetric unit of **1** contains 11 non-hydrogen atoms with one crystallographically independent Cd(II) ion, one malate ligand unit, and one water molecule. Each Cd(II) centre is surrounded by seven oxygen atoms forming a distorted pentagonal bipyramidal site. All oxygen atoms are provided by three different malate ligands and one coordinated water molecular (O1; O2; O3A; O4A; O5B; O3B; O1W). The oxygen atoms provided by the organic ligands belong to the carboxylate group, except the O5B atom and O1W, which belong to a hydroxo group in a position and water molecule, respectively. Three types of Cd–O bonds are present in the structure, the Cd–O (hydroxyl) bonds with a bond length of $2.337(16) \text{ \AA}$, the Cd–O (water) bonds with a bond length of $2.287(17) \text{ \AA}$, and Cd–O (carboxylate) bonds in the range $2.268(16)$ – $2.529(15) \text{ \AA}$ (average 2.391 \AA).

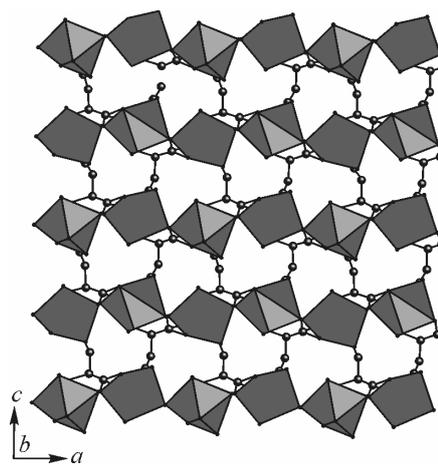
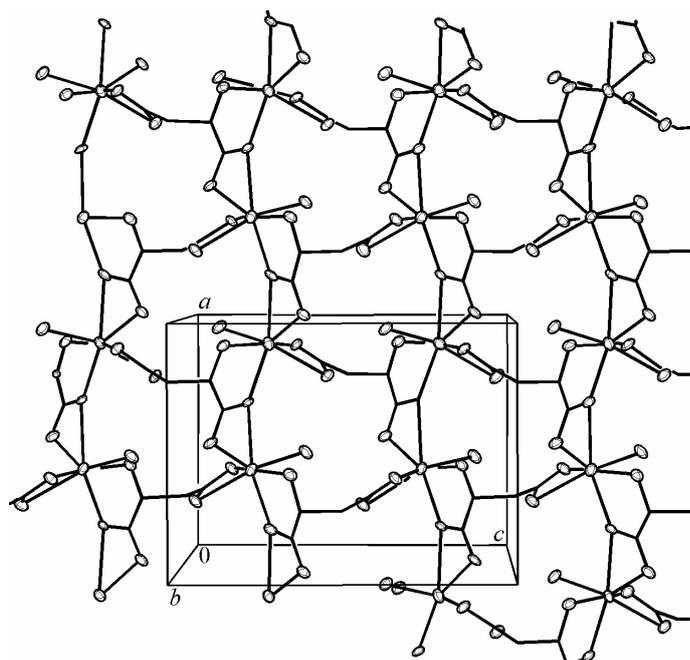
Each malate ligand is connected to three neighboring Cd(II) ions via carboxylato bidentate-chelate and oxo bridges; the corresponding cadmium-cadmium separation is $7.209(2)$ and $4.658(1) \text{ \AA}$,

Table 2

Selected bond lengths (\AA) and angles (deg.) for complex **1**

Cd1—O3B	2.268(16)	Cd1—O1W	2.287(17)	O3B—Cd1—O1W	92.4(7)	O3B—Cd1—O2	102.7(6)
Cd1—O2	2.293(18)	Cd1—O4A	2.326(16)	O1W—Cd1—O2	82.9(7)	O3B1—Cd1—O4A	121.2(6)
Cd1—O5B	2.337(16)	Cd1—O3A	2.529(15)	O1W—Cd1—O4A	134.1(7)	O2—Cd1—O4A	114.7(7)
Cd1—O1	2.527(17)			O3B—Cd1—O5B	70.3(6)	O1—Cd—O5B	81.4(7)
				O2—Cd1—O5B	162.5(7)	O4A—Cd1—O5B	82.1(7)

Symmetry code: (A) $x-1/2, -y+1/2, -z+1$; (B) $x, -y+1/2, z+1/2$.

Fig. 2 (left). Two-dimensional layer of **1**Fig. 3 (right). Polyhedral view of the layer in **1**

respectively. Here malato also acts as a quinque-dentate ligand as the oxo oxygen atoms bridge the cadmium atoms in a zigzag fashion to give an infinite edge-sharing CdO_7 polyhedron linkage along the a -directions of the unit cell. These chains are connected together by malate ligand in c directions to give a two-dimension infinite framework (Figs. 2 and 3). There is extensive $\text{O—H}\cdots\text{O}$ type hydrogen bonding in the structure of **1** (Table 3). The coordinated water molecules and alcoholic OH moieties form strong hydrogen bonds with the carboxylato oxygen atoms. The O atoms of the four carboxylato groups act as H-acceptors, while the H atom of the water molecules as H-donors. The $\text{O}\cdots\text{O}$ distances vary from 2.65(3) to 3.04(3) Å.

Photoluminescence property. At room temperature, solid **1** exhibits intense blue photoluminescence at 433 nm upon photo-excitation at 380 nm, as shown in Fig. 4. According to the structure of **1**, we suggest that the energy emission may come from the formation of $[\text{Cd}(\text{D,L-mal})\text{H}_2\text{O}]_n$ clusters and/or the ligand to metal charge transfer (LMCT). These observations suggest that polymer **1** could be anticipated as a potential fluorescent polymer material [20].

In summary, the solvothermal synthesis, single crystal structure, thermal and spectroscopic properties of a new cadmium(II) achiral coordination polymer has been reported. This structure consists in a 2D framework of oxygen edge-sharing enneahedra surrounding the metal ions that are interconnected by carboxylate bidentate-chelate and oxo groups. The malate ligand exhibits a new pentaden

Table 3

Hydrogen-bonding geometry (Å, deg.) of complex **1**

D—H...A	D—H	H...A	D...A	D—H...A
O(1W)—H(1A)...O(4) ⁱ	0.93	2.59	3.04(3)	110
O(1W)—H(1A)...O(1) ⁱⁱ	0.93	2.51	3.20(3)	131
O(1W)—H(1B)...O(1) ⁱ	0.93	2.25	2.99(3)	136
O(5)—H(5A)...O(2) ⁱⁱⁱ	0.82	1.83	2.65(3)	177

Symmetry codes: (i) $-1/2+x, y, 3/2-z$; (ii) $x, 1/2-y, 1/2+z$; (iii) $-x, 1-y, 1-z$.

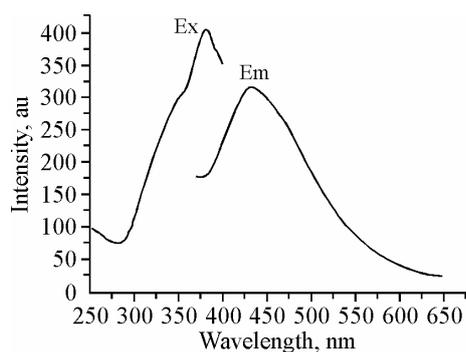


Fig. 4. Emission (right) and excitation (left) spectra of **1**

tate coordination mode with the cadmium atoms. Strong hydrogen bonds involving the coordinated water molecules and alcoholic OH moieties were observed. Complex **1** exhibits strong photoluminescence property at room temperature.

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