Synthesis and Crystal Structure of a New Cd(II) Coordination Polymer Based on a 1,10-Phenanthroline Derivative

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The new coordination polymer [Cd(oct)(L)] (H_2oct = octanedioic acid and L = 2-(4-fluorophenyl)-1H-imidazo-[4,5-f][1,10]phenanthroline) has been synthesized under hydrothermal condition and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Crystal data: $C_{27}H_{23}CdFN_4O_4$, monoclinic, space group $C2/c$, a = 21.391(4), b = 18.180(4), c = 14.031(3) Å, β = 116.50(3), V = 4883(2) Å^3, Z = 8. The flexible oct dianions bridge the Cd(II) cations to yield a double-chain structure. The L ligands are attached on both sides of the chains, and their π-π interactions between neighboring chains result in two-dimensional supramolecular layers.

Key words: Coordination Polymer, Crystal Structure, Octanedioic Acid, 2-(4-Fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline

Introduction

The rational design and synthesis of new extended supramolecular networks that can provide new shapes, sizes and chemical environments have attracted considerable attention in supramolecular chemistry [1 – 3]. Usually, these complexes can be specially designed by the careful selection of metal cations with preferred coordination geometries, the structure of the connecting ligands, and the reaction conditions [4]. Generally, two different types of interactions, such as covalent or ionic bonds and non-convalent intermolecular forces, can be used to construct a variety of supramolecular architectures [5]. In this regard, simple 1,10-phenanthroline ligands have been widely used to construct such architectures because of their excellent coordinating ability and large conjugated system that can easily form π-π interactions [6]. On this basis, a number of coordination polymers have been prepared from one-dimensional covalently bonded chains or layers, yielding extended two- or three-dimensional supramolecular structures through these interactions [7 – 9]. However, specially designed derivatives such as 2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L), which are good candidates for the construction of supramolecular architectures, have not been well studied in coordination chemistry [1]. Here, octanedioic acid (H_2oct) and L were selected as an organic linker and an N-donor chelating ligand, respectively, to yield a new coordination polymer, [Cd(oct)(L)] (**1**).

Table 1. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses[a].

Cd(1)–O(1)	2.3784(19)	Cd(1)–O(2)	2.4314(17)
Cd(1)–O(3)^{i}	2.613(2)	Cd(1)–O(4)^{i}	2.2617(19)
Cd(1)–O(3)^{ii}	2.3335(19)	Cd(1)–N(1)	2.4200(18)
Cd(1)–N(2)	2.3211(19)		
O4^{i}–Cd1–N2	170.44(8)	N2–Cd1–O3^{ii}	81.49(7)
O4^{i}–Cd1–O3^{ii}	89.89(8)	O4^{i}–Cd1–O1	92.37(7)
N2–Cd1–O1	84.90(7)	O3^{ii}–Cd1–O1	98.52(7)
O4^{i}–Cd1–N1	117.58(8)	N2–Cd1–N1	70.23(7)
O3^{ii}–Cd1–N1	114.71(6)	O1–Cd1–N1	133.78(6)
O4^{i}–Cd1–O2	102.13(7)	N2–Cd1–O2	83.70(7)
O3^{ii}–Cd1–O2	150.01(7)	O1–Cd1–O2	54.14(6)
N1–Cd1–O2	84.09(6)	O4^{i}–Cd1–O3^{i}	52.91(6)
N2–Cd1–O3^{i}	128.01(6)	O3^{ii}–Cd1–O3^{i}	77.09(8)
O1–Cd1–O3^{i}	144.57(6)	N1–Cd1–O3^{i}	76.86(6)
O2–Cd1–O3^{i}	131.85(6)		

[a] Symmetry transformations used to generate equivalent atoms: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $x, -y+1, z+1/2$.

Results and Discussion

Structure description

Single-crystal X-ray structural analysis has revealed that the compound has a two-dimensional supramolecular layer structure. Selected bond lengths and angles for **1** are given in Table 1. As illustrated in Fig. 1, the central Cd atom is coordinated by two nitrogen atoms from one L ligand, and five carboxylate oxygen atoms from three different oct ligands in a distorted pentagonal bipyramidal geometry. The Cd–O distances range from 2.2617(19) to 2.613(2) Å. The Cd(1)–N(1) and Cd(1)–N(2) distances are 2.4200(18) and 2.3211(19) Å, respectively (Table 1), which are near to the data reported for $[Cd_2(Dpq)_2(BPDC)_2]\cdot 1.5\,H_2O$ (Dpq is dipyrido[3,2-d:2,30-f]quinoxaline, and BPDC is biphenyl-4,4′-di-

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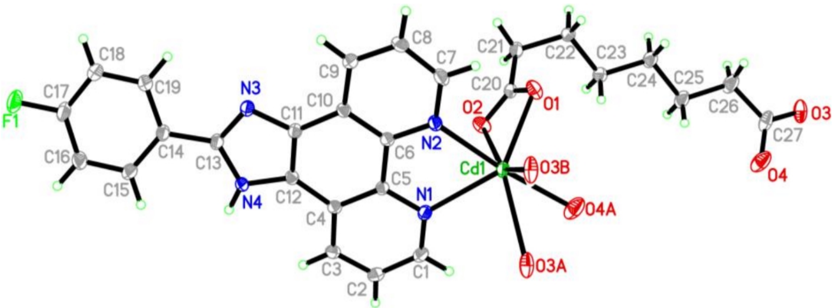

Fig. 1 (color online). The coordination environment of the Cd atom in [Cd(oct)(L)].

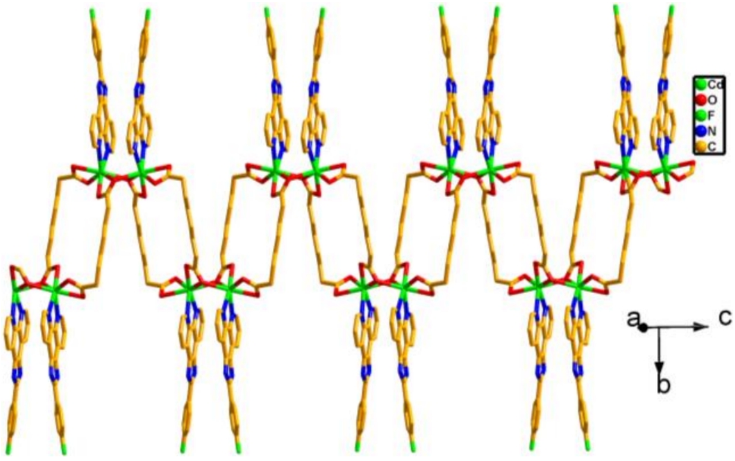

Fig. 2 (color online). View of the double-chain structure of [Cd(oct)(L)].

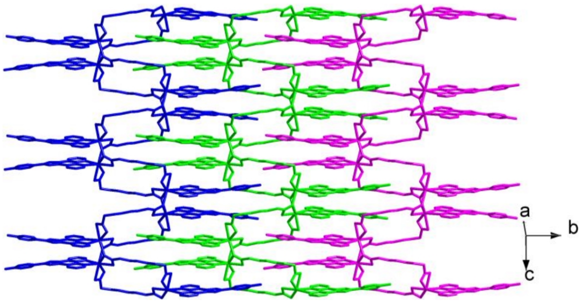

Fig. 3 (color online). A two-dimensional supramolecular layer of [Cd(oct)(L)] constructed by π-π interactions.

Table 2. Crystal structure data for **1**.

Formula	$C_{27}H_{23}CdFN_4O_4$
M_r	598.89
Crystal size, mm^3	$0.21 \times 0.18 \times 0.16$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	21.391(4)
b, Å	18.180(4)
c, Å	14.031(3)
β, deg	116.50(3)
V, Å^3	4883(2)
Z	8
D_{calcd}, g cm^{-3}	1.63
μ(MoK_α), mm^{-1}	0.9
F(000), e	2416
hkl range	$-27 \le h \le 25$; $-23 \le k \le 23$; $-18 \le l \le 18$
θ range, deg	3.0 – 27.5
Refl. collect. / unique / R_{int}	22841 / 5582 / 0.035
Data / ref. parameters	5082 / 334
$R1$ / $wR2$ [$I \ge 2\sigma(I)$]	0.0292 / 0.0636
$R1$ / $wR2$ (all data)	0.0430 / 0.0677
GoF (F^2)	1.039
$\Delta\rho_{\text{max / min}}$, e Å^{-3}	0.380 / −0.380

carboxylate) [11]. It is interesting to note that the two carboxylates of the oct anions show different coordination modes (Fig. 2): one bridges two Cd(II) atoms, while the other connects one Cd(II) atom in a chelating mode. In this way, each oct dianion bridges two Cd(II) cations to form a chain structure. In the oct unit the C(22)–C(26) chain is fully extended (all-*trans*-conformation) except for a kink at C(21). It is further noteworthy that the L ligands are attached in pairs on both sides of the chains. There is strong π-π interaction between the ligands of pairs of the chain (centroid-to-centroid distance 3.41 Å, face-to-face distance 3.35 Å). The ligands L are arranged in a parallel fashion, leading to a structure suitable to form π-π

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interactions between these pairs (Fig. 3). The lateral ligands L from adjacent chains form strong π-π interactions (centroid-to-centroid distance 3.39 Å, face-to-face distance 3.34 Å) resulting in an interesting two-dimensional supramolecular layer (Fig. 3). Obviously, the π-π stacking interactions play an important role in the formation and stabilization of the supramolecular structure. In addition, N–H···O hydrogen bonding interactions further stabilize the structure of **1**.

As far as we know several Cd(II) complexes with phen-like chelating ligands have been reported so far, however, no Cd(II) coordination polymer containing a chelating ligand L and a flexible dicarboxylate has been observed [6 – 11]. It is noteworthy that the structure of **1** is entirely different from that of the related compound $[Cd_2(Dpq)_2(BPDC)_2]\cdot 1.5\,H_2O$, in which the BPDC ligands link the Cd(II) centers to give an interesting six-connected twofold interpenetrated framework [11].

Experimental Section

General

All the materials were of analytical reagent grade and used as received without further purification. The IR spectrum was obtained on a Perkin-Elmer 2400LSII spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer.

*Synthesis of compound **1***

A mixture of $Cd(NO_3)_2 \cdot 2.5\,H_2O$ (0.5 mmol), H_2oct (0.5 mmol) and L (0.5 mmol) was dissolved in 12 mL distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to between 5 and 6. The resulting solution was stirred for about 1 h at r. t., sealed in a 23-mL Teflon-lined stainless-steel autoclave and heated at 465 K for 7 d under autogeneous pressure. Afterwards, the reaction system was slowly cooled to r. t. Pale-yellow block-shaped crystals of **1** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield: 33 % based on Cd. – Anal. for $C_{27}H_{23}CdFN_4O_4$: calcd. C 54.15, H 3.87, N 9.35; found C 54.34, H 3.49, N 9.22. – IR (KBr, cm^{-1}): ν = 1709w, 1610m, 1584s, 1457s, 1420w, 1455w, 1362w, 1343s, 847w, 723w, 650w.

X-Ray structure determination

Single-crystal X-ray diffraction data for complex **1** were recorded at a temperature of 293(2) K on a Rigaku RAXIS-RAPID diffractometer, using the ω scan technique with MoK_α (λ = 0.71073 Å) radiation. The structure was solved by Direct Methods with SHELXS-97 [12] and refined by full-matrix least-squares techniques using the program SHELXL-97 [13]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as rigid groups. Numbers pertinent to data collection and refinement are listed in Table 2.

CCDC 813008 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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