Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[[(2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2N^7,N^8)cadmium(II)]-di-μ-chlorido-[(2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2N^7,N^8)-cadmium(II)]-μ-fumarato-$\kappa^4O^1,O^{1\prime}$:-$O^4,O^{4\prime}$]: a coordination polymer with a two-dimensional supramolecular architecture

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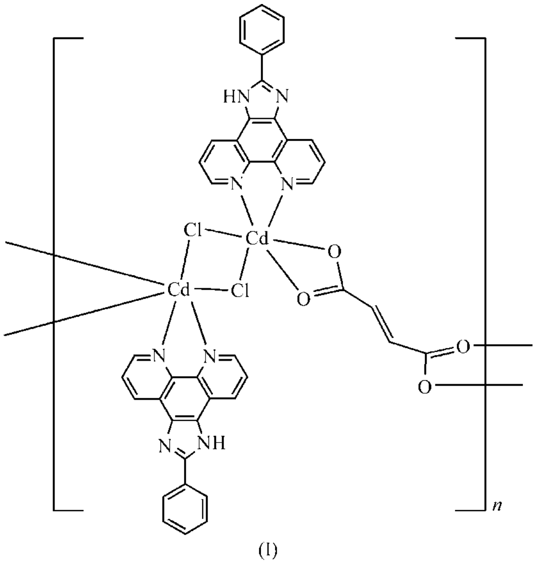
Received 13 August 2008
Accepted 19 August 2008
Online 20 September 2008

The title cadmium(II) coordination polymer, $[Cd_2(C_4H_2O_4)Cl_2(C_{19}H_{12}N_4)_2]_n$, (I), was obtained by the reaction of $CdCl_2\cdot 2.5H_2O$, fumaric acid (H_2fum) and 2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene (*L*) under hydrothermal conditions. The fum dianion is situated across an inversion centre in the space group $P\overline{1}$. The Cd^{II} atom is six-coordinated by two *L* N atoms, two fum O atoms and two Cl atoms in a distorted octahedral geometry. The μ_2-Cl atoms and the bis-chelating fum dianions bridge neighbouring Cd^{II} centres, yielding a coordination polymer chain structure along the *c* axis. N—H$\cdots$O hydrogen bonds between the N atoms of *L* and the carboxylate O atoms of fum lead to a sheet structure in the *bc* plane. Compound (I) represents a rare example of a supramolecular structure constructed by a chloride anion, a dicarboxylate anion and a 1,10-phenanthroline derivative. This work may further the development of the coordination chemistry of 1,10-phenanthroline derivatives.

Comment

Generally, two different types of interactions (covalent bonds and noncovalent intermolecular forces) can be used to construct varied supramolecular architectures. The π–π interaction, as one of the most powerful noncovalent intermolecular interactions, is operative in determining supramolecular architectures (Chen & Liu, 2002). 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 (Zhang *et al.*, 2005; Wang *et al.*, 2007).



(I)

To date, 1,10-phenanthroline (phen) and 2,2-bipyridyl have been widely used to build supramolecular architectures, due to their excellent coordinating ability and large conjugated systems that can easily form π–π interactions (Wang *et al.*, 2008; Tong *et al.*, 2000; Zheng *et al.*, 2001). However, far less attention has been given to their derivatives (Yang, Li *et al.*, 2007; Yang, Ma *et al.*, 2007). For example, the rare phen derivative 2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene (*L*) possesses a large aromatic system and is a good candidate for the construction of metal–organic supramolecular architectures (Wang *et al.*, 2007). In this contribution, we selected fumaric acid (H_2fum) as a linker and *L* as a secondary ligand, generating the novel title Cd^{II} coordination polymer, (I), which displays a two-dimensional supramolecular architecture interlinked through hydrogen bonds.

As shown in Fig. 1, the asymmetric unit of (I) contains one unique Cd^{II} cation, one unique chloride anion and one-half of a fum dianionic ligand. The fum dianion is situated across an inversion centre. Each Cd^{II} atom is six-coordinated by two N atoms (N1 and N2) from one *L* ligand, two O atoms (O1 and O2) from one fum ligand and two chloride anions [Cl1 and Cl1^{i}; symmetry code: (i) $1 - x$, $1 - y$, $-z$] in a distorted octahedral geometry. The average Cd—O and Cd—N distances in (I) (Table 1) are comparable with those observed for $[Cd_4(OH)_2(H_2O)_2(sip)_2(4,4'\text{-bpy})_4]\cdot H_2O$ (sip is 5-sulfoisophthalate and 4,4′-bpy is 4,4′-bipyridyl; Li *et al.*, 2005).

As depicted in Fig. 2, two μ_2-Cl atoms bridge two Cd^{II} centres to yield a $[Cd_2Cl_2]^{2-}$ unit. The fum dianions link neighbouring $[Cd_2Cl_2]^{2-}$ units in a bis-chelating mode, giving a one-dimensional chain structure along the *c* axis. The *L* ligands are extended on both sides of the chain, and the planes of adjacent *L* ligands are parallel. The secondary *L* ligand plays an important role in the formation of the chain structure. Two N atoms from the secondary *L* ligand occupy two coordination positions of the Cd^{II} atom, while the remaining coordination positions are available for fum ligands, allowing

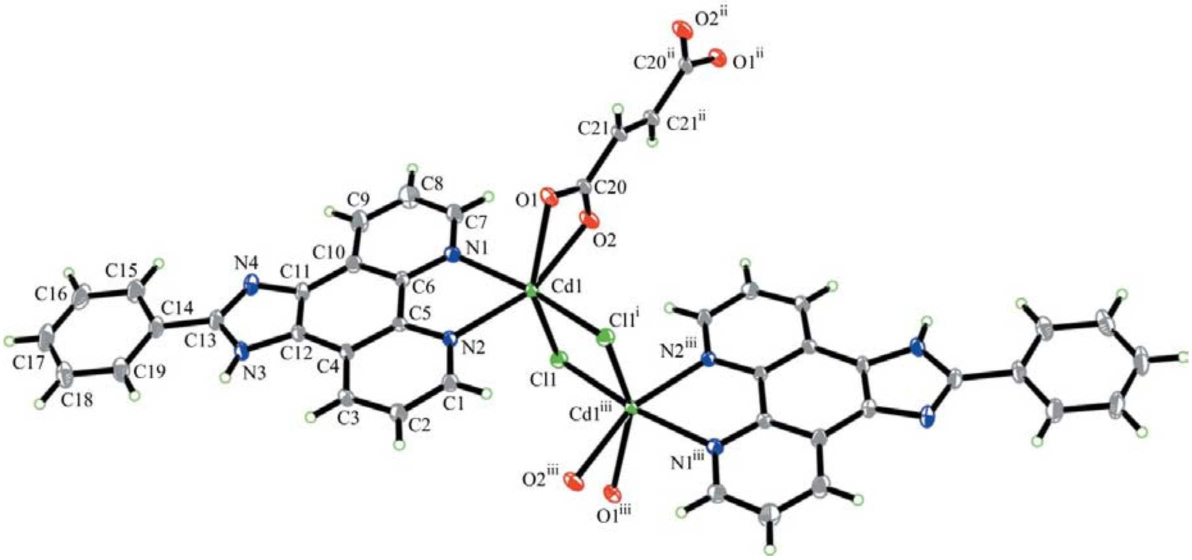


Figure 1
A view of the local coordination of the $\mathrm{Cd^{II}}$ cation in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, -y, 1 - z$.]

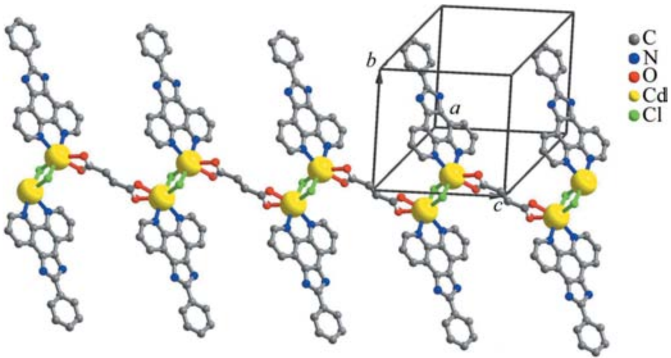


Figure 2
A view of the coordination polymer chain structure of (I) along the *c* axis.

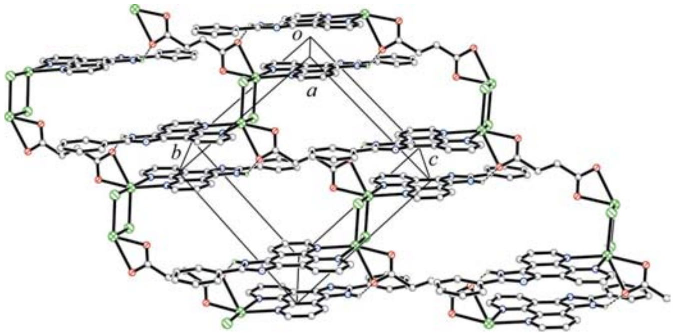


Figure 3
A view of the sheet formed by the linking of the coordination polymer chains by N—H$\cdots$O hydrogen bonds.

the formation of the chain structure. N—H$\cdots$O hydrogen bonds between the N atoms of *L* and the carboxylate O atoms of fum lead to a sheet structure in the *bc* plane (Table 2 and Fig. 3).

It is noteworthy that the structure of (I) presented here is clearly different from that of the previously reported compound [Pb(ndc)(*L*)]·0.5H_2O (ndc is naphthalene-1,4-dicarboxylate; Yang, Li *et al.*, 2007). In the latter compound, the ndc ligand links the $\mathrm{Pb^{II}}$ atoms to yield a single chain. The *L* ligands extend solely on one side of the chain in a slanted fashion, and π–π interactions between the *L* ligands result in a final wavy layer structure. The structure of (I) is also entirely different from that of [Pb(fum)(dpdp)]·H_2O (dpdp is dipyrido[3,2-*a*:2′,3′-*c*]phenazine; Yang, Ma *et al.*, 2007). In that structure, each fum ligand bridges four $\mathrm{Pb^{II}}$ centres in a tetradentate mode, generating a novel layer structure. These layers are decorated with dpdp ligands alternating on the two sides of each layer. π–π interactions between the dpdp ligands lead to a unique three-dimensional supramolecular structure.

It should be pointed out that the complex structure of (I) is not sensitive to the $\mathrm{Cd^{II}}$:*L* ratio; the same compound, with a $\mathrm{Cd^{II}}$:*L* ratio of 1:1, was isolated using $\mathrm{Cd^{II}}$:*L* reaction stoichiometries of 1, 2 and 3. We have also tried to investigate the effects of different cadmium(II) salts on the structure of the complex through reaction with $Cd(NO_3)_2$, $Cd(CH_3COOH)_2$ or $CdSO_4$, but single crystals of their products have not been obtained. Therefore, the chloride anion probably plays an important role in the formation of title complex. To the best of our knowledge, compound (I), featuring a fascinating two-dimensional superamolecular structure, is the first solid entity constructed by a chloride anion, a dicarboxylate anion and a phen derivative.

Experimental

1,10-Phenanthroline was oxidized to 1,10-phenanthroline-5,6-dione according to the reported procedure of Hiort *et al.* (1993). For the preparation of *L*, a mixture of 1,10-phenanthroline-5,6-dione (2 mmol), benzaldehyde (2.2 mmol), glacial acetic acid (15 ml) and ammonium acetate (3.2 g) was heated under reflux for 2 h, resulting in a yellow precipitate. After cooling, the mixture was diluted with water (25 ml) and the pH of the solution was adjusted with concentrated aqueous ammonia to 5.5. The yellow product was filtered off, washed with water and acetone, and oven-dried at 333 K. For the preparation of (I), $CdCl_2$·2.5H_2O (0.114 g, 0.5 mmol), H_2fum (0.058 g,

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0.5 mmol) and *L* (0.148 g, 0.5 mmol) were dissolved in distilled water (12 ml), followed by addition of triethylamine until the pH of the system was about 5.3. The resulting solution was stirred for about 3 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 463 K for 7 d under autogenous pressure. The reaction system was then cooled slowly to room temperature. Pale-yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield: 39% based on Cd^{II}). IR (ν, cm^{-1}, KBr): 3115 (*s*), 3056 (*s*), 2914 (*vs*), 1611 (*vs*), 1389 (*s*), 1340 (*s*), 1113 (*s*), 753 (*s*), 654 (*s*).

Crystal data

$[Cd_2(C_4H_2O_4)Cl_2(C_{19}H_{12}N_4)_2]$
M_r = 1002.40
Triclinic, $P\overline{1}$
a = 10.069 (3) Å
b = 10.480 (2) Å
c = 10.749 (4) Å
α = 88.59 (3)°
β = 63.20 (3)°
γ = 73.59 (5)°
V = 964.2 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.30 mm^{-1}
T = 293 (2) K
0.33 × 0.25 × 0.21 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.642, T_{max} = 0.760
9502 measured reflections
4365 independent reflections
3755 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.061
S = 1.06
4365 reflections
262 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cd1—N1	2.312 (2)	Cd1—O2	2.289 (2)
Cd1—N2	2.333 (2)	Cd1—Cl1^{i}	2.5640 (9)
Cd1—O1	2.479 (2)	Cd1—Cl1	2.5782 (14)

Symmetry code: (i) $-x+1, -y+1, -z$.

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N3—H3⋯O1^{ii}	0.86	2.09	2.820 (3)	142

Symmetry code: (ii) $-x+1, -y+2, -z$.

All H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors thank Jilin Normal University for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3238). Services for accessing these data are described at the back of the journal.

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