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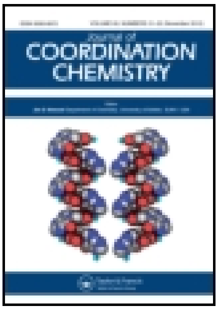

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Synthesis, crystal structure, thermal, and photoluminescence properties of Cd carboxylate coordination polymers: a new 2-D structure and reinvestigation of Cd tartrate

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Synthesis, crystal structure, thermal, and photoluminescence properties of Cd carboxylate coordination polymers: a new 2-D structure and reinvestigation of Cd tartrate

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A new 2-D coordination polymer, $[Cd(HnicO)(pyc)(H_2O)]_n$ (**1**) ($H_2nicO = $ 2-oxynicotinic acid, $pycH = $ pyridine-4-carboxylic acid), and the $[Cd_3(tartr)_3]_n$ salt (**2**) ($tartrH_2 = $ tartaric acid) have been synthesized and structurally characterized. The former is stabilized by H-bonds to give a 3-D architecture. Complex **2**, that represents a reinvestigation of Cd tartrate, has been compared with isomorphous $[Cd_3(tartr)_3]$ structures in terms of the unit cell void and the respective water content, indicating for these compounds the aptitude to crystallize with a small, but different, amount of lattice water. Thermogravimetric and luminescent characterization of **1** were performed.

Keywords: Cd(II) coordination polymer; pyridine-4-carboxylic acid; 2-oxynicotinic acid; tartaric acid; photoluminescence

1. Introduction

Considerable efforts have focused on synthesis of new multidimensional coordination polymers because of their architectures and potential applications in ion exchange, gas storage, molecular magnetism, luminescence, and heterogeneous catalysis [1]. Construction of metal organic frameworks is guided by metal ion coordination capability, ligand, and solvent [2]. The bridging ligand plays a crucial role in construction of attractive architectures. We have synthesized several coordination polymers with main group as well as d-block metals [3]. Carboxylates are commonly used bridging ligands to construct coordination polymers because of their versatile coordination behavior and ability to act as H-bond acceptors and/or donors to assemble supramolecular structures [4]. Here, we have used mono and di-carboxylates,

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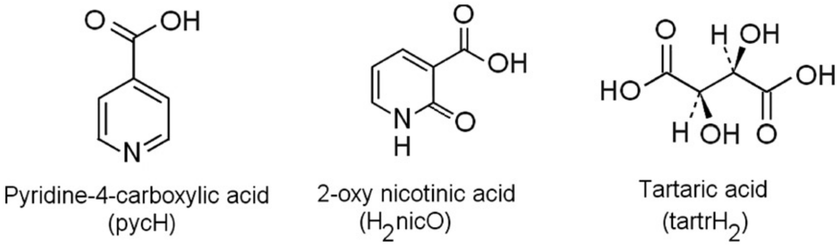

Scheme 1. The ligands.

pyridine-4-carboxylic acid (pycH), 2-oxynicotinic acid (H_2nicO, generated *in-situ* from 2-chloronicotinic acid) and tartaric acid (tartrH_2) (scheme 1). Although literature survey revealed that sole pycH or H_2nicO ligand have been frequently used for the synthesis of coordination polymers with several metal ions [5, 6], examples with mixed ligand system are uncommon [7].

In the present work, we report the synthesis, characterization, thermal, and luminescence properties of a new 2-D coordination polymer of cadmium $[Cd(HnicO)(pyc)(H_2O)]_n$ (**1**) and of the $[Cd_3(tartr)_3]_n$ salt (**2**). Since coordination polymers of Cd(II) with carboxylates [8] are interesting for their luminescent behavior, the synthesis, structural characterization, and study of luminescence of **1** are reported. Different hydrated forms of Cd tartrate have been reported [9, 10], including two structures having similar composition to **2**; a reinvestigation of these results is here presented.

2. Experimental

2.1. *Materials and instrumentation*

Cadmium acetate dehydrate and L(+)-tartaric acid were purchased from Merck. Isonicotinic acid and 2-chloro-nicotinic acid were purchased from SIGMA-ALDRICH Inc. FT-IR spectra were recorded as KBr pellets from 4000–400 cm^{-1} with a Perkin Elmer Spectrum-100 FT-IR spectrometer. Elemental analyses (C, H, and N) were carried out on a 240 C Elemental analyzer. Thermogavimetric analysis (TGA) was done under nitrogen flow (30 mL min^{-1}) with a Shimadzu DTG-60 simultaneous DTA-TG apparatus. Fluorescence spectra of the ligand and complex were measured in the solid state at room temperature using a HITACHI F-7000 spectrofluorimeter.

2.2. *Synthesis of $[Cd(HnicO)(pyc)(H_2O)]_n$ (1)*

Cadmium acetate dihydrate $[Cd(CH_3COO)_2{\cdot}2H_2O]$ (0.1332 g, 0.5 mmol), isonicotinic acid (0.0615 g, 0.5 mmol), and 2-chloro-nicotinic acid (0.078 g, 0.5 mmol) were dissolved in 10 mL of deionized water in 1 : 1 : 1 ratio. Triethyl amine (0.14 mL, 1 mmol) was added dropwise to the solution with constant stirring. The transparent solution was then transferred into a 25 mL Teflon-lined stainless steel vessel and heated at 160°C for 72 h. The mixture was allowed to cool to room temperature and colorless block-shaped crystals were isolated by decanting the supernatant liquid, washed with deionized water, ethanol and dried in air. Yield: 68%. Anal. Calcd for $C_{12}H_{10}CdN_2O_6$ (390.62): C, 36.89; H, 2.58; N, 7.17. Found: C, 36.87; H, 2.55; N, 7.19. IR (cm^{-1}): 891 s, 1017 w, 1092 s, 1152 w, 1257 w, 1396 w, 1474 s, 1527 w, 1573 s, 1651 s, 1698 w, 1750 w, 1771 w, 1791 w, 1875 w, 1833 w, 1911 w, 2281 w, 3197 w, 3242 w, 3400 w, 3566 m, 3613 m, 3648 m, 3675 m, 3686 m, 3753 m, 3801 m, 3818 m, 3820 m, 3841 m, 3857 w, 3868 w, 3903 w.

2.3. *Synthesis of $[Cd_3(tartr)_3]_n$ (2)*

Cadmium acetate dihydrate $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.1332 g, 0.5 mmol) and L(+)-tartaric acid (0.075 g, 0.5 mmol) were dissolved in 10 mL deionized water. To this mixture triethyl amine (0.14 mL, 1 mmol) was added dropwise. The resultant transparent solution was poured into a 25 mL Teflon-lined stainless steel vessel and heated at 160°C for 72 h. After cooling the solution to room temperature colorless needle-shaped crystals were isolated by decanting the supernatant liquid. The isolated crystals were washed with deionized water, ethanol, and dried in air. Yield: 52%. Anal. Calcd for $C_{12}H_{12}Cd_3O_{18}$ (781.42): C, 18.44; H, 1.54. Found: C, 18.42; H, 1.57. IR (cm^{-1}): 834 w, 850 w, 902 m, 959 w, 1011 m, 1042 w, 1089 m, 1162 w, 1391 w, 1459 w, 1474 s, 1516 s, 1542 s, 1573 s, 1659 s, 1709 m, 1750 m, 1771 w, 1797 w, 1828 w, 1870 w, 2292 w, 3197 w, 3332 w, 3405 w, 3509 w, 3546 w, 3576 w, 3629 w, 3649 w, 3675 w, 3738 m, 3753 m, 3800 w, 3831 w, 3862 w, 3899 w. Two similar complexes have been reported earlier [8]; however, in this case the synthesis was different.

2.4. *X-ray crystallography*

Diffraction data for **1** and **2** were collected at room temperature on a Nonius DIP-1030H system equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing, and scaling of the data sets were carried out using Denzo [11] and Scalepack [11] programs. The structures were solved by using direct methods and subsequent Fourier analyses [12] and refined by full-matrix least-squares based on F^2 with all observed reflections [12]. Hydrogen atoms were placed at calculated positions with exception of those of water in **1**, which were fixed from the ΔF map. Hydrogen atoms of disordered water molecules in **2** were not located. All calculations were performed using the WinGX System, Ver 1.80.05 [13]. Crystal data as well as details of data collection and refinement are given in table 1.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. $[Cd(HnicO)(pyc)(H_2O)]_n$ (1). The X-ray analysis of **1** shows Cd in a highly distorted octahedral coordination sphere (figure 1) of two pyridine-4-carboxylates, two oxynicotinates, and a water. H_2nicO has enol-ketonic tautomerism and here the anion is in its keto form, stabilized upon coordination and hydrogen bonding, a feature usually found in solid state [14, 15]. The pyridine carboxylate is a bridging connector while the

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

	1	**2** $\cdot 0.75(H_2O)$
Empirical formula	$C_{12}H_{10}CdN_2O_6$	$C_{12}H_{12}Cd_3O_{18.75}$
Formula weight	390.62	793.42
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$C222_1$
Unit cell dimensions (Å)		
a	8.9120(10)	11.271(3)
b	16.166(2)	10.788(3)
c	9.6490(10)	30.697(5)
Volume (Å^3), Z	1390.1(3), 4	3732.5(16), 8
Calculated density (g cm^{-3})	1.866	2.824
Absorption coefficient (mm^{-1})	1.599	3.493
$F(000)$	768	3024
θ range (°)	2.46–28.26	2.61–24.71
Reflections collected	12,980	9111
Independent reflection	3158	2958
R_{int}	0.0480	0.0880
Number of reflections ($I > 2\sigma(I)$)	2596	1715
Number of refined parameters	196	313
Goodness-of-fit (F^2)	0.976	0.862
R_1, wR_2 ($I > 2\sigma(I)$)	0.0352, 0.0873	0.0418, 0.0685
Flack parameter	0.02(4)	0.02(5)
Residuals (e Å^{-3})	0.685, −0.383	0.686, −0.784

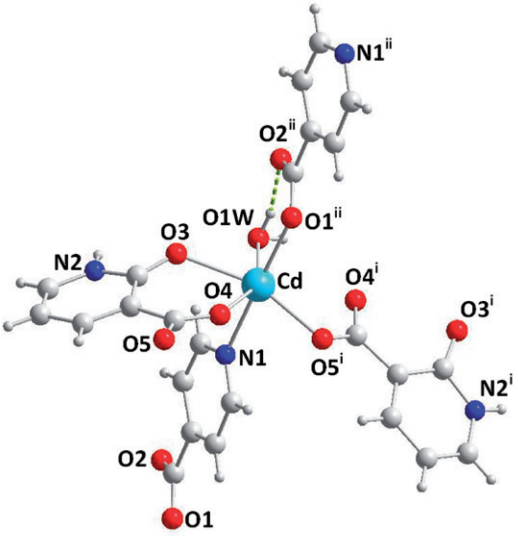

Figure 1. Coordination sphere about Cd with labeling scheme of non carbon atoms for **1** (symmetry codes: (i) $x + 1/2$, $-y + 3/2$, z; (ii) x, y, $z + 1$).

oxynicotinate chelates (through O(3) and O(4)) towards one Cd and monodentate (O(5)) to a symmetry related one with the distance of 2.311(3) and 2.336(4) Å, respectively. The oxynicotinates bridge two cadmiums through pyridine and an oxygen donor. These connections lead to a corrugated 2-D sheet structure, as shown in figure 2, having a 4,4 topology with metals at nodes and ligands at sides. The intermetallic

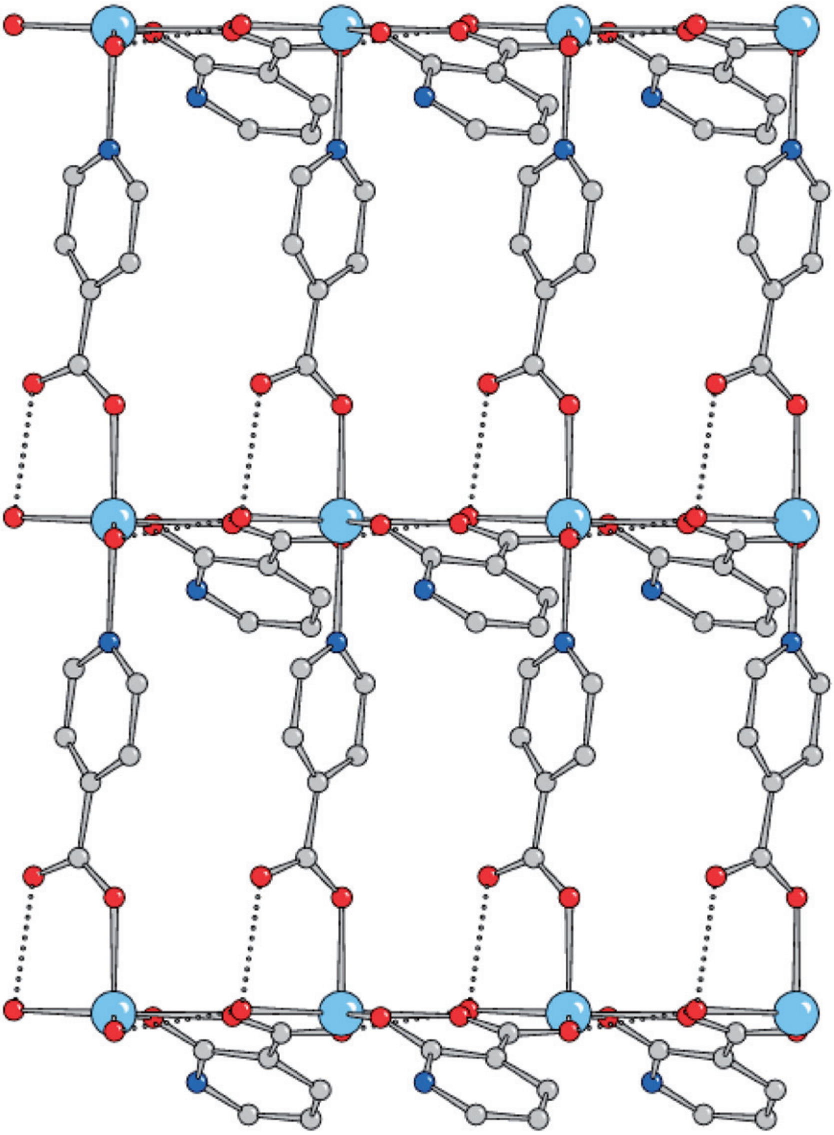

Figure 2. 2-D polymer in **1** viewed down the *b* axis showing intramolecular H-bonds.

distance is 4.9195(5) Å through the oxynicotinate and 9.649(1) Å through the pyridine-4-carboxylate. The 2-D arrangement is reinforced by intramolecular H-bond interactions having O1w as donor towards O2 (figure 2) and symmetry related O5. A peculiar feature of the structure is represented by the strong bending conformation (with respect to an expected linear coordination) assumed by the oxynicotinates, clearly evident from figure 3. The dihedral angle between the nicotinate ring and the O3/O4/O5/O1w equatorial plane is 33.92°. This arrangement is likely induced to favor formation of a strong H-bond between the protonated N2 and O2 of pyc (N···H distance of 2.771 Å) of the side layer giving rise to a 3-D architecture (figure 4).

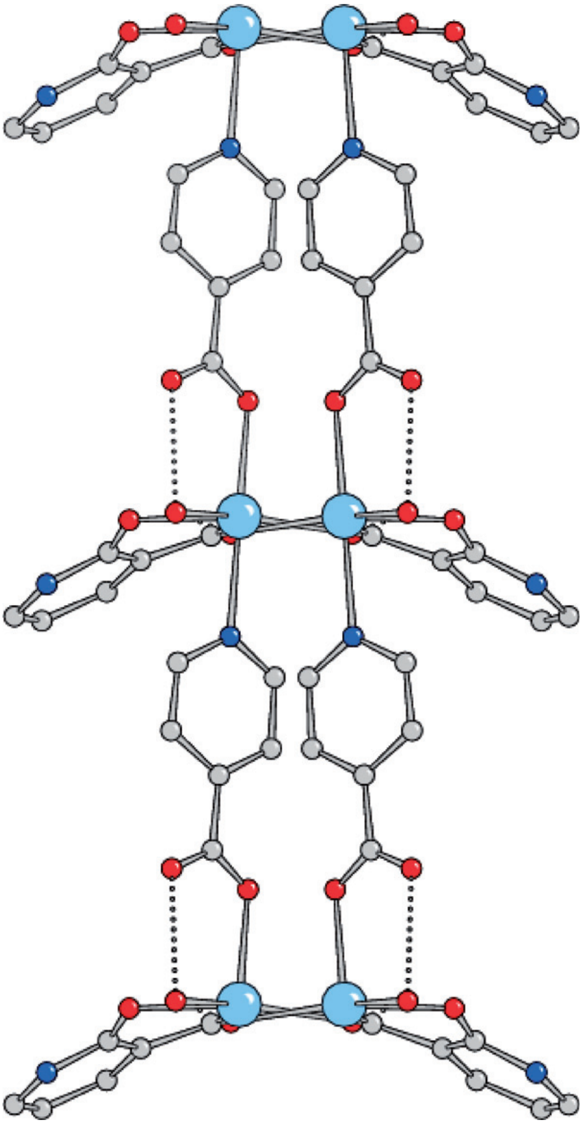

Figure 3. Strong bending conformation (with respect to an expected linear coordination) assumed by the oxynicotinates in **1**.

The structure does not have π–π stacking interactions. Selected bond lengths and angles of **1** are given in table 2.

3.1.2. $[Cd_3(tartr)_3]_n$ (2).

The structure comprises four crystallographically independent cadmium centers: two are located on general positions (Cd3, Cd4), two on the crystallographic two-fold axis (Cd1, Cd2), and three tartrates having an anti conformation of the carbon skeleton. The cadmiums have a distorted octahedral coordination sphere with Cd–O bond lengths that vary from 2.222(8) to 2.505(7) Å (table 3). Due to

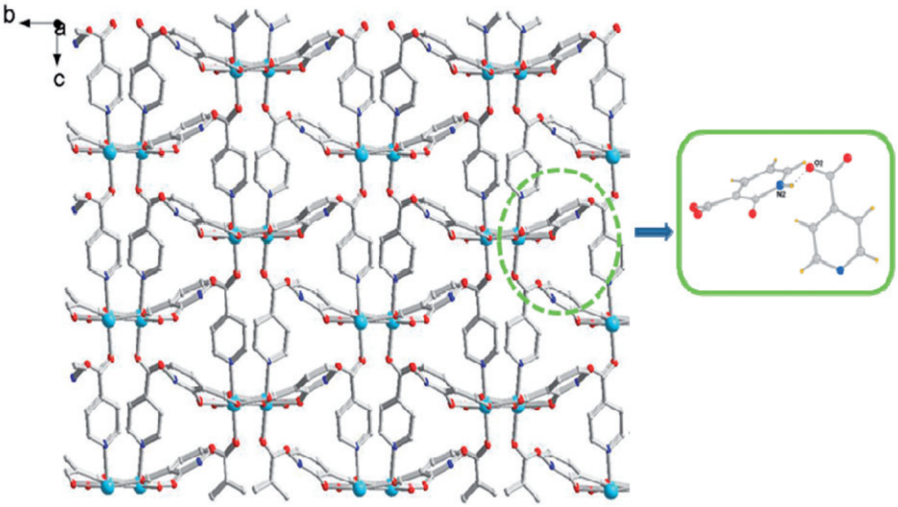

Figure 4. Packing of the 2-D layers giving origin to a 3-D architecture through N(2)–H···O interactions (shown with a slightly different orientation in the callout).

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cd–O(1^{ii})	2.279(7)	Cd–O(5^{i})	2.276(3)
Cd–O(3)	2.311(3)	Cd–O(1w)	2.327(4)
Cd–O(4)	2.336(4)	Cd–N(1)	2.384(9)
O(1^{ii})–Cd–O(3)	96.06(18)	O(3)–Cd–N(1)	84.8(2)
O(1^{ii})–Cd–O(4)	90.5(3)	O(4)–Cd–O(5^{i})	84.50(13)
O(1^{ii})–Cd–O(5^{i})	94.25(15)	O(4)–Cd–O(1w)	152.32(11)
O(1^{ii})–Cd–O(1w)	91.0(2)	O(4)–Cd–N(1)	91.3(3)
O(1^{ii})–Cd–N(1)	178.14(15)	O(5^{i})–Cd–O(1w)	122.91(13)
O(3)–Cd–O(4)	75.50(11)	O(5^{i})–Cd–N(1)	85.53(18)
O(3)–Cd–O(5^{i})	157.53(15)	O(1w)–Cd–N(1)	87.6(2)
O(3)–Cd–O(1w)	76.86(11)		

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

Table 3. Selected coordination bond lengths (Å) for **2**.

Cd(1)–O(8)/O(8^{i})	2.236(8)	Cd(2)–O(7)/O(7^{iv})	2.328(8)
Cd(1)–O(10^{ii})/O(10^{iii})	2.390(8)	Cd(2)–O(9)/O(9^{iv})	2.410(10)
Cd(1)–O(11^{ii})/O(11^{iii})	2.283(7)	Cd(2)–O(14)/O(14^{iv})	2.354(9)
Cd(3)–O(2)	2.284(9)	Cd(4)–O(1)	2.259(10)
Cd(3)–O(3)	2.320(8)	Cd(4)–O(4^{vi})	2.480(7)
Cd(3)–O(6^{v})	2.222(8)	Cd(4)–O(5^{vi})	2.249(7)
Cd(3)–O(12^{ii})	2.231(8)	Cd(4)–O(13^{vi})	2.298(7)
Cd(3)–O(16)	2.505(7)	Cd(4)–O(15^{vi})	2.467(8)
Cd(3)–O(18)	2.268(9)	Cd(4)–O(17^{vii})	2.259(9)

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

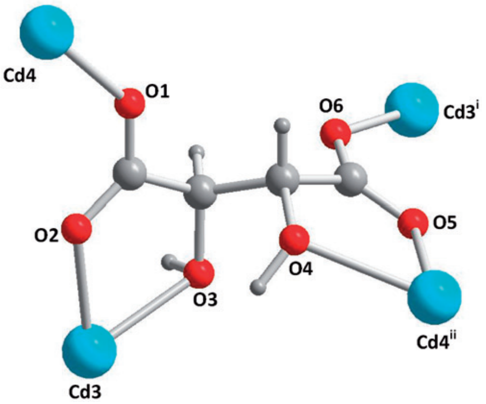

Figure 5. Coordination mode of one of the three independent tartrate anions in **2**. A similar pattern is applicable also to the other anions (symmetry codes: (i) $-x+3/2$, $y-1/2$, $-z+3/2$; (ii) $x+1/2$, $y-1/2$, z).

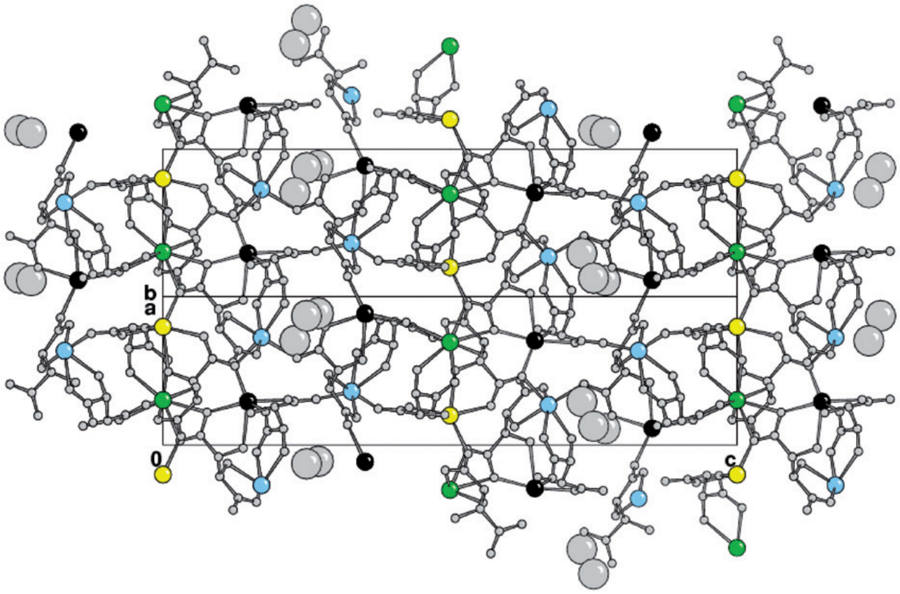

Figure 6. View normal to crystallographic [110] planes of the 3-D architecture of **2**. Cd1 yellow, Cd2 green, Cd3 light blue, Cd4 black, big spheres indicate lattice water molecules. (Available in color online.).

their conformational freedom, tartrates are polydentate ligands with coordination mode ($\eta^6\mu_4$), showing *bis* chelating behavior through hydroxyl groups and carboxylate oxygen atoms and monofunctional ligand with the other carboxylate oxygen atoms, thus connecting four cadmiums (figure 5). All the carboxylate oxygen atoms have an endo and exo coordination type. With the described linkages, the resulting crystal packing is a 3-D coordination network arrangement as illustrated in figure 6. The packing is reinforced by a H-bonding scheme through hydroxyl as H-bond donors. Two of these interactions are

Table 4. Hydrogen bonds parameters (Å) for **1** and **2**.

Complex **1**						
O1w–H1w	0.851	1.899	174.05	2.747	O5	$x+1, y, z$
O1w–H2w	0.848	1.816	165.92	2.647	O2	$x, y, z+1$
N2–H2	0.860	1.978	152.82	2.771	O2	$-x+1, -y+1, z+1/2$
Complex **2**						
O3–H3a	0.850	1.953	179.12	2.803	O5	$-x+3/2, y+1/2, -z+3/2$
O4–H4a	0.984	1.971	179.79	2.955	O16	
O10–H10a	0.916	1.823	177.97	2.739	O14	$x-1/2, -y+1/2, -z+1$
O15–H15a	1.028	1.578	160.94	2.572	O2	$x+1/2, y-1/2, z$
O16–H16a	0.864	2.060	130.56	2.703	O11	$x+1/2, y+1/2, z$

rather strong (O15···O2 and O16···O11 of 2.572 and 2.703 Å, respectively). Selected bond lengths and angles for **2** are given in table 3. Hydrogen bond parameters of **1** and **2** are listed in table 4.

Figure 6 shows the positions of the crystallographic independent metals: parallel to the ab-plane Cd1 and Cd2 ions form an almost coplanar metal layer that alternates with the layers comprising cadmium Cd3 and Cd4. One of the independent tartrates (i.e., C1–C4 of figure 5) connect only Cd3 and Cd4, building a structure as indicated in figure 7.

A search in CCDC allowed to retrieve Cd tartrate polymorphs of different stoichiometry containing a varied amount of water, $[\mathrm{Cd(tartr)}]\cdot 5\mathrm{H_2O}$ [9a,b], $[\mathrm{Cd_2(tartr)_2(H_2O)}]\cdot 3\mathrm{H_2O}$ [9c,d] and $[\mathrm{Cd_3(tartr)_3}]\cdot x\mathrm{H_2O}$ [10a,b]. All these are 3-D structures with polydentate behavior of the anion. The present crystal structure is isomorphous with that of the previously reported compounds [10], indicating that enantiomerically pure tartrate salts of Cd are inclined to include water in their unit cells, but in different quantity affected by crystallization conditions. Compound **2** was initially regarded as an anhydrous salt of the naturally occurring form of the L-(+)-tartaric acid. However, a small void corresponding to 7% (259.0 Å^3) of the unit cell was detected as potentially available area for solvent and two small residuals in the Fourier map were successfully refined as water oxygen atoms with occupancy factor of 0.5 and 0.25 (the latter located on a two-fold axis), based on the respective electron density height, thus 0.75 per unit formula.

Two isomorphous structures were reported as dehydrated [10a] and with a content of water of 0.50 per unit formula [10b]. Since in the former the excellent final R factors [$R_1=0.0287$, $wR_2=0.0547$] support the presence of no residuals in the electron density map, the void of 6.5% of the unit cell volume still indicates a porous structure capable to include a small amount of water between 0.75 (found in **2**) and 0.50 [10b]. Table 5 reports the comparison among the cell volumes and voids in these structures showing a linear trend between the unit cell volumes and the void cavities in the 3-D architecture.

3.2. *TGA study*

Thermogravimetric analysis of **1** was done from 30°C to 800°C under flowing N_2 at a heating rate of 10°C min^{-1}. The TGA curve is given in "Supplementary material." The TG profile shows that deaquation takes place from 140°C to 160°C (experimental mass

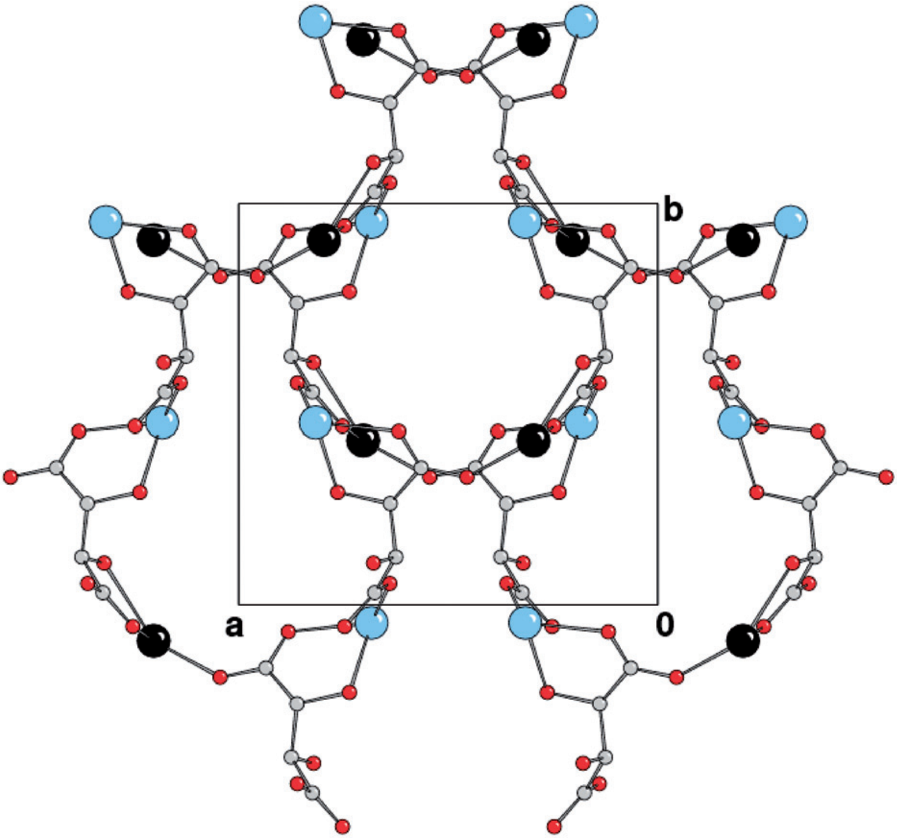

Figure 7. The 2-D arrangement formed by Cd3 and Cd4 parallel to the *ab*-plane in **2**.

Table 5. Comparison of unit cell of **2** with that of the isomorphous structures reported.

	2	Ref. [8a]	Ref. [8b]
Cell volume (Å^3)	3732.5	3710.5	3696.4
Unit cell void (Å^3)	259.0	241.4	195.1
% void	6.9	6.5	5.3
Water per unit formula [$Cd_3(tartr)_3$]	0.75	–	0.50

loss *ca* 4% and Calcd, *ca* 4.6%). Then in the temperature range 330–620°C complete decomposition of the complex takes place with formation of cadmium oxide.

3.3. *Luminescence study*

Emission spectra of ligand and **1** have been studied at room temperature (Supplementary material). For free pycH, the strongest emission is found at 370 nm

($\lambda_{ex} = 280$ nm), whereas for the complex a strong emission is observed at 380 nm when excited at 307 nm. Emission of **1** is very similar to the free pycH ligand transition and may be predominantly ligand-centered electronic transitions perturbed by coordination to Cd^{+2} ions. This observation suggests that **1** will be a potential photoactive material [16].

4. Summary

We report two luminescent cadmium carboxylate coordination polymers. The former is built up by pyridine-4-carboxylate and oxynicotinate where oxynicotinate displays unusual bending conformation in the crystal packing likely to favor a hydrogen bonding scheme giving a 3-D network. The emission spectral behavior is ligand centered. The second complex is a 3-D tartrate salt where the ligand is polydentate showing $\eta^6\mu_4$ coordination with the formation of small voids occupied by disordered water molecules. A small but different content of lattice water was observed in the present reinvestigation compared to the previous reports of polymorph Cd tartrate salts, a feature likely affected by the crystallization conditions.

Supplementary material

CCDC-820607 and CCDC-820610 contains the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: 44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

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