



Supramolecular architecture of cadmium(II)–terephthalate complexes having a tridentate or tetradentate Schiff base as blocking coligand

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Abstract

Two new cadmium(II)–terephthalate complexes, $\infty^1\{[\text{Cd}_2(\mu\text{-terephthalate})_2(\text{L}^1)_2] \cdot 9\text{H}_2\text{O}\}$ (**1**) and $\{[\text{Cd}(\text{H}_2\text{O})(\text{L}^2)]_2(\mu\text{-terephthalate})\}(\text{terephthalate}) \cdot 10\text{H}_2\text{O}$ (**2**), where $\text{L}^1 = (E)\text{-}N^1,N^1\text{-diethyl-}N^2\text{-}(1\text{-pyridin-2-yl)ethylidene)ethane-1,2\text{-diamine}$; $\text{L}^2 = N,N'\text{-bis-}(1\text{-pyridin-2-yl-ethylidene)ethane-1,2\text{-diamine}$; terephthalate = benzene-1,4-dicarboxylate $^-\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2^-$) have been synthesized by a conventional solution method. Characterization by single crystal X-ray crystallography shows that compound **1** is composed of 1-D polymeric zig-zag chains with distorted pentagonal-bipyramidal cadmium centers. Compound **2** consists of centrosymmetric dinuclear complexes with a distorted pentagonal-bipyramidal cadmium center in which one terephthalate ligand bridges the metal centres and another terephthalate anion with water of crystallization forms a H-bonding network.

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Keywords: Cadmium(II); Terephthalate; Schiff base; Crystal structures; Coordination polymer

1. Introduction

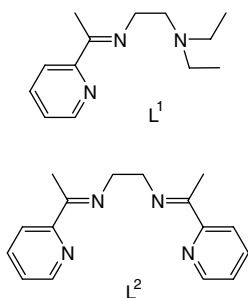
Metal-organic coordination frameworks (coordination polymers) with various intriguing topologies have been extensively studied for their versatile chemical and physical properties and potential applications in functional materials [1–9]. The combination of metal–ligand coordination and non-covalent interactions, such as hydrogen bonding, provides a powerful method for creating complex structures from simple building blocks [10–13]. In addition, the π -interactions and host–guest solvent interactions offer the propensity for packing control in the solid crystalline state [14–17]. Usually bi- or multidentate ligands containing N or O donors, e.g., 4,4'-bipyridine, azide, pyrazine, 4,4'-trimethylenedi-

pyridine and polyaromatic acids, etc., are used to bridge metal centres [18–22]. Multi-carboxylic ligands with suitable spacers are good choices as building blocks, especially benzoic acid based ligands [23,24]. As an example, terephthalates (ta) have been used in many synthetic systems because they can form short bridges via one carboxylate end or long bridges via the benzene ring, leading to a great variety of structures [25,26]. Among the metal ions, Cd(II) coordination polymers with terephthalate have varying topologies as the metal coordination number can be expanded up to seven and the directional property of the coordination bond is somewhat relaxed by the absence of any crystal field stabilization energy in the d^{10} electronic configuration [27–29]. The terminal or blocking co-ligands, which are usually used along with the bridging ligand to complete the metal coordination sphere, can alter the supramolecular assembly and consequently the type of structure formed. The literature data show that for

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cadmium–terephthalate systems either monodentate or chelating bidentate terminal ligands have been used [26,27]. Only one compound has been reported with a tetradentate terminal ligand and the resulting compound is mononuclear [30]. No compound with a tridentate blocking ligand is reported to date. Schiff base type ligands are easily prepared, highly variable and offer a good control on the metal coordination sphere by occupying a square plane of an octahedron or trigonal plane of a trigonal bipyramid and leaving the axial bonding sites free for the desired extended coordination [31,32].

In this paper, we report the synthesis of two complexes of cadmium terephthalate using a tridentate (L^1) and a tetradentate (L^2) terminal Schiff base type ligand by the conventional solution method and their crystal structure analyses.



2. Experimental

2.1. Materials and physical measurements

Commercially available solvents, 2-acetyl-pyridine, N,N' -diethylethylenediamine, ethylenediamine, cadmium acetate dihydrate and sodium terephthalate were used without further purification. Elemental analyses were carried out using a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded in KBr (4500–500 cm^{-1}) using a Perkin–Elmer R XI FT-IR spectrophotometer. The thermal analyses (TG-DTA) were carried out on a Mettler Toledo TGA/SDTA 851 thermal analyser in a dynamic atmosphere of dinitrogen (flow rate: 30 $\text{cm}^3 \text{min}^{-1}$). The sample was heated in an alumina crucible.

2.2. Preparations

2.2.1. (*E*)- N^1,N^1' -diethyl- N^2 -(1-(pyridin-2-yl)-ethylidene)-ethane-1,2-diamine (L^1)

N,N' -diethylethylenediamine (1.74 g, 15 mmol) and 2-acetylpyridine (1.815 g, 15 mmol) in a 1:1 molar ratio were refluxed in 30 mL of dry methanol for 4 h. The resulting solution was evaporated under reduced pressure to obtain a yellow semi-solid mass. The mass was then extracted thrice ($3 \times 10 \text{ mL}$) with *n*-hexane which

on slow evaporation gave a pale yellow product. Yield: 2.792 g (85%). *Anal. Calc.* for $\text{C}_{13}\text{H}_{21}\text{N}_3$: C, 71.23; H, 9.58; N, 19.17. Found: C, 71.10; H, 9.75; N, 19.02%. IR (ν/cm^{-1}): 1648 ($\nu_{\text{C}=\text{N}}$).

2.2.2. N,N' -bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine (L^2)

This ligand was prepared by a procedure similar to that for L^1 , by starting with ethylenediamine (0.9 g, 15 mmol) and 2-acetyl-pyridine (3.639 g, 30 mmol) in a 1:2 molar ratio to obtain a yellow liquid. Light yellow microcrystals were obtained by recrystallization from *n*-hexane. Yield: 90%. *Anal. Calc.* for $\text{C}_{16}\text{H}_{18}\text{N}_4$: C, 72.22; H, 6.75; N, 21.09. Found: C, 72.05; H, 6.88; N, 21.01%. IR (ν/cm^{-1}): 1681 ($\nu_{\text{C}=\text{N}}$).

2.2.3. Catena-poly[bis{ $(\mu$ -terephthalato- $\kappa^4 O^1, O^{1'}:O^4, O^{4'})$ -(*E*)- N^1,N^1' -diethyl- N^2 -(1-(pyridin-2-yl)ethylidene)-ethane-1,2-diamine)-cadmium (II)}nonahydrate], $\infty^1 \{ [\text{Cd}_2(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)_2 \{ 2\text{-C}_5\text{H}_4\text{N-C}(\text{CH}_3) = \text{N-CH}_2\text{CH}_2\text{-N}(\text{C}_2\text{H}_5)_2 \}_2] \cdot 9\text{H}_2\text{O} \}$ (**1**)

A methanolic solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.532 g, 2 mmol) and a hot methanolic solution (10 ml) of ligand L^1 (0.438 g, 2 mmol) were added to an aqueous solution of sodium terephthalate (0.42 g, 2 mmol) with constant stirring. The resulting solution was filtered and the filtrate allowed to stand at room temperature for two days to yield colorless plate-like crystals. Yield: 1.976 g (87%). *Anal. Calc.* for $\text{C}_{42}\text{H}_{68}\text{Cd}_2\text{N}_6\text{O}_{17}$: C, 43.72; H, 5.94; N, 7.28. Found: C, 43.54; H, 5.65; N, 7.36%. IR (ν/cm^{-1}): 3410 (br, $\nu_{\text{H}_2\text{O}}$), 1572 and 1398 (ν_{CO_2}), 1653 ($\nu_{\text{C}=\text{N}}$).

2.2.4. [Di-aqua-bis{ N,N' -bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine}(μ -terephthalato- $\kappa^4 O^1, O^{1'}:O^4, O^{4'})$ -di-cadmium(II)]-terephthalate decahydrate, $[\{ \text{Cd}(\text{H}_2\text{O})_2 \{ 2\text{-C}_5\text{H}_4\text{N-C}(\text{CH}_3) = \text{N-CH}_2\text{CH}_2\text{-N}(\text{C}_2\text{H}_5)_2 \}_2 \} (\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)] (\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2) \cdot 10\text{H}_2\text{O}$ (**2**)

The title compound was prepared by a similar procedure as for **1** using ligand L^2 (0.532 g, 2 mmol) to give colorless crystals. Yield: 1.106 g (85%). *Anal. Calc.* for $\text{C}_{24}\text{H}_{34}\text{Cd}_2\text{N}_4\text{O}_{10}$: C, 44.24; H, 5.26; N, 8.61. Found: C, 44.30; H, 5.11; N, 8.75%. IR (ν/cm^{-1}): 3410 (br, $\nu_{\text{H}_2\text{O}}$), 1570 and 1381 (ν_{CO_2}), 1654 ($\nu_{\text{C}=\text{N}}$).

2.3. X-ray crystallography

Diffraction data was collected at $T = 293(2) \text{ K}$ for **1** and at $T = 227(2) \text{ K}$ for **2** by the ω -scan method with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and the use of a graphite monochromator on a Bruker AXS CCD diffractometer. Data collection and cell refinement were done with SMART [33], data reduction with SAINT [33]. An experimental absorption correction was performed with SADABS [34]. The structure was solved by direct

methods (SHELXS-97) [35]; refinement was done by full-matrix least-squares on F^2 using the SHELXL-97 program suite [35]. All non-hydrogen positions were found and refined with anisotropic temperature factors. In **1** and **2** the hydrogen atoms were calculated with appropriate riding models (AFIX 43 for aromatic hydrogens on pyridine and terephthalate, AFIX 23 for CH_2 , AFIX 33 for CH_3) and $U_{\text{eq}(\text{H})} = 1.2 U_{\text{eq}(\text{C})}$ for CH and CH_2 and $U_{\text{eq}(\text{H})} = 1.5 U_{\text{eq}(\text{C})}$ for CH_3 . In **1** the hydrogen atoms on the oxygen atoms of water of crystallization (nine disordered oxygen atoms per formula unit) were neither found nor calculated. In **2** the hydrogen atoms on the aqua ligand and solvent water molecules were found and refined with $U_{\text{eq}(\text{H})} = 1.5 U_{\text{eq}(\text{O})}$. In **1** and **2** the five and six strongest peaks, respectively, of the residual electron density are in the near vicinity (within 1.0 Å) of the cadmium atom. Graphics were computed with DIAMOND [36]. Supramolecular interactions (hydrogen bonds, C–H... π contacts) were calculated with PLATON for windows [37–39]. For complex **1** the quality of the overall crystallographic refinement is not too good, due to

incorporated and disordered water of crystallization. The water of crystallization (nine H_2O per formula unit) is not discussed further nor included in the figures below for reasons of clarity. The metal–ligand moiety could be clearly refined, however. Crystal data are listed in Table 1 and bond angles in Tables 2 and 3 for complexes **1** and **2**, respectively.

3. Results and discussions

3.1. IR spectra

For complexes **1** and **2** strong absorption bands appear at 1572 and 1570 cm^{-1} for the asymmetric stretching and 1398 and 1381 cm^{-1} for the symmetric stretching of the carboxylate groups, respectively. The binding modes of the carboxylate ligands can be accessed on the basis of the difference (Δ) between the asymmetric stretching $\nu_{\text{a}}(\text{CO}_2^-)$ and symmetric stretching $\nu_{\text{s}}(\text{CO}_2^-)$ [40]. The Δ value for **1** is 174 cm^{-1} and for

Table 1
Crystal data for complexes **1** and **2**

Complex	1	2
Formula	$\text{C}_{42}\text{H}_{50}\text{Cd}_2\text{N}_6\text{O}_{17}^{\text{a}}$	$\text{C}_{24}\text{H}_{34}\text{CdN}_4\text{O}_{10}$
M (g mol^{-1})	1135.70 ^a	650.95
Crystal size (mm)	$0.26 \times 0.14 \times 0.06$	$0.19 \times 0.14 \times 0.09$
θ Range ($^\circ$)	2.18–26.10	1.77–28.86
h,k,l range	–25,25; –17,17; –23,22	–15,14; –16,16; –16,16
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	20.668(7)	11.522(2)
b (Å)	14.172(5)	12.089(2)
c (Å)	18.985(6)	12.567(2)
α ($^\circ$)	90.00	108.139(3)
β ($^\circ$)	106.121(5)	94.999(3)
γ ($^\circ$)	90.00	117.517(3)
V (Å ³)	5342(3)	1418.7(5)
Z	4	2
D_{calc} (g cm^{-3})	1.412	1.524
$F(000)$	2304 ^a	668
μ (mm^{-1})	0.864	0.829
Max/minimum transmission	0.9500/0.8065	0.9291/0.8584
Reflections collected	41 335	13 011
Independent reflections (R_{int})	10 571 (0.0801)	6691 (0.0190)
Observed reflections [$I > 2\sigma(I)$]	5668	5448
Parameters refined	615	388
Maximum/minimum $\Delta\rho^{\text{b}}$ (e \AA^{-3})	1.048/–0.808	1.280/–0.724
R_1/wR_2^{c} [$I > 2\sigma(I)$]	0.0610, 0.1492	0.0334, 0.0670
R_1/wR_2^{c} (all data)	0.1385, 0.2020	0.0449, 0.0715
Goodness-of-fit on F^2^{d}	1.030	1.082
Weight scheme w ; a/b^{e}	0.0961/0.1243	0.0311/0.0000

^a Hydrogen atoms on the oxygen atoms of the water of crystallization (nine disordered oxygen atoms per formula unit) were neither found nor calculated and, hence, are not included in the chemical formula, molar mass M or in $F(000)$.

^b Largest difference peak and hole.

^c $R_1 = [\sum(|F_o| - |F_c|)] / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

^d Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$.

^e $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$.

Table 2
Selected distances (Å) and angles (°) for **1**

Cd1–O2	2.255(5)
Cd1–N2	2.276(6)
Cd1–O6	2.280(6)
Cd1–N1	2.358(7)
Cd1–N3	2.373(7)
Cd1–O1	2.622(6)
Cd1–O5	2.653(6)
Cd2–O8 ⁴	2.253(6)
Cd2–N5	2.286(7)
Cd2–O3	2.331(6)
Cd2–N4	2.377(7)
Cd2–N6	2.430(7)
Cd2–O4	2.508(6)
Cd2–O7 ⁴	2.638(8)
O2–Cd1–N2	133.1(2)
O2–Cd1–O6	92.6(2)
N2–Cd1–O6	129.7(2)
O2–Cd1–N1	94.0(2)
N2–Cd1–N1	69.9(2)
O6–Cd1–N1	90.7(2)
O2–Cd1–N3	109.5(3)
N2–Cd1–N3	76.4(2)
O6–Cd1–N3	111.3(3)
N1–Cd1–N3	146.2(2)
O2–Cd1–O1	52.3(2)
N2–Cd1–O1	81.5(2)
O6–Cd1–O1	143.3(2)
N1–Cd1–O1	82.7(2)
N3–Cd1–O1	92.7(2)
N3–Cd1–O1	92.7(2)
O2–Cd1–O5	143.8(2)
N2–Cd1–O5	82.1(2)
O6–Cd1–O5	51.5(2)
N1–Cd1–O5	91.3(2)
N3–Cd1–O5	83.8(2)
O1–Cd1–O5	163.6(2)
O8 ⁴ –Cd2–N5	131.5(3)
O8 ⁴ –Cd2–O3	84.21(3)
N5–Cd2–O3	144.0(3)
O8 ⁴ –Cd2–N4	116.7(3)
N5–Cd2–N4	69.5(3)
O3–Cd2–N4	91.3(2)
O8 ⁴ –Cd2–N6	93.1(3)
N5–Cd2–N6	73.6(3)
O3–Cd2–N6	115.3(3)
N4–Cd2–N6	142.4(2)
O8 ⁴ –Cd2–O4	132.7(3)
N5–Cd2–O4	94.2(3)
O3–Cd2–O4	53.4(2)
N4–Cd2–O4	87.3(2)
N6–Cd2–O4	88.3(2)
O8 ⁴ –Cd2–O7 ⁴	49.7(2)
N5–Cd2–O7 ⁴	84.7(3)
O3–Cd2–O7 ⁴	126.1(3)
N4–Cd2–O7 ⁴	87.8(3)
N6–Cd2–O7 ⁴	95.9(4)
O4–Cd2–O7 ⁴	175.1(3)

Symmetry transformations: ⁴ = $x - 2, -y + 3/2, z - 1/2$.

2 is 189 cm⁻¹. The separation is consistent with binding modes as found in the structural analysis. The broad band in the region of 3410 cm⁻¹ for both complexes could be assigned to the stretching vibration of the water

Table 3
Selected distances (Å) and angles (°) for **2**

Cd–O10	2.254(2)
Cd–N3	2.368(2)
Cd–N2	2.373(2)
Cd–N4	2.391(2)
Cd–N1	2.402(2)
Cd–O1	2.4318(16)
Cd–O2	2.4579(16)
O10–Cd–N3	107.98(9)
O10–Cd–N2	94.28(9)
N3–Cd–N2	70.96(7)
O10–Cd–N4	84.36(7)
N3–Cd–N4	67.84(7)
N3–Cd–N4	136.01(7)
O10–Cd–N1	82.88(8)
N3–Cd–N1	138.30(7)
N2–Cd–N1	68.10(7)
N4–Cd–N1	153.63(8)
O10–Cd–O1	113.05(10)
N2–Cd–O1	136.20(6)
N4–Cd–O1	82.36(6)
N1–Cd–O1	81.57(6)
O10–Cd–O2	164.95(9)
N3–Cd–O2	86.83(7)
N2–Cd–O2	93.15(6)
N4–Cd–O2	99.25(6)
N1–Cd–O2	87.79(6)
O1–Cd–O2	53.58(5)

molecules involved in hydrogen bonding. The imine (C=N) vibration appears at 1653 and 1654 cm⁻¹ for complexes **1** and **2**, respectively.

3.2. Description of the structures

Compound **1** is a 1D polymeric zig-zag chain. Two crystallographically different cadmium centers (Cd1 and Cd2 along with their ligands) alternate along the chain (Fig. 1).

Each cadmium atom is coordinated by three nitrogen donors from the tridentate chelating (neutral) (*E*)-*N*¹, *N*¹-diethyl-*N*²-(1-(pyridin-2-yl)ethylidene)ethane-1,2-diamine ligand and four oxygen donors from two bis-bidentate bridging (crystallographically different)

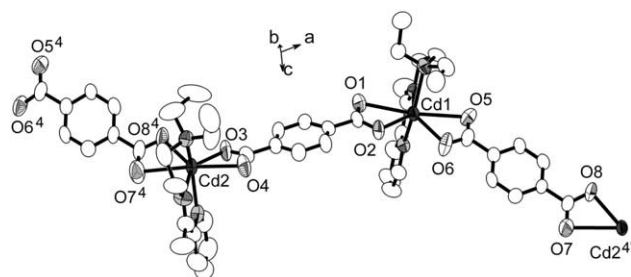


Fig. 1. Short chain segment of **1** with the two different cadmium centers. Symmetry transformations: ⁴ = $x - 2, -y + 3/2, z - 1/2$; ^{4'} = $x - 1, -y + 3/2, z + 1/2$.

terephthalate ligands. The coordination environment around cadmium can be described as a distorted trigonal bipyramid (Figs. 2 and 3). The repeat unit along the chain encompasses four cadmium centers (Fig. 4).

There is no element of helicity along the chain propagation axis. The chains do not run along the 2_1 -crystallographic axes (parallel to the b -axis) but perpendicular to the b -axis. All chains are parallel to each other (Fig. 5). Neighbouring chains can be thought of as stacked in planes coplanar with the ac -plane. Along the b -axis these “planes” are shifted with respect to each other (Fig. 5). The space in-between neighbouring chains – visible in the space-filling representation in

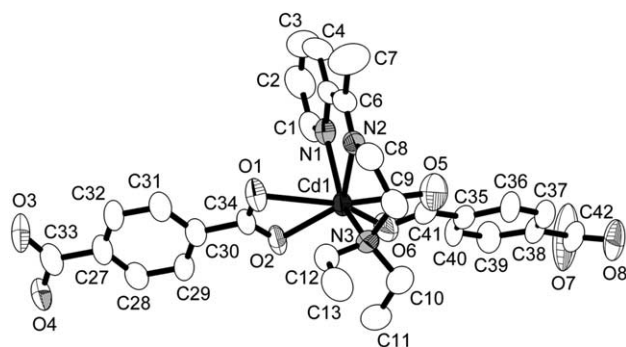


Fig. 2. Coordination environment around Cd1 in **1**; 50% thermal ellipsoids. Symmetry transformation: $^4 = x - 2, -y + 3/2, z - 1/2$.

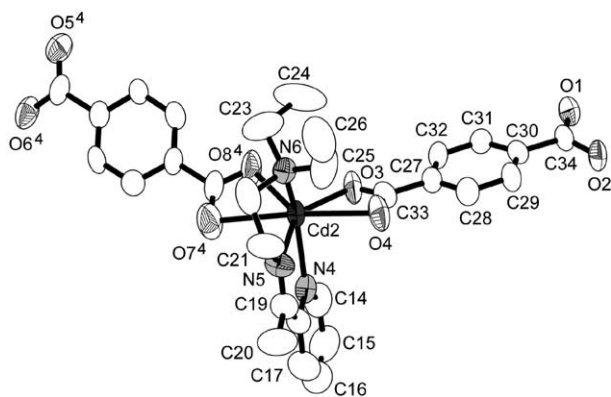


Fig. 3. Coordination environment around Cd2 in **1**; 50% thermal ellipsoids. Symmetry transformation: $^4 = x - 2, -y + 3/2, z - 1/2$.

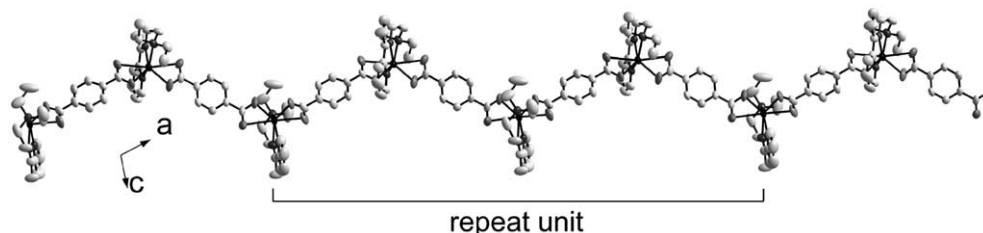


Fig. 4. Longer chain segment of **1** showing the repeat unit of four cadmium centers.

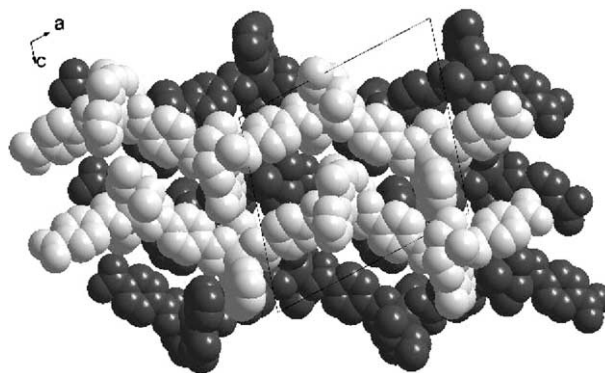


Fig. 5. Packing diagram for the parallel chains (space-filling representation) in **1** with the unit-cell outline included. Chains in different “planes” are differentiated by dark and light grey shading.

Fig. 5 – is filled by water molecules of crystallization (nine H_2O molecules per formula unit). The water arrangement cannot be discussed in more detail because neither could a certain disorder of the oxygen atoms be clearly resolved nor the hydrogen atoms be determined. There are no π - π interactions discernable in the inter-chain packing in **1**. The shortest centroid-centroid contact for two almost parallel aromatic rings (interplanar angle 8.9°) is found between the pyridyl moieties on the two different Cd1 and Cd2 centers in adjacent chains (symmetry relation $-x, -1/2 + y, 1/2 - z$ or $-x, 1/2 + y, 1/2 - z$). The centroid-centroid contact of 5.36 \AA together with the “slip angle” between the centroid-centroid vector and the normal to the plane of $\sim 50^\circ$ excludes any meaningful π -overlap (see below) [14h].

With respect to the Cd-terephthalate zigzag chain structure in **1**, similar chains with bis-bidentate benzene-1,4-dicarboxylate (bdc) bridges are found in $\infty^1[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ [26] and $\infty^1\{[\text{Cd}(\mu\text{-bdc})(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O}\}$, both with an interchain hydrogen-bonding network [41], or in $\infty^3\{[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{Cd}(\mu\text{-bdc})\text{Cl}] \cdot 2\text{H}_2\text{O}\}$ as part of a 3D framework with bridging chloro ligands [27d]. Other terephthalato-bridged cadmium coordination polymers contain tetrakis-monodentate ligands in $\infty^3[\text{Cd}(\mu_4\text{-bdc})_{1/2}\text{Cl}(1,10\text{-phen})]$ [27c] or bis-tridentate terephthalato ligands in $\infty^3[\text{Cd}(\mu_4\text{-bdc})(\text{pyridine})]$

[27a], bridging between four cadmium ions as part of a 3D framework. Noteworthy, the last two structures have been obtained through hydrothermal reactions of 1,4-dicyanobenzene by its slow hydrolysis into terephthalic acid.

Compound **2** consists of centrosymmetric dinuclear (“dimeric”) and cationic complexes with each of the two (symmetry related) cadmium atoms being coordinated by the tetradentate chelating *N,N'*-bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine ligand and an aqua ligand (Fig. 6). The terephthalato ligand bridges between the two cadmium atoms utilizing all of its four oxygen donor atoms. Both of the two carboxylate oxygen atoms coordinate to a cadmium atom with equal

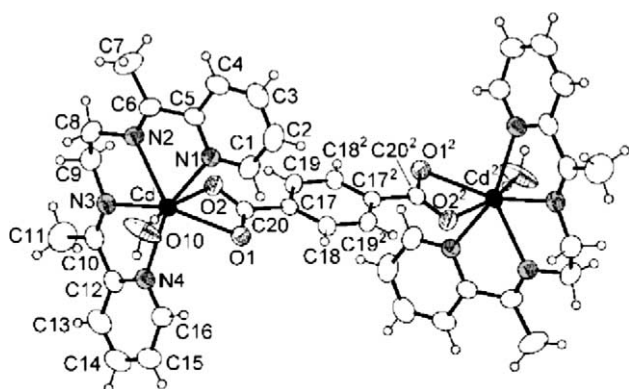


Fig. 6. Molecular structure of the centrosymmetric cationic dinuclear complex of **2**; 50% thermal ellipsoids. Symmetry transformation: $^2 = -x + 1, -y + 2, -z$.

Cd–O bond lengths to give a four-membered chelate ring. Thus, each cadmium atom is coordinated by four nitrogen and three oxygen donors in what could be described as a distorted pentagonal bipyramid. The atoms O10–Cd–O2, which form the largest angle (165°) around Cd, present the axis of the bipyramid. The distorted pentagonal plane is formed by Cd–N1–N2–N3–N4–O1 (the largest deviation from that plane is 0.66 \AA). From the plane formed by the nitrogen chelating ligand with the metal (Cd–N1–N2–N3–N4), the largest deviation would be 0.21 \AA and the axis Cd–O1 would form an angle of 39.4° with that plane. The center of the bridging terephthalate ligand is also a center of inversion which renders the two halves of the dinuclear complex symmetry equivalent.

The dinuclear complex still has a single positive charge which is balanced by a “free”, that is, hydrogen-bonded terephthalate anion. The dinuclear complexes form layers parallel to the *ac*-plane of the crystal lattice (Fig. 7). In between, that is sandwiched by the complex layers, are the terephthalate anions together with the water molecules of crystallization. The hydrogen-bonding network, where the aqua ligand and the carboxylate oxygen atoms of the bridging terephthalato ligand also participate, is shown in Fig. 7. Details of the hydrogen-bonding interactions are listed in Table 4.

The intermolecular packing between the complexes of **2**, within the layers formed parallel to the *ac*-plane, shows a rather strong π -stacking interaction [14h] between the parallel (because they are symmetry related) pyridyl planes of N4–C12–C13–C14–C15–C16 with a slip angle of 20.3° , a vertical displacement between the

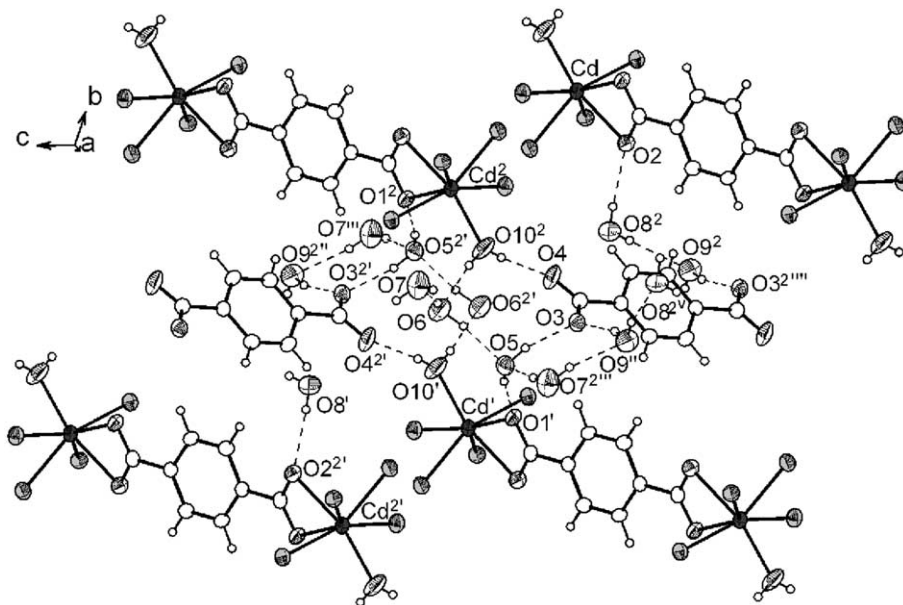


Fig. 7. Hydrogen bonding interaction in **2**. For clarity only the nitrogen atoms of the chelate ligand are shown; 40% thermal ellipsoids; symmetry transformations: $^1 = x, y - 1, z$; $^2 = x, y - 1, z - 1$; $^3 = x - 1, y, z$; $^4 = -x + 1, -y + 2, -z + 1$; $^5 = -x + 1, -y + 1, -z + 1$; $^6 = -x + 1, -y + 2, -z + 2$; $^7 = -x + 2, -y + 1, -z + 1$; $^8 = -x + 1, -y + 1, -z$; $^{2b} = -x + 2, -y + 2, -z + 1$.

Table 4
Hydrogen bonding interactions in **2**

D–H...O	D–H (Å)	H...O (Å)	D...O (Å)	D–H...O (°)
O5–H5A...O3	0.87(3)	1.85(3)	2.700(3)	166(3)
O5–H5B...O1'	0.87(3)	1.97(4)	2.835(3)	170(3)
O6–H6A...O7	0.90(4)	1.94(4)	2.813(4)	164(4)
O6–H6B...O5	0.93(4)	1.88(4)	2.774(3)	161(4)
O7'''–H7D...O9 ^{2''}	0.84(4)	2.14(4)	2.947(4)	159(4)
O7–H7E...O5 ^{2'''}	0.83(4)	2.03(4)	2.855(3)	172(4)
O8–H8C...O2 ²	0.78(4)	2.05(4)	2.830(3)	175(4)
O8–H8D...O9	0.71(3)	2.12(3)	2.809(4)	166(5)
O9''–H9C...O3	0.87(4)	1.87(4)	2.708(3)	163(4)
O9''–H9D...O8 ^{2v}	0.72(4)	2.09(4)	2.792(3)	163(5)
O10–H10A...O4 ²	0.78(4)	1.88(4)	2.648(3)	166(5)
O10–H10B...O6 ²	0.78(4)	1.96(4)	2.736(3)	173(5)

D, donor, H, hydrogen bond acceptor; symmetry relations: ' = $x, y - 1, z$; '' = $x, y - 1, z - 1$; ''' = $x - 1, y, z$; ² = $-x + 1, -y + 2, -z + 1$; ^{2''} = $-x + 1, -y + 2, -z + 2$; ^{2'''} = $-x + 2, -y + 1, -z + 1$; ^{2v} = $-x + 2, -y + 2, -z + 1$.

ring centroids of 1.3 Å, a centroid separation of 3.76 Å and an interplanar separation of 3.53 Å. In comparison the pyridyl planes of N1–C1–C2–C3–C4–C5 exhibit no π -interaction because of their very large slip angle of 37.5°, despite an interplanar distance of 3.60 Å. The symmetry related pyridyl planes of N1 have a vertical displacement between the ring centroids of 2.75 Å (centroid separation 4.53 Å) [14h,42–47]. π -Interactions with rather long centroid–centroid distances >3.9 Å, large slip angles (>30°) and vertical displacements (>2.0 Å) between the ring centroids are very weak to negligible.

To the best of our knowledge, among the plethora of terephthalate bridged architectures compound **2** is only the second example where one dicarboxylate ligand joins the metal centers through coordination bonds while a second dicarboxylate anion connects through H-bonds. Here, the terephthalate anions have both a discrete coordination and a H-bonding role in the supramolecular framework construction. The other example is [$\{Zn(tmtsc)(OH_2)\}_2(\mu\text{-terephthalate})(\text{terephthalate}) \cdot 2H_2O$] [tmtsc = 1,1,4-trimethylthiosemicarbazide] [48]. Also, a copper complex, $[Cu_2(2,2'\text{-bipy})_4(\mu\text{-terephthalate})(\text{terephthalate})]$ is known where one terephthalate links the Cu-centers and the second one balances the charge as a free anion [49].

3.3. Thermal analysis

The simultaneous TG-DTA curves of complex **1** reveal that upon heating it starts to lose water molecules at 30 °C and the dehydration continues up to 80 °C (Fig. 8). The observed weight loss (13.0%) is slightly lower than the calculated one (14.1%, corresponding to nine water molecules of crystallization per formula unit) because the loss of water molecules starts at room temperature and during drying of the sample some of the water molecules are lost. The crystalline sample

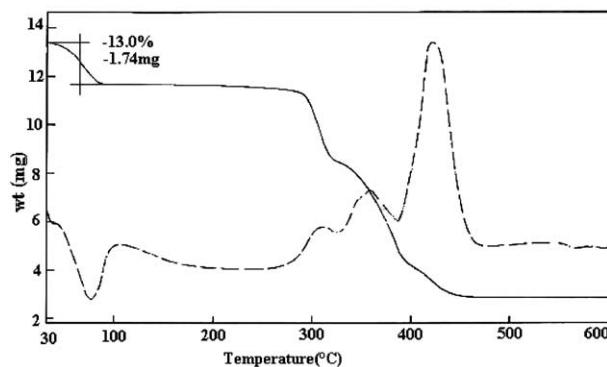


Fig. 8. The TG (—) and DTA (----) curves of compound **1** (heating rate: 5 °C/min).

turns into amorphous powders upon removal of water molecules. The dehydrated species is stable up to 260 °C and does not re-absorb any water on exposure to humid atmosphere suggesting that the framework integrity breaks down once the water molecules are lost. Compound **2** starts to lose its water molecules ca. 30 °C and both the crystalline and coordinated water are lost completely at 80 °C in a single step. The observed percentage of weight loss of a freshly prepared sample (16.5%) corresponds to the loss of six water molecules (per reduced formula unit, calc: 16.6%). However, on keeping the sample at room temperature the water molecules are lost gradually and consequently the percentage of water loss may not correspond to the molecular formulae if the sample is not freshly prepared. The anhydrous species is stable up to 240 °C. Here also re-absorption of water molecules does not take place on exposure of the anhydrous species to open air.

4. Conclusion

Herein, we reported two cadmium(II) complexes of terephthalate having nitrogen containing tridentate and tetradentate Schiff-base blocking ligands. Compound **1**, with a tridentate ligand, is a 1D polymeric chain whereas compound **2** with tetradentate ligand is a very rare type of dinuclear complex. In both complexes the water of crystallization is involved in a strong H-bonding network. In complex **2** the intermolecular packing is controlled by typical π -stacking interactions between pyridyl planes.

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Appendix A. Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 267613 (compound **1**), 267614 (compound **2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.06.038.

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