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Towards rational synthesis of polar solids. Synthesis and X-ray structures of cadmium(II) *meta*-pyridinecarboxylate coordination polymers †

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Two cadmium(II) coordination polymers, $Cd_2L^1{}_4(\mu\text{-}H_2O)$ **1** and $Cd_2L^2{}_4(\mu\text{-}H_2O)$ **2** [L^1 = (*E*)-4-(2-thiazolyl)ethenylbenzoate, L^2 = (*E*)-4-(3-pyridyl)ethenylbenzoate] based on *meta*-pyridinecarboxylate bridging ligands, were synthesized by the reactions of cadmium perchlorate and the corresponding benzonitrile precursor ligands under hydro(solvo)thermal conditions. Although both compounds **1** and **2** are constructed from the $Cd_2L^n{}_4(\mu\text{-}H_2O)$ building block, X-ray single crystal structure determinations show that **1** adopts a 2-D polymeric network structure while **2** exhibits a 3-D framework structure as a result of the slightly different configurations of the bridging pyridinecarboxylate ligands. Owing to the presence of the bridging water molecules, both **1** and **2** crystallize in centrosymmetric space groups.

Introduction

Non-centrosymmetric organization of molecular building blocks is an essential requirement for many solid state properties including second-order nonlinear optical (NLO) effects.[1] The synthesis of such acentric supramolecular assemblies still presents a significant challenge for synthetic chemists.[2] On the other hand, construction of metal–organic coordination frameworks *via* metal coordination-directed self-assembly processes has become an area of intense research in recent years.[3] Strong metal–ligand coordination bonds and their directionality can be exploited for the rational design of extended solid materials.[4] Moreover, both the network structures and properties of these coordination networks can be fine-tuned *via* a systematic change of the organic linking ligands.[5] In our work, we have become particularly interested in utilizing metal–ligand coordination to counteract unfavorable centric interactions (such as dipole–dipole repulsions) and thus developing general strategies for the construction of acentric polymeric coordination networks for second-order NLO applications.[6]

Our approach to the rational synthesis of transparent polar polymeric coordination networks is very straightforward. First, we focus on d^{10} metal centers Zn(II) and Cd(II) for their transparency and their favorable thermal and oxidative stabilities. Second, we have chosen pyridinecarboxylate groups as bridging ligands. We hypothesize that polymeric coordination networks will result if these pyridinecarboxylate ligands can use both the pyridyl and carboxylate functionalities to coordinate to Zn(II) or Cd(II) centers. Third, the unsymmetrical structure and conjugate nature of pyridinecarboxylate groups will impart electronic asymmetry to the resulting coordination networks. Such electronic asymmetry is an essential requirement for second-order NLO properties. We have thus far identified three different structure motifs with which we can rationally construct polar solids containing pyridinecarboxylate ligands: (a) 3-D diamondoid networks; (b) 2-D grid structures; (c) 2-D networks composed of "basic" trinuclear carboxylates with 3-fold rotational symmetry. By using *para*-pyridinecarboxylates, we have successfully designed acentric diamondoid coordination networks [Fig. 1(a)].[6a] Interestingly, when "bent" linking groups such as *meta*-pyridinecarboxylates were used, acentric coordination polymers with 2-D grid structures were obtained [Fig. 1(b)].[6b] We have recently discovered that acentric 2-D coordination networks containing an unprecedented "basic" tricadmium carboxylate structural motif could be prepared under basic conditions [Fig. 1(c)].[6c] Because of the 3-fold rotational symmetry of the "basic" tricadmium carboxylate chromophoric building blocks, these 2-D coordination networks are octupolar in nature and are expected to have a superior transparency/non-linearity tradeoff.

In order to test the generality of the above crystal engineering approaches to polar solids, we have recently systematically examined the reactions of a series of pyridinecarboxylic acids (and their precursors) with Zn(II) and Cd(II) salts. We report in this contribution the synthesis and X-ray structures of two Cd(II) coordination polymers, $Cd_2L^1{}_4(\mu\text{-}H_2O)$ **1** and $Cd_2L^2{}_4(\mu\text{-}H_2O)$ **2** [L^1 = (*E*)-4-(2-thiazolyl)ethenylbenzoate, L^2 = (*E*)-4-(3-pyridyl)ethenylbenzoate] based on *meta*-pyridinecarboxylate bridging ligands. Owing to the presence of bridging water molecules, **1** and **2** do not adopt any of the three structures in Fig. 1 and are both centrosymmetric. Detailed studies of the subtle differences among these solids should lead to better understanding of the above crystal engineering approaches and ultimately result in superior second-order NLO materials.

Experimental

Materials and methods

2-Bromothiazole and 4-bromopyridine hydrochloride were purchased from TCI America and all other chemicals were purchased from Aldrich Chemical Company. 4-Ethynylbenzonitrile was synthesized according to the published procedure.[7] The IR spectra were recorded as KBr pellets on a Paragon 1000 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were taken on a Varian Unity-Plus 400 spectrometer. Thermogravimetric analyses were performed in air at a scan speed of 10 °C min^{-1} on a Shimadzu TGA-50 TG analyzer.

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003441j/

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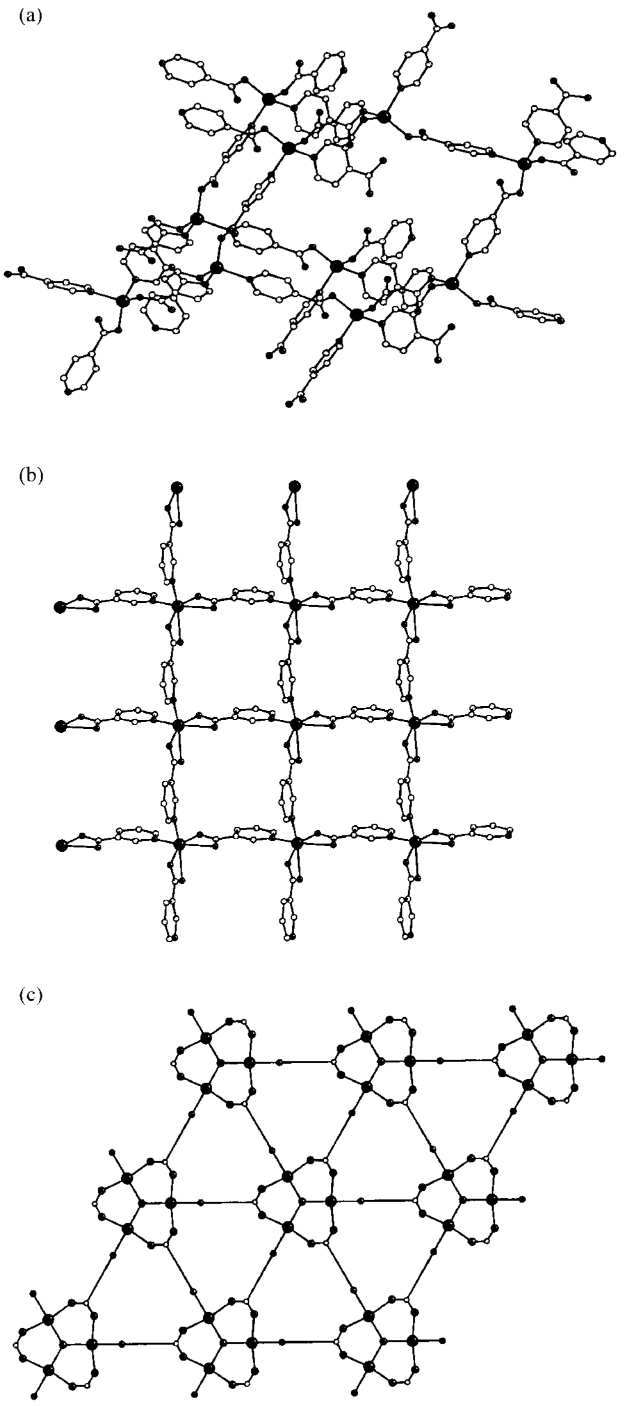
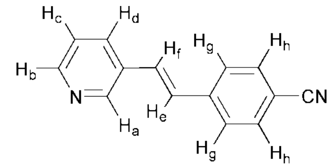


Fig. 1 Three structural motifs for the rational synthesis of polar solids. (a) A 3-D diamondoid network; (b) a 2-D grid structure; (c) a 2-D polymeric network of "basic" trinuclear carboxylates with 3-fold rotational symmetry.

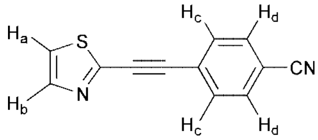
Synthesis of (*E*)-4-(3-pyridyl)ethenylbenzonitrile

A mixture of (4-cyanobenzyl)triphenylphosphonium bromide (7.786 g, 17 mmol) and 3-pyridinecarbaldehyde (1.66 g, 15.5 mmol) in 30 mL of methylene chloride was stirred vigorously in a 250 mL Erlenmeyer flask. To this suspension was added 10 mL of 50% aqueous NaOH dropwise over the course of 1 h. After stirring vigorously for one additional hour, the mixture was washed with three portions of deionized water (150 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The resulting white solid was then transferred to a 100 mL round bottom flask containing iodine crystals (0.1 g, 0.788 mmol) and 40 mL of nitrobenzene, and the mixture was refluxed for 3 h. Upon cooling, the reaction mixture was extracted with dilute hydrochloric acid. The aqueous phase was removed and made alkaline with 3 M NaOH, and extracted with ethyl acetate. The extract was dried over $MgSO_4$ and evaporated to dryness to afford 2.426 g of pure product (76% yield); mp 124–126 °C. ^1H NMR: δ 8.71 (br s, 1H, H_a), 8.51 (d, 1H, $J = 4.6$ Hz, H_b), 7.82 (d, 1H, $J = 1.8$ Hz, H_d), 7.62 (d, 2H, $J = 8.3$ Hz, H_g), 7.57 (d, 2H, $J = 8.3$ Hz, H_h), 7.28 (dd, 1H, $J_{cb} = 4.9$, $J_{cd} = 4.9$ Hz, H_c), 7.18 (d, 1H, $J = 16.5$ Hz), 7.11 (d, 1H, $J = 16.5$ Hz). $^{13}C\{^1H\}$ NMR: δ 149.4, 148.8, 141.0, 132.9, 132.5, 131.9, 128.7, 128.5, 127.0, 123.6, 118.8, 111.1.

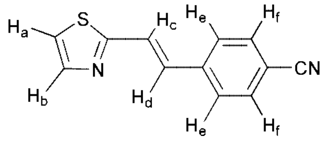


Synthesis of (*E*)-4-(2-thiazolyl)ethenylbenzonitrile

A mixture of 4-ethynylbenzonitrile (2.58 g, 15.7 mmol) and 2-bromothiazole (2.02 g, 10 mmol) in 50 mL of diethylamine was refluxed in the presence of dichlorobis(triphenylphosphine)palladium (40 mg, 0.06 mmol) and copper(I) iodide (10 mg, 0.05 mmol) for 12 h. Diethylamine was removed under reduced pressure, and the residue dissolved in 50 mL of ethyl acetate and washed twice with 50 mL of water. The organic layer was dried over $MgSO_4$ and evaporated to dryness. Silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (4:1 v/v) afforded 2.68 g of pure 4-(2-thiazolyl)ethynylbenzonitrile (81% yield); mp 149–150 °C. ^1H NMR: δ 7.90 (d, 1H, $J = 3.4$ Hz, H_b), 7.66 (br s, 4H, $H_c + H_d$), 7.45 (d, 1H, $J = 3.4$ Hz, H_a). $^{13}C\{^1H\}$ NMR: δ 147.7, 144.1, 132.4, 132.2, 126.3, 121.7, 118.2, 112.8, 91.5, 85.9.



4-(2-Thiazolyl)ethynylbenzonitrile (1.0 g, 4.8 mmol) in 50 mL of methylene chloride was hydrogenated in the presence of Lindlar's catalyst under 40 psi of H_2 for 12 h. Methylene chloride was removed *in vacuo* to yield crude (*Z*)-4-(2-thiazolyl)ethenylbenzonitrile, which was refluxed in nitrobenzene (25 mL) containing a trace of iodine (0.3 g) for 3 h. The mixture was then extracted with dilute hydrochloric acid, and then made alkaline with 3 M NaOH. The alkaline aqueous phase was extracted with ethyl acetate, dried over $MgSO_4$, and evaporated to dryness. Silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (4:1 v/v) afforded 0.75 g of pure product (74% yield); mp 134–136 °C. ^1H NMR: δ 7.82 (d, 1H, $J = 3.0$ Hz, H_b), 7.61 (d, 2H, $J = 8.6$ Hz, H_f), 7.56 (d, 2H, $J = 8.6$ Hz, H_e), 7.38 (d, 1H, $J = 16.2$ Hz, H_c), 7.34 (d, 1H, $J = 16.2$ Hz, H_d), 7.30 (d, 1 H, $J = 3.0$ Hz, H_a). $^{13}C\{^1H\}$ NMR: δ 143.9, 140.1, 132.5, 131.7, 127.3, 124.4, 119.3, 118.6, 111.7.



Synthesis of $Cd_2L^1_4(\mu\text{-}H_2O)$ 1

A mixture of $Cd(ClO_4)_2\cdot 6H_2O$ (0.110 g, 0.25 mmol) and (*E*)-4-(2-thiazolyl)ethenylbenzonitrile (0.104 g, 0.5 mmol) was thoroughly mixed with methanol (0.07 mL), water (0.3 mL) and pyridine (0.1 mL) in a heavy-walled Pyrex tube. The tube was

Table 1 X-Ray diffraction data for **1** and **2**[a]

Chemical formula	$Cd_2C_{48}H_{34}N_4O_9S_4$, **1**	$CdC_{28}H_{21}N_2O_{4.5}$, **2**
M	1163.89	567.85
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Z	4	8
T/°C	−75(1)	−75(1)
λ(Mo-Kα)/Å	0.71073	0.71073
a/Å	15.099(1)	11.458(2)
b/Å	20.340(1)	16.087(2)
c/Å	15.116(1)	25.536(4)
β/°	97.982(1)	91.230(3)
V/Å^3	4597.3(4)	4705.9(2)
D_c/g cm^{-3}	1.682	1.609
μ(Mo-Kα)/cm^{-1}	11.7	9.69
N_{ref} (total)	8106	3996
N_{ref} (obs.) [$I > 2\sigma(I)$]	4721	2238
N_{par}	612	325
$R1$[a]	0.061	0.066
$wR2$[a]	0.142	0.173
Goodness of fit (GOF)	1.02	0.98
Min., max. residual density/e Å^{-3}	−0.63, 2.22	−1.33, 1.67

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{ref}(\text{obs.}) - N_{par})]^{1/2}$ where N_{ref}(obs.) = number of observed reflections and N_{par} = number of parameters.

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

1			
Cd1–O1	2.350(6)	Cd2–O2	2.226(6)
Cd1–O4	2.224(6)	Cd2–O3	2.352(6)
Cd1–O5	2.280(6)	Cd2–O7	2.239(6)
Cd1–O9	2.314(5)	Cd2–O9	2.336(5)
Cd1–N3c	2.332(7)	Cd2–N1a	2.440(6)
Cd1–N2d	2.442(6)	Cd2–N4b	2.320(6)
O1–Cd1–O4	105.2(2)	O2–Cd2–O3	111.6(2)
O1–Cd1–O5	81.1(2)	O2–Cd2–O7	165.1(2)
O1–Cd1–O9	90.7(2)	O2–Cd2–O9	86.0(2)
O1–Cd1–N3c	85.0(2)	O2–Cd2–N1a	82.6(2)
O1–Cd1–N2d	173.6(2)	O2–Cd2–N4b	99.9(2)
O4–Cd1–O5	172.1(2)	O3–Cd2–O7	80.3(2)
O4–Cd1–O9	87.5(2)	O3–Cd2–O9	87.9(2)
O4–Cd1–N3c	97.8(2)	O3–Cd2–N1a	165.6(2)
O4–Cd1–N2d	81.1(2)	O3–Cd2–N4b	84.1(2)
O5–Cd1–O9	87.8(2)	O7–Cd2–O9	85.6(2)
O5–Cd1–N3c	87.4(2)	O7–Cd2–N1a	86.1(2)
O5–Cd1–N2d	92.7(2)	O7–Cd2–N4b	89.9(2)
O9–Cd1–N3c	173.9(2)	O9–Cd2–N1a	95.8(2)
O9–Cd1–N2d	91.0(2)	O9–Cd2–N4b	171.4(2)
N2d–Cd1–N3c	92.9(2)	N1a–Cd2–N4b	91.2(2)
2			
Cd1–O1	2.281(6)	Cd1–O2e	2.313(6)
Cd1–O3	2.324(6)	Cd1–N1f	2.332(7)
Cd1–O5	2.318(6)	Cd1–N2g	2.354(8)
O1–Cd1–O3	170.7(2)	O3–Cd1–N2g	94.1(2)
O1–Cd1–O5	104.06(19)	O2e–Cd1–O5	86.0(2)
O1–Cd1–O2e	96.3(2)	O5–Cd1–N1f	167.7(2)
O1–Cd1–N1f	87.5(2)	O5–Cd1–N2g	86.6(2)
O1–Cd1–N2g	87.3(2)	O2e–Cd1–N1f	88.5(2)
O3–Cd1–O5	85.22(19)	O2e–Cd1–N2g	172.4(2)
O2e–Cd1–O3	83.5(2)	N1f–Cd1–N2g	98.4(3)
O3–Cd1–N1f	83.2(2)		

Symmetry codes: a = $-x$, $-1/2 + y$, $3/2 - z$; b = $-x$, $1/2 + y$, $3/2 - z$; c = $1 - x$, $-1/2 + y$, $3/2 - z$; d = $1 - x$, $1/2 + y$, $3/2 - z$; e = $2 - x$, y, $3/2 - z$; f = x, $-y$, $-1/2 + z$; h = $-1/2 + x$, $1/2 - y$, $1/2 + z$.

frozen under liquid nitrogen, sealed, and heated inside an oven at 140 °C. After 72 h of heating, the tube was opened, and colorless crystals were obtained. Yield: 80 mg (28%). IR (cm^{-1}): 1646s, 1595s, 1572m, 1551s, 1474w, 1431w, 1378s, 1176w, 1127w, 1047w, 1027w, 970m, 955m, 799m, 768m, 699m.

Synthesis of $Cd_2L^2_4(\mu\text{-}H_2O)$ 2

A mixture of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.055 g, 0.125 mmol) and (*E*)-4-(3-pyridyl)ethenylbenzonitrile (0.053 g, 0.25 mmol) was thoroughly mixed with methanol (0.07 mL) and water (0.3 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and heated inside an oven at 130 °C. After 1 week of heating, the tube was opened, and pale yellow crystals were obtained. Yield: 32 mg (22%). IR (cm^{-1}): 1595s, 1551s, 1485m, 1382s, 1231w, 1145m, 948m, 797w, 776m, 717m, 670w, 628w.

X-Ray data collections and structure determinations

Data collection for **1** (**2**) was carried out with a colorless crystal of dimensions of 0.05 × 0.16 × 0.22 (0.05 × 0.10 × 0.24 mm) on a Siemens SMART system equipped with a CCD detector using Mo-Kα radiation. Of the 8106 (3996) unique reflections measured, 4721 (2238) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement for **1** (**2**). The structures were solved by direct methods using SHELX-TL[8] and refined on F^2 by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms.[8] All the hydrogen atoms in **1** and **2** were located by geometric placing. Final refinement gave an $R1 = 0.061$ (0.066), $wR2 = 0.142$ (0.173) and goodness of fit = 1.02 (0.98) for **1** (**2**). Experimental details for X-ray data collections of **1** and **2** are tabulated in Table 1, while selected bond distances and angles for **1** and **2** are listed in Table 2. All the drawings were made using either XP[8] or CAMERON[9] programs.

CCDC reference number 186/2070.

See http://www.rsc.org/suppdata/dt/b0/b003441j/ for crystallographic files in .cif format.

Results and discussion

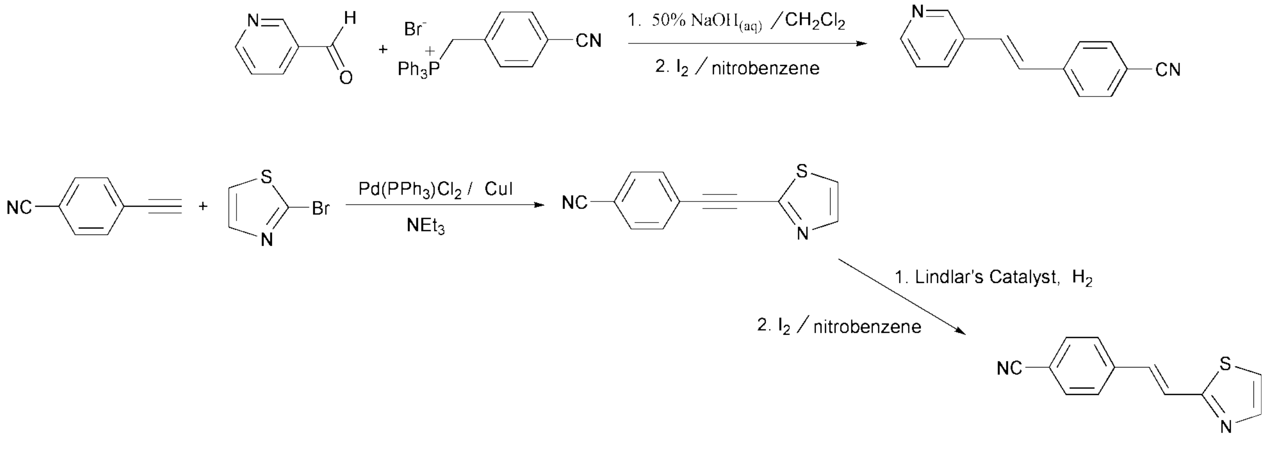
Synthesis

The ligand precursor (*E*)-4-(3-pyridyl)ethenylbenzonitrile was synthesized *via* a Wittig reaction[10] between (4-cyanobenzyl)-triphenylphosphonium bromide and 4-pyridinecarbaldehyde, using 50% aqueous sodium hydroxide to generate the ylide, as illustrated in Scheme 1. The reaction gave a mixture of (*E*)- and (*Z*)-products. Refluxing this mixture in nitrobenzene in the presence of iodine for 3 h afforded the pure (*E*)-product in 76% overall yield.[11] Pure (*E*)-4-(3-pyridyl)ethenylbenzonitrile was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

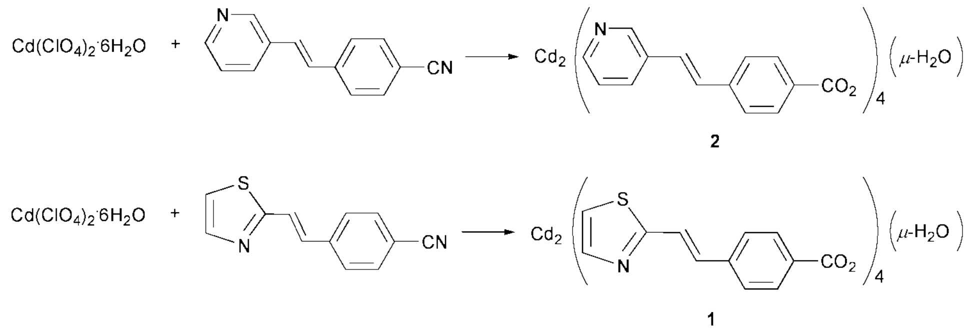
The ligand precursor (*E*)-4-(2-thiazolyl)ethenylbenzonitrile was synthesized by a Heck coupling reaction[12] between 4-ethynylbenzonitrile and 2-bromothiazole, followed by hydrogenation in the presence of Lindlar's catalyst. The hydrogenation afforded the pure (*Z*)-isomer, which was converted to the desired (*E*)-isomer by refluxing in nitrobenzene in the presence of iodine. Pure (*E*)-4-(2-thiazolyl)ethenylbenzonitrile was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

$Cd_2L^1_4(\mu\text{-}H_2O)$ **1**, was obtained as large colorless crystals in 28% yield by a hydro(solvo)thermal reaction between $Cd(ClO_4)_2 \cdot 6H_2O$ and (*E*)-4-(2-thiazolyl)ethenylbenzonitrile in a mixture of methanol, water and pyridine at 140 °C (Scheme 2). The IR spectrum of **1** exhibits peaks at 1572 and 1378 cm^{-1} that can be assigned to the antisymmetric and symmetric C=O stretches, respectively.[13] Carboxylate formation in **1** has evidently resulted from the *in situ* hydrolysis of ligand during the hydro(solvo)thermal synthesis.[14] The presence of bridging water molecules in **1** is clearly indicated in the TGA results which exhibited a weight loss of 1.54% in the temperature range 219–259 °C [calc. 1.55% for the loss of one water molecule per $Cd_2L^1_4(\mu\text{-}H_2O)$ unit].

$Cd_2L^2_4(\mu\text{-}H_2O)$ **2** was obtained similarly by hydro(solvo)-thermal reaction between $Cd(ClO_4)_2 \cdot 6H_2O$ and (*E*)-4-(3-pyridyl)ethenylbenzonitrile (Scheme 2). The structure of **2** can be inferred from the IR spectrum showing strong peaks at 1551



Scheme 1



Scheme 2

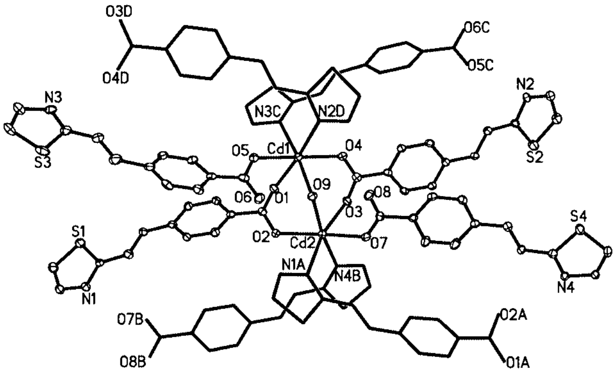


Fig. 2 Coordination environment of **1**. The asymmetric unit is shown with ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

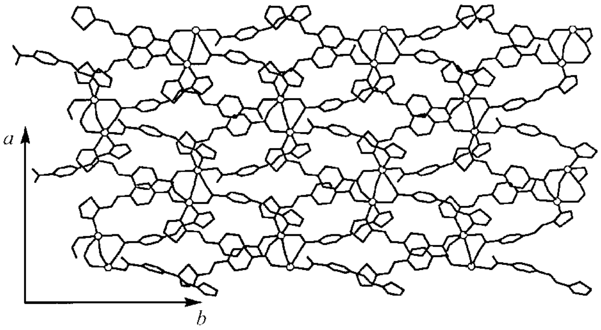


Fig. 3 2-D sheet of **1** as viewed down the *c* axis. Open circles represent Cd atoms.

and 1382 cm^{-1} which are characteristic of the antisymmetric and symmetric C=O stretches. TGA results indicated that **2** exhibited a weight loss of 1.57% in the temperature range 229–302 °C [calc. 1.58% for the loss of one water molecule per $Cd_2L^2_4(\mu\text{-}H_2O)$ unit].

Single crystal X-ray structures

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **1** consists of two cadmium atoms, four 4-(2-thiazolyl)ethenylbenzoate (L^1) ligands, and one bridging water molecule (Fig. 2). The thiazolyl nitrogen atoms of all the four L^1 ligands coordinate to Cd centers. Two of these L^1 ligands adopt exotridentate bridging mode (with μ,η^2-carboxylato groups), while the other two L^1 ligands are exobidentate (with monodentate carboxylato groups). With a bridging water molecule (O9), each Cd center in **1** is coordinated to three carboxylate oxygen atoms, to one oxygen atom of the bridging water molecule, and to two pyridyl nitrogen atoms in a *cis* geometry. The geometry around both Cd(II) centers can be described as a highly distorted octahedron. The bond angles around the central Cd1 atom and the *cis* ligands lie in the range 81.1–102.5° while the bond angles around the central Cd2 atom and the *cis* ligands lie in the range 80.3–111.6°. All the Cd–O and Cd–N bond distances are normal. The Cd1–Cd2 distance in **1** is 3.74 Å. The dihedral angles between the thiazolyl and phenyl rings for the four L^1 ligands are 19.6, 18.1, 14.2 and 6.6°.

The structure of **1** is based upon the $Cd_2L^1_4(\mu\text{-}H_2O)$ building block. The $Cd_2L^1_4(\mu\text{-}H_2O)$ unit uses a pair of the eight different L^1 ligands to connect to an adjacent $Cd_2L^1_4(\mu\text{-}H_2O)$ unit. Each $Cd_2L^1_4(\mu\text{-}H_2O)$ unit is thus connected to four neighboring $Cd_2L^1_4(\mu\text{-}H_2O)$ units in the *ab* plane to form a 2-D sheet structure (Fig. 3). Adjacent $Cd_2L^1_4(\mu\text{-}H_2O)$ units along the *b* axis adopt the same orientation and form an infinite chain structure. These infinite chains are related by a 2_1 operation along the *b* axis. Overall, each 2-D sheet lacks a center of symmetry. However, the adjacent 2-D sheets are related by an inversion center and **1** crystallizes in the centrosymmetric space group $P2_1/c$. It is interesting that within each 2-D sheet, Cd centers are encased between L^1 ligands to form a sandwich structure (Fig. 4); such sandwich structures are presumably favorable for

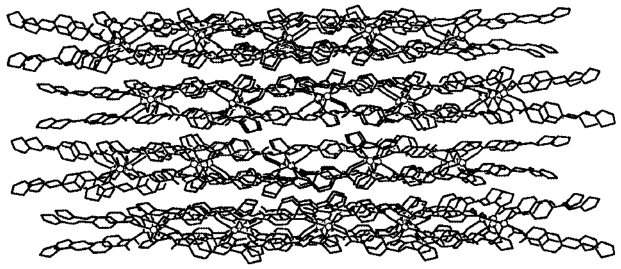


Fig. 4 Stacking of 2-D sheets of **1** viewed down the *a* axis.

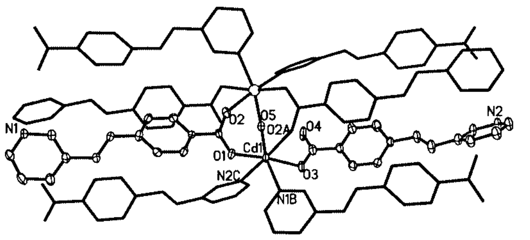


Fig. 5 Coordination environment of **2**. The asymmetric unit is shown with ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

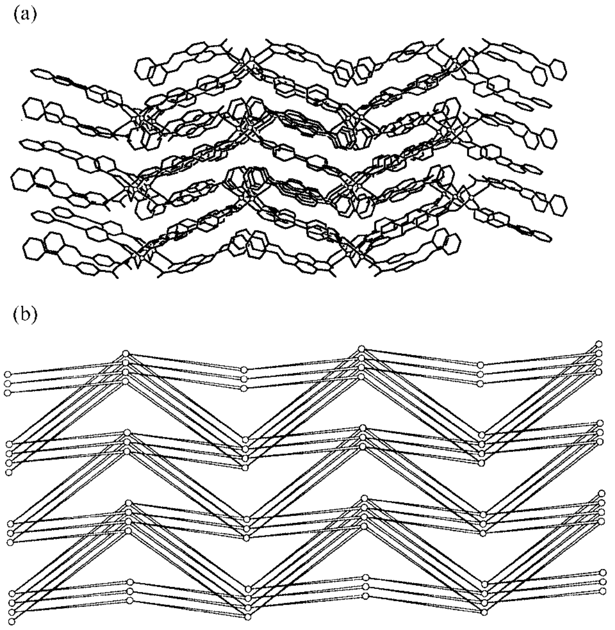


Fig. 6 (a) Perspective view of **2** down the *a* axis. The Cd atoms are represented with open circles. (b) 3-D network connectivity in **2**. Open circles represent the $Cd_2L^2_4(\mu\text{-}H_2O)$ units.

the packing of the 2-D sheets owing to the hydrophobic–hydrophobic interactions.

Compound **2** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of **2** contains one Cd atom, two 4-(3-pyridyl)ethenylbenzoate (L^2) ligands, and one water molecule sitting on a two-fold axis. One L^2 ligand adopts exotridentate bridging mode, while the other L^2 ligand is exobidentate. The C_2 symmetry operation generates a $Cd_2L^2_4(\mu\text{-}H_2O)$ unit which constitutes the building block of **2** (Fig. 5). The coordination geometry of **2** is essentially identical to that of **1**: each Cd center in **2** is coordinated to three carboxylate oxygen atoms, to one oxygen atom of the bridging water molecule and to two pyridyl nitrogen atoms in a *cis* geometry. Each Cd center adopts a distorted octahedral geometry with the bond angles around the central Cd1 atom and the *cis* ligands in the range 83.2–104.1°. The Cd–Cd distance in the $Cd_2L^2_4(\mu\text{-}H_2O)$ unit is 3.72 Å. In contrast to **1**, the phenyl and pyridyl rings for the two L^2 ligands in **2** are very non-coplanar with dihedral angles of 62.5 and 46.5°.

Although compounds **1** and **2** contain similar building blocks, they have drastically different network topologies. Each $Cd_2L^2_4(\mu\text{-}H_2O)$ unit in **2** is also connected to four neighboring $Cd_2L^2_4(\mu\text{-}H_2O)$ units *via* four different pairs of L^2 bridging ligands. Unlike **1**, these $Cd_2L^2_4(\mu\text{-}H_2O)$ units in **2** are not in the same plane. Three of these $Cd_2L^2_4(\mu\text{-}H_2O)$ units are in the same zigzag chains along the *c* axis which are linked to the two $Cd_2L^2_4(\mu\text{-}H_2O)$ units from two other zigzag chains to result in a highly regular 3-D network (Fig. 6). There are inversion centers relating these zigzag chains. We believe this drastic structure difference between **1** and **2** is a result of the isomerism of the bridging ligands. While the coordinated oxygen (O5 and O7) and nitrogen (N3 and N4) atoms in exobidentate L^1 ligands in **1** are *cis* to each other (Fig. 1), the coordinated oxygen (O3) and nitrogen (N2) atoms in exobidentate L^2 ligands in **2** are *trans* to each other (Fig. 2). Such a *trans* configuration of the L^2 ligands is responsible for the linking of one zigzag $Cd_2L^2_4(\mu\text{-}H_2O)$ chain to two different zigzag $Cd_2L^2_4(\mu\text{-}H_2O)$ chains to result in a 3-D network structure of **2**.

In summary, we have synthesized two Cd(II) coordination polymers based on *meta*-pyridinecarboxylate bridging ligands. Subtle configurational isomerism between the two *meta*-pyridinecarboxylate bridging ligands in **1** and **2** is responsible for the drastic difference of the resulting coordination polymers. Both **1** and **2** are centrosymmetric presumably as a result of the presence of bridging water molecules.

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