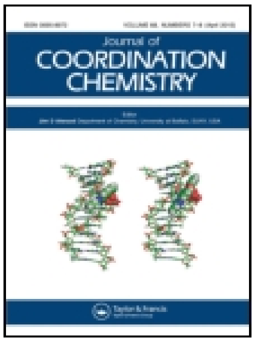

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One-dimensional and two-dimensional coordination polymers constructed from Cd^{2+} ions and flexible bipyridyl bridging ligands

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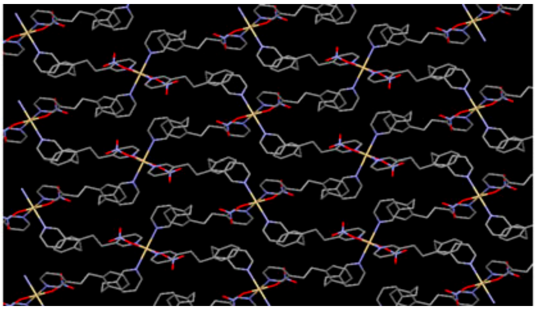

The syntheses and structures of the coordination polymers $[Cd(ppeb)_2(H_2O)_2]_n\cdot(NO_3)_{2n}$ (**1**), $[Cd(ppeb)_2(ClO_4)_2]_n$ (**2**), $[Cd(opeb)_2(NO_3)_2]_n$ (**3**), and $[Cd(opeb)_2(H_2O)_2]_n\cdot(ClO_4)_{2n}$ (**4**), where ppeb and opeb represent the 1,4- and 1,2-isomers of *bis*[2-(3-pyridyl)ethyl]-benzene, $C_{20}H_{20}N_2$, respectively, are described. Each structure contains *trans*-CdO_2N_4 octahedra. In **1** and **2**, they are bridged by pairs of ligands to generate looped chains, whereas in **3** and **4** the ligands link the metal nodes into squashed 4^4 polymeric sheets. In **1** and **4**, O–H…O hydrogen bonds from the coordinated water molecules to the uncoordinated anions help to consolidate the structures.

Keywords: Cadmium; Coordination polymer; Flexible ligand

1. Introduction

An important class of ligands for constructing new metal–organic frameworks and coordination networks are bipyridyls in which the pyridine rings are connected by a flexible alkyl linker, which can readily adopt different conformations and result in a great variety of extended structures [1–20]. These neutral ligands necessitate the presence of anions to charge-balance the metal ion, which may exert own influences on structure. As part of our ongoing studies in this area [21, 22], we now describe the syntheses and

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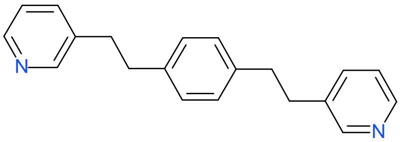
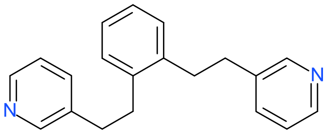
*Corresponding author. Email: w.harrison@abdn.ac.uk crystal structures of the coordination polymers $[Cd(C_{20}H_{20}N_2)_2(H_2O)_2]_n{\cdot}(NO_3)_{2n}$ (**1**), $[Cd(C_{20}H_{20}N_2)_2(ClO_4)_2]_n$ (**2**), $[Cd(C_{20}H_{20}N_2)_2(NO_3)_2]_n$ (**3**), and $[Cd(C_{20}H_{20}N_2)_2(H_2O)_2]_n{\cdot}(ClO_4)_{2n}$ (**4**). In **1** and **2**, $C_{20}H_{20}N_2$ = 1,4-*bis*[2-(3-pyridyl)ethyl]-benzene (ppeb) and in **3** and **4**, $C_{20}H_{20}N_2$ = the isomeric 1,2-*bis*[2-(3-pyridyl)ethyl]-benzene (opeb).



ppeb



opeb

2. Experimental

2.1. *Ligand syntheses and characterization*

Pyridine-3-carboxaldehyde (2.72 g, 25.4 mmol) was added to a solution of 1,4-*bis*(methyltriphenylphosphonium)benzene dibromide (10 g, 12.7 mmol) in dry ethanol (50 mL). A freshly prepared solution of sodium ethoxide was slowly added to the stirred mixture over 30 min. After a further 3.5 h, the ethanol was removed and water (80 mL) followed by CH_2Cl_2 (8 mL) was added. The triphenylphosphine oxide that remains as a precipitate was filtered off and washed with water. The aqueous washings were combined and neutralized with 2 M sodium hydroxide and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The CH_2Cl_2 was removed *in vacuo* to give a brown solid that was dissolved in ethanol (15 mL) to which 10% palladium on carbon (200 mg) was added. The mixture was hydrogenated at 1 atmosphere pressure and 24 °C with vigorous stirring until no more hydrogen was absorbed. The ethanol was removed and the crude product was purified by column chromatography (silica gel; eluent 90% EtOH: 10% EtOAc) to give 1,4-*bis*[2-(3-pyridyl)ethyl] benzene (2.6 g, 72%) as a white solid, m.p. 125–126 °C. ν_{max} (KBr)/cm^{-1}: 3017w, 2924w, 1570w, 1511w, 1419s, 1189w, 1142w, 1023w, 816s, 715s and 534s; δ_H (250 MHz; $CDCl_3$) 2.8 (8H, s), 6.9 (4H, s), 7.1–7.2 (2H, m), 7.36–7.39 (2H, m), 8.35 (2H, s) and 8.38–8.40 (2H, m); δ_c (62.9 MHz; $CDCl_3$) 34.8, 36.9, 123.2, 128.5, 135.9, 136.8, 138.5, 147.2 and 149.8; m/z 289 (CI) ($[M + H]^+$, 100%) $C_{20}H_{21}N_2$ requires 289.1699 Found 289.1698.

Pyridine-2-carboxaldehyde (2.72 g, 25.4 mmol) was added to a solution of 1,2-*bis*(methyltriphenylphosphonium)benzene dibromide (10 g, 12.7 mmol) in dry ethanol (50 mL). A fresh solution of sodium ethoxide was slowly added to the stirred mixture over 30 min. After a further 3.5 h, the ethanol was removed and water (80 mL) followed by CH_2Cl_2 (8 mL) was added. The remaining triphenylphosphine oxide was filtered off and washed with water. The aqueous washings were combined and neutralized with sodium hydroxide (2 mL) and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The CH_2Cl_2 was removed *in vacuo* to give a brown solid that was dissolved in ethanol (15 mL) to which 10% palladium on carbon (200 mg) was added. This rigorously stirred mixture was hydrogenated at 1 atmosphere pressure and at 24 °C until no more hydrogen was absorbed. The ethanol was removed and the crude product was purified by column chromatography (silica gel; eluent 90% EtOH: 10% EtOAc) to give 1,2-*bis*[2-(3-pyridyl)ethyl]benzene (3.1 g, 85%) as a light brown oil; λ_{max} (MeOH)/nm 285 (log ε 4.1) and 239 (log ε 3.4); ν_{max} (KBr)/cm^{-1}: 3027s, 2932s, 2866m, 1575s, 1479vs, 1423vs, 1191s, 1026m, 803s, 752m and 716s; δ_H (250 MHz; DMSO-d_6) 2.85 (8H, m, CH_2CH_2), 7.11–7.19 (4H, m), 7.27 (2H, dd, *J* 4.8, 3.0), 7.63 (2H, dd, *J* 2.0, 1.5) and 8.40 (4H, m); δ_c (62.9 MHz; DMSO-d$_6$) 34.7, 36.3, 123.1, 126.2, 129.2, 135.9, 136.9, 138.8, 147.3 and 149.7; *m/z* 289.1701 ($[M + H]^+$. $C_{20}H_{21}N_2$ requires 289.1704), 289.0 ($[M + H]^+$, 100%).

2.2. *Coordination polymer synthesis and characterization*

1,4-*Bis*[2-(3-pyridyl)ethyl]benzene (0.1 g, 0.35 mmol) was dissolved in ethanol (5 mL) and layered onto a solution of $Cd(NO_3)_2{\cdot}xH_2O$ (0.107 g, ~0.35 mmol) in water (5 mL). The solution was left to stand for two weeks and during this time small colorless cuboids of **1** grew at the layer interface. These were harvested and air dried (0.127 g, 61%). (Found: C, 56.3; H, 5.1; N, 9.8%, $C_{40}H_{44}CdN_6O_8$ requires C, 56.6; H, 5.2; N, 9.9%); ν_{max} (KBr)/cm^{-1}: 3111s, 2852s, 1603w, 1513w, 1484w, 1431s, 1190w, 1056w, 816w, 711w and 647s.

1,4-*Bis*[2-(3-pyridyl)ethyl]benzene (0.1 g, 0.35 mmol) was dissolved in ethanol (5 mL) and layered onto a solution of $Cd(ClO_4)_2{\cdot}xH_2O$ (0.108 g, ~0.35 mmol) in water (5 mL). The solution was left to stand for two weeks and during this time colorless blocks of **2** grew at the layer interface, which were recovered and air dried (0.158 g, 76%). (Found: C, 54.0; H, 4.5; N, 6.1%. $C_{40}H_{40}CdCl_2N_4O_8$ requires C, 54.1; H, 4.5; N, 6.3%); ν_{max} (KBr)/cm^{-1}: 3434s, 2918w, 2852w, 1603w, 1486w, 1433w, 1198s, 1061s, 929s, 814s, 706s and 619s. **Caution!** Although we did not encounter any problems in this work, all perchlorate salts are potentially explosive especially when in contact with organic material. Only small quantities should be manipulated and handled with all applicable safety precautions in place.

1,2-*Bis*[2-(3-pyridyl)ethyl]benzene (0.1 g, 0.35 mmol) was dissolved in ethanol (5 mL) and layered onto a solution of $Cd(NO_3)_2{\cdot}xH_2O$ (0.107 g, ~0.35 mmol) in water (5 mL). The solution was left to stand for one month and during this time colorless crystals of **3** grew at the layer interface, which were harvested and air dried (0.072 g, 51%). (Found: C, 58.6; H, 5.2; N, 9.1. $C_{40}H_{40}CdN_6O_6$ requires C, 59.1; H, 5.0; N, 10.3%); ν_{max} (KBr)/cm^{-1}: 3479w, 3417w, 3057m, 3023m, 2925s, 2872m, 1602w, 1482m, 1433vs, 1384s, 1289vs, 1193w, 1050w, 1029m, 804m, 754s and 711m.

1,2-*Bis*[2-(3-pyridyl)ethyl]benzene (0.1 g, 0.35 mmol) was dissolved in ethanol (5 mL) and layered onto a solution of $Cd(ClO_4)_2{\cdot}xH_2O$ (0.108 g, ~0.35 mmol) in water (5 mL). The solution was left to stand for one month and during this time colorless blocks of **4** grew at the layer interface, which were harvested and air dried (0.080 g, 56%). (Found: C, 52.0; H, 4.8; N, 5.8. $C_{40}H_{44}CdCl_2N_4O_{10}$ requires C, 52.0; H, 4.8; N, 6.1%); ν_{max} (KBr)/cm^{-1}: 3456s, 3411s, 3066w, 3017w, 2929m, 2869w, 1604m, 1486m, 1433s, 1196m, 1112vs, 1092vs, 1055s, 925w, 806m, 756w, 708m and 628m.

2.3. *Crystallographic studies*

The intensity data for **1–4** were collected using a Nonius KappaCCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å, $T = -153$ °C). For **1**, a colorless cuboid of side-length ~0.05 mm was chosen for data collection; for **2**, a colorless block, 0.15 × 0.15 × 0.10 mm was used; for **3**, a colorless block, 0.30 × 0.30 × 0.15 mm was used; for **4**, a colorless slab, 0.20 × 0.20 × 0.10 mm was used. Empirical (multi-scan) absorption corrections were applied at the data-reduction stage with SADABS [23].

Each structure was readily solved by direct methods using SHELXS-97 (space group $P\bar{1}$ for **1**, $P2_1/n$ for **2**, $P2_1/c$ for **3,** and $C2/c$ for **4** and the atomic models were developed and refined against $|F|^2$ with SHELXL-97 [24]. The water hydrogens in **1** were found in

Table 1. Key crystallographic data for **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{40}H_{44}CdN_6O_8$	$C_{40}H_{40}CdCl_2N_4O_8$	$C_{40}H_{40}CdN_6O_6$	$C_{40}H_{44}CdCl_2N_4O_{10}$
M_r	849.21	888.06	813.18	924.09
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	8.8031(3)	8.7092(2)	8.7574(3)	22.2618(9)
b (Å)	10.0598(4)	16.8466(4)	9.0611(3)	8.4599(3)
c (Å)	12.1942(5)	12.8886(3)	23.1667(9)	21.7280(9)
α (°)	107.495(3)	90	90	90
β (°)	103.678(2)	101.8890(14)	100.475(1)	98.906(2)
γ (°)	101.5309(17)	90	90	90
V (Å^3)	956.98(6)	1850.46(7)	1807.68(11)	4042.8(3)
Z	1	2	2	4
ρ_{Calcd} (g cm^{-3})	1.474	1.594	1.494	1.518
μ (mm^{-1})	0.632	0.795	0.661	0.735
Data collected	7261	12,563	10,044	14,466
Unique data	3722	3622	3527	3954
R_{Int}	0.107	0.056	0.073	0.060
$R(F)$	0.060	0.027	0.035	0.058
$wR(F^2)$	0.143	0.072	0.083	0.159
CCDC deposition number[a]	1021192	1021193	1022202	1022203

[a] Full crystallographic data for these structures including atom positions and geometrical parameters can be accessed at: http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx by citing the deposition number shown.

difference maps and the positions freely refined with the constraint $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{O})$ applied. In **4**, the water hydrogens were geometrically placed and refined as riding. The C-bound H atoms in all structures were geometrically placed and modeled as riding with C–H = 0.95–0.99 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. There was a suggestion of disorder of some of the ligand atoms in **4**, but efforts to model this did not result in a significant improvement in fit. The structures were verified and analyzed with PLATON [25] and the molecular graphics were generated with ORTEP-3 [26] and ATOMS [27]. Crystal data for **1–4** are summarized in table 1 and full details are available as Supplementary Material (cif format).

3. Results

3.1. *Structure of 1*

The asymmetric unit of **1** consists (figure 1) of a Cd^{2+} ion (site symmetry $\bar{1}$), a ppeb bridging ligand, a water molecule, and a nitrate. The coordination polyhedron about the metal ion is an almost regular *trans*-CdO_2N_4 octahedron (table 2), arising from two waters and four pbp N. The bond-valence sum (BVS) [28] for Cd1 is 2.04 (expected value = 2.00), the octahedral volume is 17.07 Å^3, and the angular variance [29] for the *cis* X–Cd–Y octahedral bonds is 4.6°^{2}.

The dihedral angle between *cis*-orientated N1- and N2-pyridine-ring planes bonded to the metal ion is 82.04(14)°. The dihedral angles between the central benzene ring of the ligand and the N1- and N2-pyridine rings are 24.4(14)° and 74.01(17)°, respectively. Both its ethyl chains adopt extended (*anti*) conformations as indicated by the C2–C6–C7–C8 and C11–C14–C15–C16 torsion angles of 170.2(4)° and −170.7(4)°, respectively. The bonded metal ion is displaced from the planes of the N1- and N2-rings by 0.445(6) and 0.118(6) Å, respectively.

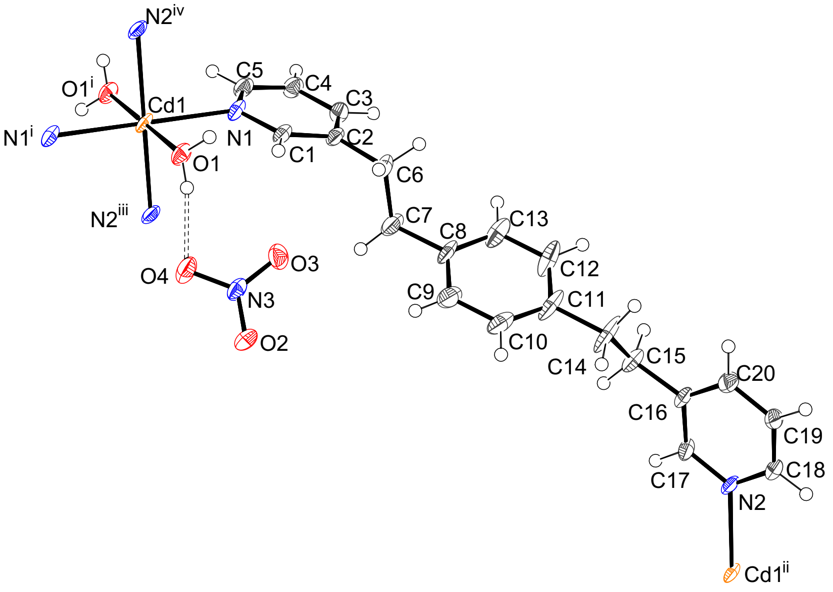


Figure 1. The asymmetric unit of **1** expanded to show the complete metal coordination sphere (50% displacement ellipsoids). Hydrogen bonds are indicated by double-dashed lines. Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-2, y-1, z-1$; (iii) $-1-x, -y, -z$; (iv) $x+2, y+1, z+1$.

Table 2. Selected geometrical data (Å, °) for **1**.

Cd1–O1	2.337(3)	Cd1–N2^{a}	2.343(3)	
Cd1–N1	2.343(3)			
C2–C6–C7–C8	170.2(4)	C11–C14–C15–C16	−170.7(4)	
O1–H10···O3^{b}	0.85(5)	1.96(5)	2.807 (4)	173(5)
O1–H20···O4	0.80(5)	1.92(5)	2.713(5)	170(5)
C3–H3···O4^{c}	0.95	2.47	3.192(6)	133
C5–H5···O1^{d}	0.95	2.58	3.249(6)	127
C18–H18···O2^{e}	0.95	2.43	3.202(7)	138
C20–H20···O2^{f}	0.95	2.54	3.438(6)	157

Symmetry codes: $^{a}2+x, 1+y, 1+z$.
$^{b}-x, 1-y, 1-z$.
$^{c}x, y-1, z$.
$^{d}1-x, 1-y, 1-z$.
$^{e}-2-x, -y, -z$.
$^{f}x-1, y-1, z$.

In the extended structure of **1**, pairs of bridging ppeb ligands link adjacent metal nodes into infinite looped chains (figure 2), which propagate in the [2 1 1] direction. Each loop consists of 30 atoms (14 per ligand + two Cd atoms). The separation of adjacent cadmium ions in the chain is 17.7137(7) Å, which is much greater than the shortest inter-chain Cd···Cd separation of 8.8031(4) Å. The nitrate ions accept O–H···O hydrogen bonds from the water molecules to crosslink the chains (figure 3), resulting in centrosymmetric $R_4^4(12)$ loops [30]. Several C–H···O interactions are also observed. The shortest centroid–centroid separation between aromatic rings of 4.371(3) Å is far too long to regard as a bonding interaction.

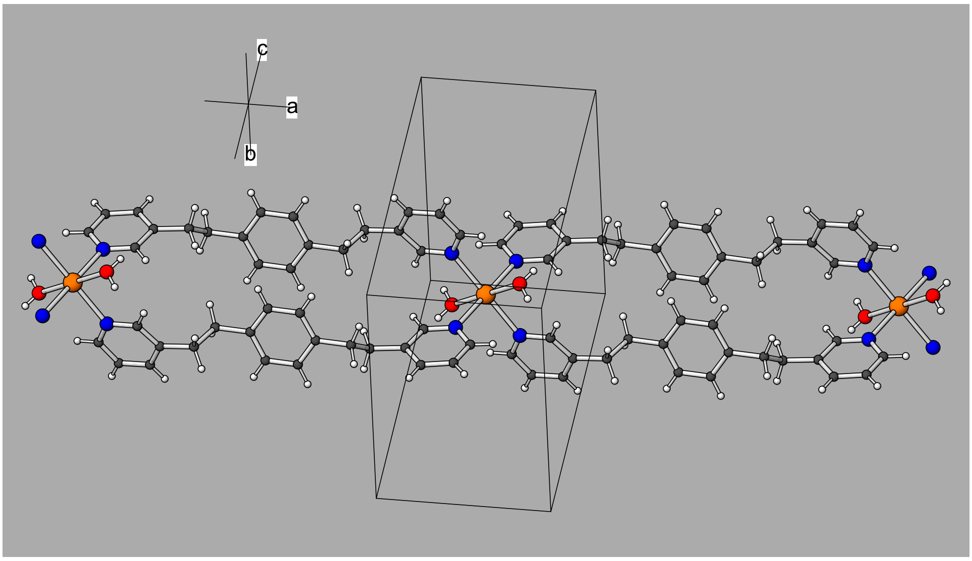


Figure 2. Part of a looped [2 1 1] polymeric chain in the structure of **1**.

3.2. *Structure of 2*

The asymmetric unit of **2** consists of the cadmium ion (site symmetry $\bar{1}$), a ppeb ligand, and a perchlorate ion (figure 4). A fairly regular *trans*-CdO_2N_4 octahedron (table 3) results from the bonded perchlorate ions and the bridging ppeb ligands: the Cd^{2+} BVS is 1.96, the octahedral volume is 17.34 $Å^3$, and the angular variance of the X–Cd–Y bonds is $31.8^{\circ 2}$. The dihedral angle between the *cis*-bonded py rings is 68.51(5)°. In the perchlorate, the Cl–O bond length of 1.4616(15) Å for O1, which is also bonded to the metal ion, is significantly longer than the others (mean = 1.428 Å).

The dihedral angles between the central benzene ring and terminal N1- and N2-pyridine rings of ppeb in **2** are 34.62(10)° and 82.45(7)°, respectively. The conformations of the inter-ring ethyl linkages are both *anti* [C2–C6–C7–C8 = −159.83(18)° and C11–C14–C15–C16 = 177.5(2)°]. The bonded cadmium ion is displaced from the planes of the N1- and N2-rings by 0.427(3) and 0.252(3) Å, respectively.

The extended structure of **2** consists of looped chains [Cd···Cd separation = 11.3080(4) Å] (figure 5), which propagate in the [1 0 $\bar{1}$] direction. The shortest inter-chain metal–metal separation is 8.7092(2) Å. Weak inter-chain C–H···O interactions (table 3) may help to consolidate the structure but there is no aromatic *π*–*π* stacking [shortest ring-centroid separation = 4.2944(11) Å].

3.3. *Structure of 3*

The asymmetric unit of **3** consists of the cadmium ion (site symmetry $\bar{1}$), an opeb ligand, and a nitrate (figure 6). A fairly regular *trans*-CdO_2N_4 octahedron (table 4) results from the bonded nitrate ions and the bridging opeb ligands: the Cd^{2+} BVS is 2.02, the octahedral volume is 16.97 $Å^3$, and the angular variance of the X–Cd–Y bonds is $32.7^{\circ 2}$. The dihedral

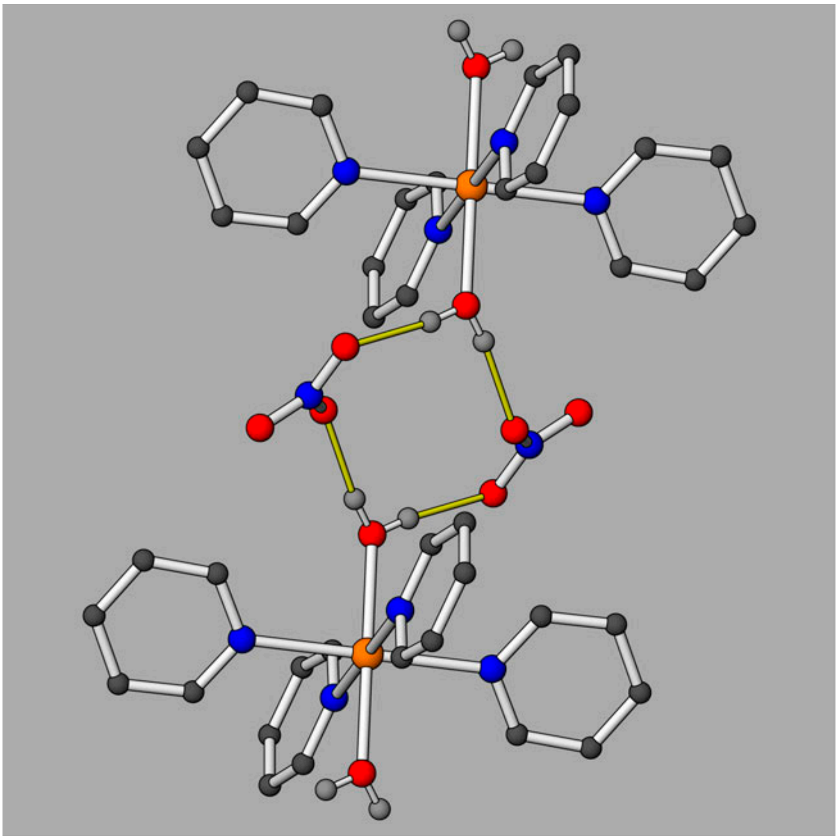


Figure 3. Fragment of the structure of **1** showing pairs of nitrate ions accepting hydrogen-bonded bridges (yellow lines) from adjacent metal ion nodes. The bridging via two different O atoms and the N atom of the nitrate group leads to centrosymmetric $R_4^4(12)$ loops (see http://dx.doi.org/10.1080/00958972.2015.1028381 for color version).

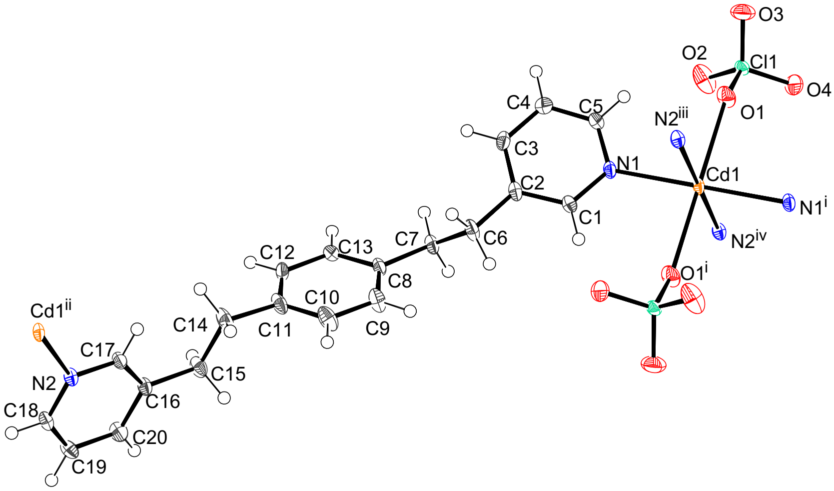


Figure 4. The asymmetric unit of **2** expanded to show the complete metal coordination sphere (50% displacement ellipsoids). Symmetry codes: (i) $1 - x, 1 - y, 1 - z$, (ii) $x - 1, y, z + 1$; (iii) $x + 1, y, z - 1$; (iv) $-x, 1 - y, 2 - z$.

Table 3. Selected geometrical data (Å, °) for **2**.

Cd1–N2^{a}	2.3296(16)	Cd1–N1	2.3297(16)	
Cd1–O1	2.4295(14)			
C2–C6–C7–C8	–159.83(18)	C11–C14–C15–C16	177.5(2)	
C1–H1···O1^{b}	0.95	2.56	3.240(3)	129
C14–H14b···O4^{c}	0.99	2.48	3.312(3)	142
C17–H17···O4^{c}	0.95	2.57	3.429(2)	151

Symmetry codes: $^{a}x + 1, y, z$.
$^{b}1 - x, 1 - y, 1 - z$.
$^{c}x - 1, y, z + 1$.

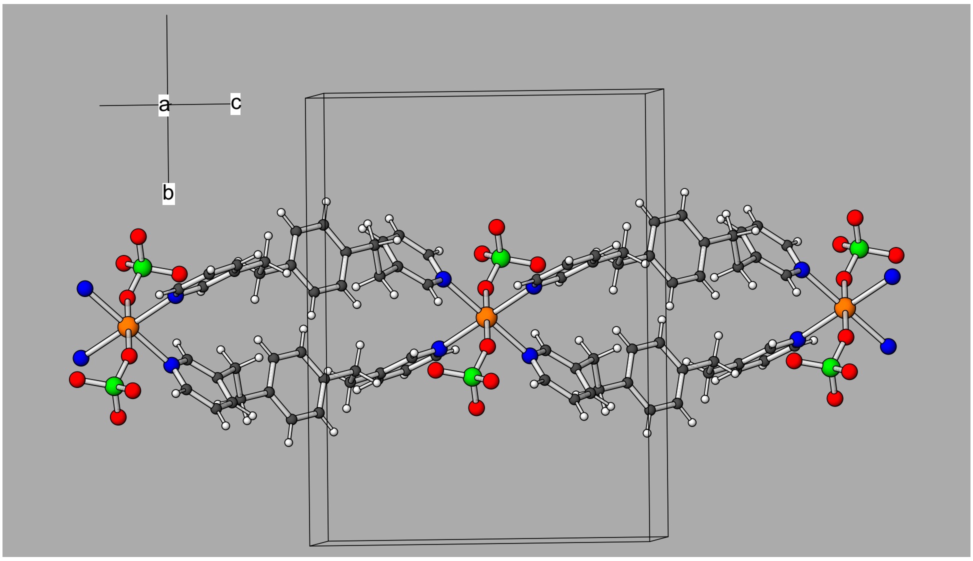


Figure 5. Part of a looped [1 0 $\bar{1}$] polymeric chain in the structure of **2**.

angle between the *cis*-bonded N1- and N2-py rings is 85.65(7)°. In the nitrate, the N–O bond length of 1.280(3) Å for O3, which is also bonded to the metal ion, is significantly longer than the others (mean = 1.228 Å).

The dihedral angles between the central (C8) benzene ring and terminal N1- and N2-pyridine rings of opeb in **3** are 9.52(14)° and 43.49(10)°, respectively. The conformations of the inter-ring ethyl linkages are *anti* for C2–C6–C7–C8 [torsion angle = −175.8(2)°] and *gauche* for C13–C14–C15–C16 [63.3(3)°]. The bonded cadmium ion is displaced from the planes of the N1- and N2-rings by 0.047(4) and 0.499(4) Å, respectively.

The extended structure of **3** consists of an extremely squashed and contorted 4^4 grid [31], which propagates in the (1 0 0) plane (figure 7). Each out-and-back loop consists of 52 atoms (12 atoms per ligand and four Cd atoms). The short and long Cd···Cd separations across a loop are 9.0611(4) and 23.1667(9) Å, respectively. Weak C–H···O interactions (table 4) may help to consolidate the structure and aromatic π–π stacking is

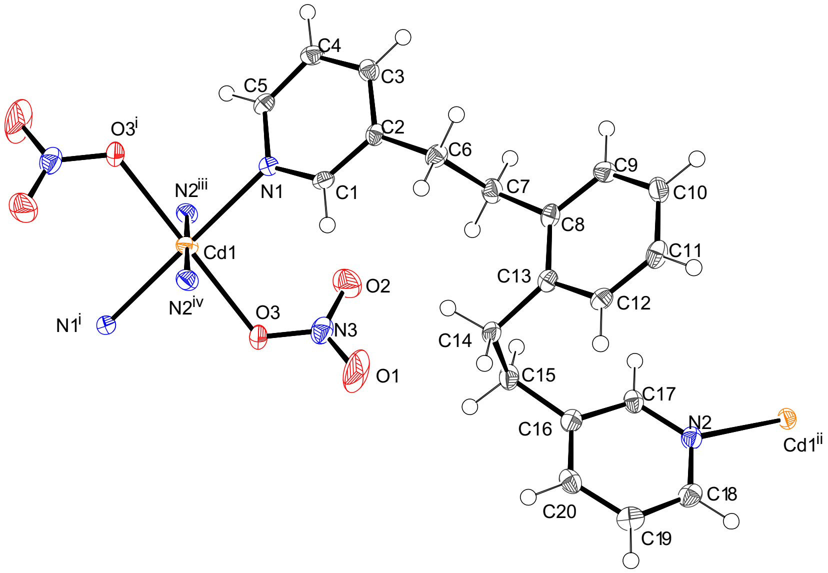


Figure 6. The asymmetric unit of **3** expanded to show the complete metal coordination sphere (50% displacement ellipsoids). Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, 3/2-y, \frac{1}{2}+z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Table 4. Selected geometrical data (Å, °) for **3**.

Cd1–N1	2.321(2)	Cd1–O3	2.3341(18)	
Cd1–N2[a]	2.383(2)			
C2–C6–C7–C8	–175.8(2)	C13–C14–C15–C16	63.3(3)	
C14–H14b···O2[a]	0.99	2.50	3.415(3)	153
C17–H17···O3[b]	0.95	2.54	3.182(3)	125
C18–H18···O2[c]	0.95	2.55	3.374(4)	145

Symmetry codes: [a] $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.
[b] $1-x, y+\frac{1}{2}, \frac{1}{2}-z$.
[c] $x, 3/2-y, z-\frac{1}{2}$.

suggested by a centroid–centroid separation of 3.6188(15) Å between inversion-related pairs of N1-rings.

3.4. *Structure of 4*

The asymmetric unit of **4** consists of the cadmium ion (site symmetry 2), an opeb ligand, two waters (both with O atom site symmetry 2), and a perchlorate (figure 8). A fairly regular *trans*-CdO_2N_4 octahedron (table 5) results from the bonded water molecules and the bridging opeb ligands: the Cd^{2+} BVS is 2.10, the octahedral volume is 16.79 Å^3, and the angular variance of the X–Cd–Y bonds is 11.6$°^2$. The dihedral angle between the *cis*-bonded N1- and N2-py rings is 71.09(17)°; that between the two bonded N1-rings related by the twofold axis is 59.04(16)°. In the perchlorate, the mean Cl–O bond length is 1.405 Å.

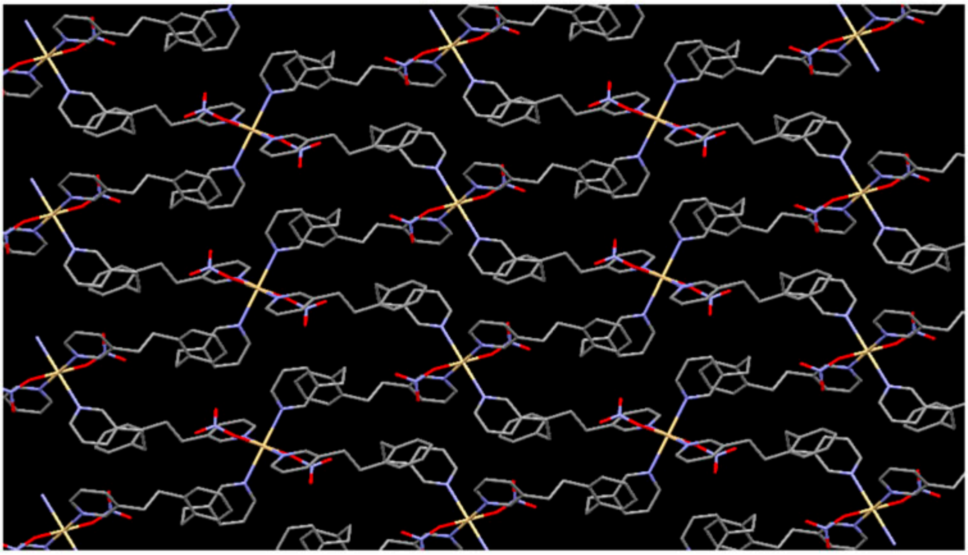


Figure 7. View approximately down [1 0 0] showing a fragment of a 4^4 polymeric (1 0 0) grid in the structure of **3**. Hydrogens omitted for clarity.

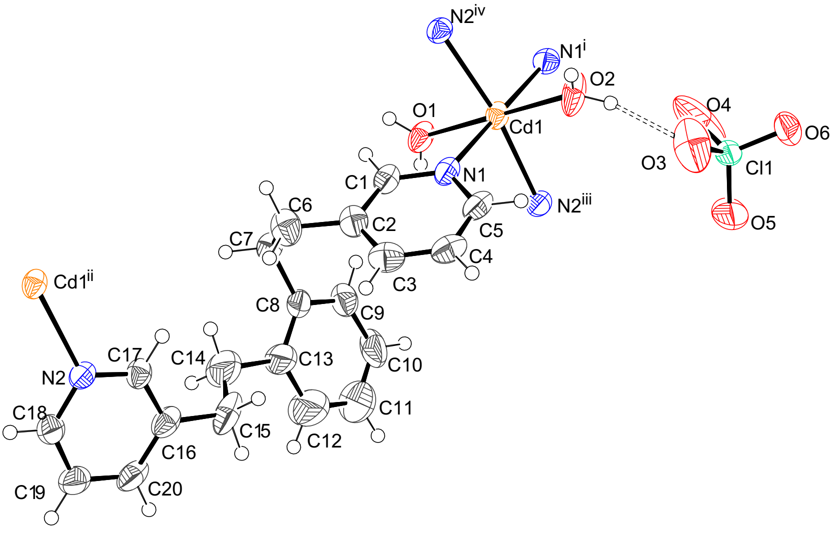


Figure 8. The asymmetric unit of **4** expanded to show the complete metal coordination sphere (50% displacement ellipsoids). Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The dihedral angles between the central (C8) benzene ring and terminal N1- and N2-pyridine rings of the opeb ligand in **4** are 63.0(3)° and 22.8(3)°, respectively. The conformations of the inter-ring ethyl linkages are *gauche* for C2–C6–C7–C8 [torsion angle = 54.8(7)°] and *anti* for C13–C14–C15–C16 [−177.7(7)°]. The bonded cadmium

Table 5. Selected geometrical data (Å, °) for **4**.

Cd1–N2[a]	2.334(4)	Cd1–N1	2.336(4)	
Cd1–O2	2.295(5)	Cd1–O1	2.347(5)	
C2–C6–C7–C8	54.8(7)	C13–C14–C15–C16	−177.6(7)	
O2–H2···O3	0.84	2.09	2.867(7)	155
O1–H1···O3[b]	0.84	1.92	2.757(6)	173
C1–H1a···O6[c]	0.95	2.52	3.393(7)	153
C17–H17···O4[d]	0.95	2.50	3.268(7)	138
C19–H19···O5[e]	0.95	2.37	3.237(8)	152

Symmetry codes: [a]*x* + ½, *y* − ½, *z*.
[b]*x*, *y* + 1, *z*.
[c]−*x*, 1 + *y*, ½ − *z*.
[d]*x* − ½, *y* + ½, *z*.
[e]−½ − *x*, ½ − *y*, −*z*.

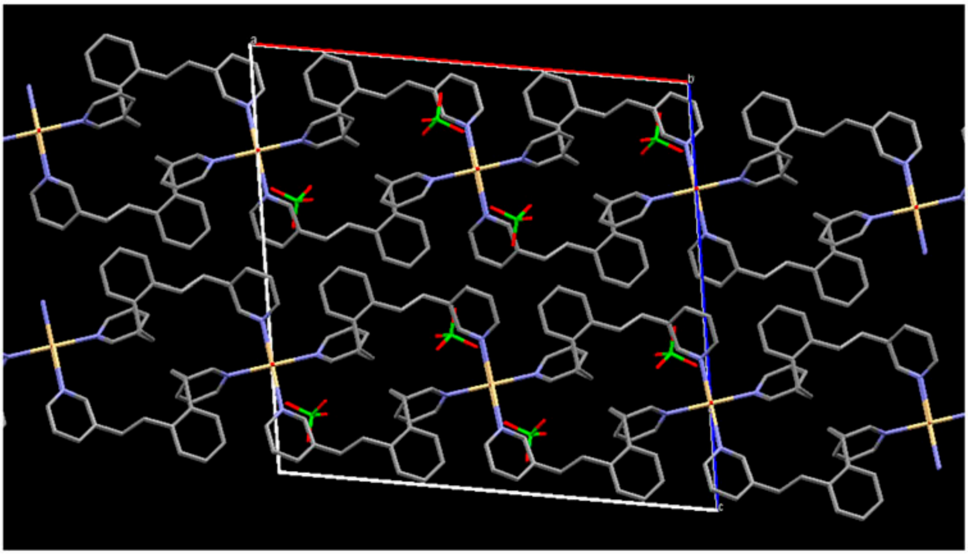


Figure 9. View down [0 1 0] of the packing in **4** showing parts of two (0 0 1) polymeric sheets.

ion is displaced from the planes of the N1- and N2-rings by 0.459(8) and 0.345(8) Å, respectively.

The extended structure of **4** consists of a squashed and contorted 4^4 grid, which propagates in the (0 0 1) plane (figure 9). As with **3**, each out-and-back loop consists of 52 atoms: the short and long Cd···Cd separations across a loop are 8.4599(8) and 22.2618(9) Å, respectively. The water molecules form O–H···O hydrogen bonds to perchlorate (figure 10) to crosslink cadmium nodes in the [0 1 0] direction and generate $R_4^2(8)$ loops (note that this graph-set motif is different to that for **1**, because here the same O of the anion accepts two hydrogen bonds). Weak C–H···O interactions (table 5) are also observed but there is no aromatic *π*–*π* stacking [shortest centroid–centroid separation = 4.332(3) Å].

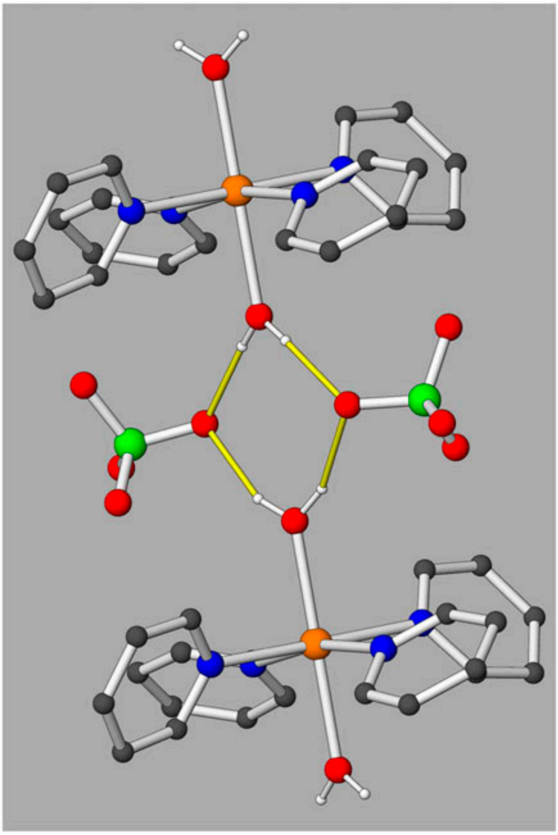


Figure 10. Fragment of the structure of **4** showing how the perchlorate ion accepts O–H···O hydrogen bonds from water molecules to generate $R_4^2(8)$ loops with twofold symmetry.

4. Conclusion

The crystal structures of coordination polymers $[Cd(C_{20}H_{20}N_2)_2(H_2O)_2]_n \cdot 2n(NO_3)$ (**1**), $[Cd(C_{20}H_{20}N_2)_2(ClO_4)_2]_n$ (**2**), $[Cd(C_{20}H_{20}N_2)_2(NO_3)_2]_n$ (**3**), and $[Cd(C_{20}H_{20}N_2)_2(H_2O)_2]_n \cdot (ClO_4)_{2n}$ (**4**) have been described. Compounds **1** and **2** (ligand = ppeb) are 1-D polymers, whereas **3** and **4**, containing the isomeric opeb are layered. The occurrence of *trans*-CdO_2N_4 octahedra is common to all structures (in **1–3** this *motif* has crystallographic inversion symmetry, whereas in **4** it has twofold symmetry), but the O is variously part of a water molecule, a nitrate ion, and a perchlorate ion. It is interesting to note that the contributions of anions and water molecules to these structures have essentially swapped over when comparing **1** (bonded water molecule + non-bonded nitrate) and **2** (bonded perchlorate) *versus* **3** (bonded nitrate) and **4** (bonded water molecule + non-bonded perchlorate). The influence of the strong O–H···O water-to-anion hydrogen bonds in the structures of **1** and **4** is very clear but it is less obvious to us how the weak C–H···O interactions, which are present in all these structures, influence the packing.

The ligand conformations in these structures are very different, with the ppeb adopting an extended *anti–anti* conformation in **1** and **2,** whereas the opeb in **3** and **4** adopts twisted *gauche–anti* arrangements. The dihedral angles between the central benzene ring and the terminal pyridine rings show considerable variation and more data are needed before any structural conclusions can be drawn on this point. Despite the profusion of aromatic rings in these compounds, aromatic π–π stacking appears to play a very minor role in consolidating the structures, with only **3** showing such possible bonds.

The Cambridge structural database (version 5.31) does not contain any crystal structures incorporating opeb and apart from recently reported $[Mn(C_5HO_2F_6)_2(C_{20}H_{20}N_2)]_n$ (**5**) [22], and we are not aware of any other structures containing ppeb. It is interesting to note that the complete bridging ligand in the crystal of **5** is generated by crystallographic inversion symmetry and the conformation of the alkyl chain linking the rings is *gauche*, giving it a contorted Z-shape rather than the extended conformations seen in **1** and **2**.

$Cd(C_5H_5N)_4(ClO_4)_2$ [32], where C_5H_5N = pyridine, is a molecular complex containing CdO_2N_4 octahedra and bound perchlorate ions. In $[Cd(C_{13}H_{14}N_2)_2(H_2O)_2]_n{\cdot}n(C_4O_4){\cdot}8n(H_2O)$ [33], where $C_{13}H_{14}N_2$ = 1,3-bis(4-pyridyl)propane, looped chains occur, as also seen in **1**. $[Cd(C_{18}H_{12}F_4N_2)_2(NO_3)_2]_n{\cdot}2n(C_{10}H_{14}){\cdot}n(C_2H_6O){\cdot}n(H_2O)$ [34], where $C_{18}H_{12}F_4N_2$ = 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene, is one example of a large family of coordination polymers that contain *trans*-CdO_2N_4 octahedra with bonded nitrate ions as parts of polymeric chains, sheets and three-dimensional networks, which incorporate various clathrated/included species. $[Cd(C_{20}H_{20}N_2)(NO_3)_2]_n$ [35], where $C_{20}H_{20}N_2$ = 1,2-bis(2-(4-pyridyl)ethyl)benzene, an isomeric ligand to those incorporated in the title compounds with an *ortho* linkage to the central ring and *para* N atoms in the terminal rings, also contains *trans*-CdO_2N_4 octahedra (with bonded nitrate anions) and infinite 4^4 sheets in the crystal.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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