

Hydrothermal synthesis and crystal structures of three-dimensional co-ordination frameworks constructed with mixed terephthalate (tp) and 4,4'-bipyridine (4,4'-bipy) ligands: $[M(tp)(4,4'-bipy)]$ ($M = Co^{II}$, Cd^{II} or Zn^{II})

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Three new metal–organic co-ordination frameworks formulated as $[M(tp)(4,4'-bipy)]$ [$M = Co^{II}$ **1**, Cd^{II} **2** or Zn^{II} **3**; tp = terephthalate; 4,4'-bipy = 4,4'-bipyridine] have been hydrothermally prepared and structurally characterized. Each pair of metal atoms in the three compounds are bridged by bis-bidentate or chelating/bridging bis-bidentate tp ligands to form a linear or zigzag co-ordination chain, and adjacent chains are further linked by chelating or monodentate bis-bidentate tp ligands to form two-dimensional rectangular or parallelogram-like $[M(tp)]$ sheets with dimensions of 10.30×11.37 , 10.08×11.68 and 10.28×10.98 Å for complexes **1**, **2** and **3**, respectively. Adjacent sheets are pillared by 4,4'-bipy spacers into a three-dimensional co-ordination network through the covalently linking mode of $\cdots 4,4'-bipy-M^{II}-4,4'-bipy-M^{II}\cdots$, which feature cuboidal $[M_{16}(tp)_8(4,4'-bipy)_8]$ structural units. Twofold interpenetration of the above three-dimensional co-ordination networks results in stable crystal structures of the three compounds.

Introduction

Research on metal-directed supramolecular complexes has rapidly been expanding due to their interesting topologies¹ and potential applications as functional materials.² Usually bi- or multi-dentate ligands containing N- or O-donors are used to bind metal centers, for example, 4,4'-bipyridine (4,4'-bipy) is an excellent bridging ligand, and a number of one-, two- and three-dimensional infinite metal–4,4'-bipy frameworks have been generated.¹ Polycarboxylates have also been used to form moderately robust (“zeolitic”) frameworks,^{3–5} in which terephthalate (tp), exhibiting a variety of bridging abilities (Scheme 1) and strong tendency to form large, tightly bound metal cluster aggregates, has been used as a building block to construct some porous co-ordination frameworks.^{6–18} On the other hand, so far most of the co-ordination polymers are built with homoleptic ligands. Although several interesting examples have been reported, including the ligand combinations of pyrazine and 4,4'-bipy,^{19a} oxalate and pyrazine,^{19b} oxalate and 4,4'-bipy,^{19c,d} pyridine-4-carboxylate and 4,4'-bipy,^{19e} and phthalate and 4,4'-bipy,^{19f} the development of synthetic routes to systems containing two or more different bridging ligands is much less well explored, and it is generally not yet possible to predict either the composition or structure of the product, much work is required for the rational design and synthesis.

We have been pursuing synthetic strategies for the preparation of non-interpenetrating open frameworks with variable cavities or channels, in which rod-like rigid spacers such as 4,4'-bipy, pyrazine and related species are chosen as building blocks.^{19a,20} Here we report the outcome of three reactions in mixed ligand systems using the rigid rod-like spacers 4,4'-bipy and terephthalate.

Experimental

All reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin-

Elmer 240 elemental analyser. The FT-IR spectra were recorded from KBr pellets in range $4000\text{--}400\text{ cm}^{-1}$ on a Nicolet 5DX spectrometer. Thermogravimetric data were collected on a Perkin-Elmer TGS-2 analyser in flowing nitrogen at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Syntheses

[Co(tp)(4,4'-bipy)] 1. An aqueous mixture (8 cm^3) containing Na_2tp (0.105 g, 0.5 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.5 mmol) and 4,4'-bipy (0.078 g, 0.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm^3), and the vessel was sealed and heated to $210\text{ }^\circ\text{C}$ for 16 h, then cooled at $5\text{ }^\circ\text{C h}^{-1}$ to $120\text{ }^\circ\text{C}$, held at this temperature for 10 h, followed by slow cooling to room temperature. From the light red powder, red block-like crystals of complex **1** were mechanically separated and washed with water (yield: 0.057 g, ca. 30%). Calc. for $C_{18}H_{12}CoN_2O_4$: C 57.01, H 3.19, N 7.39. Found: C 57.45, H 3.10, N, 7.13%. FT-IR data (cm^{-1}): 3059w, 1607s, 1554s, 1519m, 1424vs, 1396s, 1221w, 1159w, 1073w, 1017m, 842m, 816m, 745m, 631w, 512m and 466w.

[Cd(tp)(4,4'-bipy)] 2. An aqueous mixture (8 cm^3) containing H_2tp (0.083 g, 0.5 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol) and 4,4'-bipy (0.078 g, 0.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm^3). Triethylamine (0.7 cm^3 , 5 mmol) was added, and then the vessel was sealed and heated to $140\text{ }^\circ\text{C}$ for 20 h, cooled to $100\text{ }^\circ\text{C}$ at a rate of $5\text{ }^\circ\text{C h}^{-1}$, and held for 10 h, followed by further cooling to room temperature. Colourless plate-like crystals of the product were collected, washed with water and dried in air (yield: 0.173 g, 80%). Calc. for $C_{18}H_{12}CdN_2O_4$: C 49.97, H 2.80, N 6.47. Found: C 49.79, H 2.98, N 6.61%. FT-IR data (cm^{-1}): 3056w, 1598s, 1567vs, 1500 (sh), 1392vs, 1220m, 1073w, 1008w, 807m, 747m, 628m and 508m.

[Zn(tp)(4,4'-bipy)] 3. An aqueous mixture (8 cm^3) containing H_2tp (0.083 g, 0.5 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.150 g, 0.5 mmol)

and 4,4'-bipy (0.078 g, 0.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm³). Pyridine (1.0 cm³) was added, and then the vessel was sealed and heated to 180 °C for 7 days, and then cooled to 100 °C at a rate of 5 °C h⁻¹, and held for 10 h, followed by further cooling to room temperature. Colourless plate-like crystals of the product were collected, washed with water and dried in air (yield: 0.125 g, *ca.* 65%). Calc. for C₁₈H₁₂N₂O₄Zn: C 56.05, H 3.14, N 7.26. Found: C 55.78, H 3.17, N 7.26%. FT-IR data (cm⁻¹): 3047w, 1603vs, 1541 (sh), 1503m, 1394vs, 1220m, 1153w, 1069w, 1013w, 821m, 751m, 630m and 521m.

X-Ray crystallography

Diffraction intensities for the three complexes were collected at 21 °C on a Bruker CCD diffractometer employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and absorption corrections were applied.²¹ The structures were solved with direct methods and refined by full-matrix least squares using the SHELXS 97 and SHELXL 97 programs, respectively.^{22,23} Non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated.²⁴ The crystallographic data for complexes 1–3 are listed in Table 1, selected bond lengths (Å) and bond angles (°) in Table 2. Drawings were produced with SHELXTL.²⁵

CCDC reference number 186/2157.

See <http://www.rsc.org/suppdata/dt/b0/b005438k/> for crystallographic files in .cif format.

Results and discussion

Characterization

The IR spectrum of complex 1 shows characteristic bands of the dicarboxylate groups in the usual region at 1607 and 1554 cm⁻¹ for the antisymmetric stretching and at 1424vs, 1396s for symmetric stretching. The separations (Δ) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ are at 183 and 158 cm⁻¹, respectively. For complex 2, the characteristic bands of the dicarboxylate groups are shown at 1598 and 1567 cm⁻¹ for antisymmetric stretching and at 1392 cm⁻¹ for symmetric stretching. The Δ values are at 206 and 175 cm⁻¹, respectively. For complex 3, the characteristic bands of the dicarboxylate units are shown at 1603vs and 1541 (sh) cm⁻¹ for the antisymmetric stretching and at 1394 cm⁻¹ for symmetric stretching. The Δ values are 204 and 147 cm⁻¹, respectively. The splitting of $\nu_{\text{asym}}(\text{CO}_2)$ in each complex indicates that the tp carboxylate groups function in two different co-ordination fashions,²⁶ consistent with the crystal structures of 1, 2 and 3.

Thermogravimetric analysis (TGA) was performed on polycrystalline samples in a nitrogen atmosphere. There was no chemical decomposition up to 366 and 403 °C for complexes 2 and 3, respectively, suggesting that the hydrothermal products are more stable than the related ones synthesized by the solution method at room temperature.^{20h}

Crystal structures

Complexes 1, 2 and 3 are structurally very similar, being made up of twofold interpenetrating three-dimensional co-ordination networks. In 1 two equivalent Co atoms related by a twofold axis with an interatomic distance of 4.151(1) Å are bridged by two bis-bidentate tp ligands, as shown in Fig. 1(a). The Co atom is in a distorted octahedral geometry, being co-ordinated by two *trans*-related N atoms [Co–N 2.143(2) and 2.153(2) Å] of two 4,4'-bipy ligands, two oxygen atoms [Co–O 2.183(2) Å] of one chelating bis-bidentate tp ligand (Scheme 1(A)) and two oxygen atoms [Co–O 2.005(1) Å] from different bridging bis-bidentate tp ligands (Scheme 1(D)).

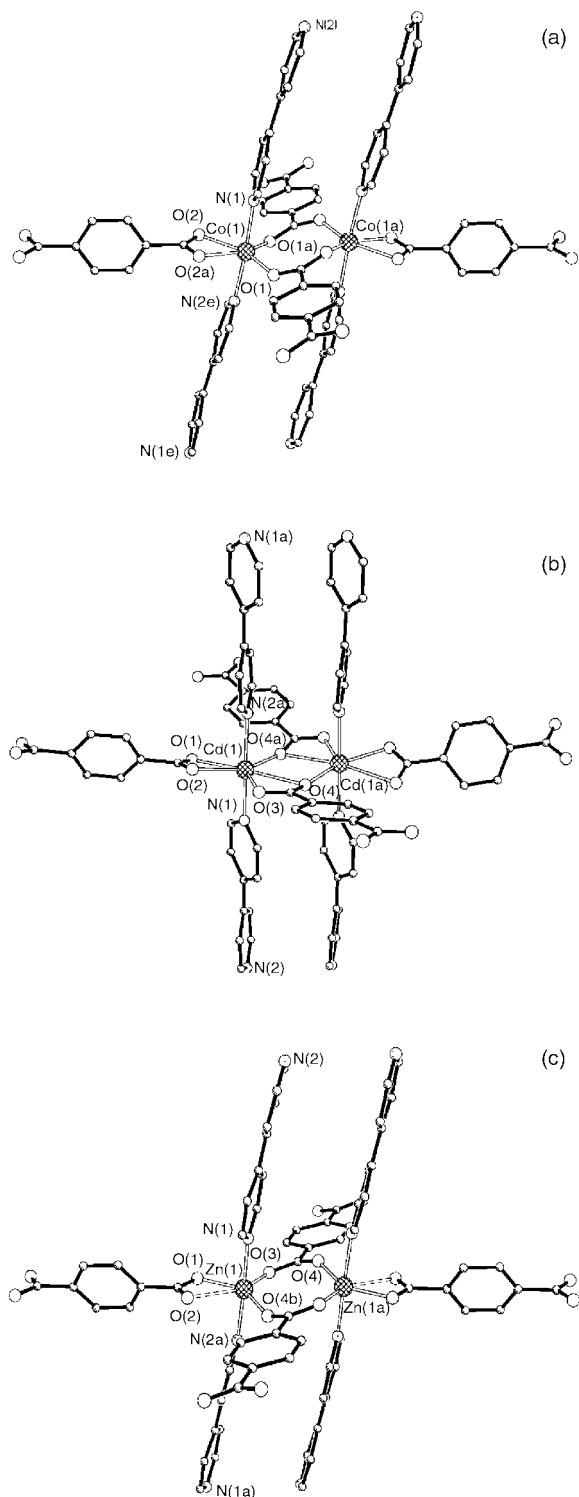


Fig. 1 Perspective views of co-ordination environments in complexes 1 (a), 2 (b) and 3 (c) with atom numberings.

The most interesting structural feature in complex 1 is that the binuclear subunits are inter-connected through tp ligands that bridge the Co₂ centers to generate an unprecedented rectangular sheet with dimensions of 10.30 × 11.37 Å, as shown in Fig. 2(a). The structural motif is not only different from the reported rectangular sheets generated by metal ions and mixed ligands,¹⁹ but also different from the reported metal(II)–tp co-ordination polymers which are composed of one-dimensional chains or three-dimensional co-ordination networks.^{10,11,14,18b} The sheets are aligned parallel to the crystallographic *ab* plane. The axial positions of the cobalt octahedron are occupied by two N atoms from two μ -4,4'-bipy ligands, which further

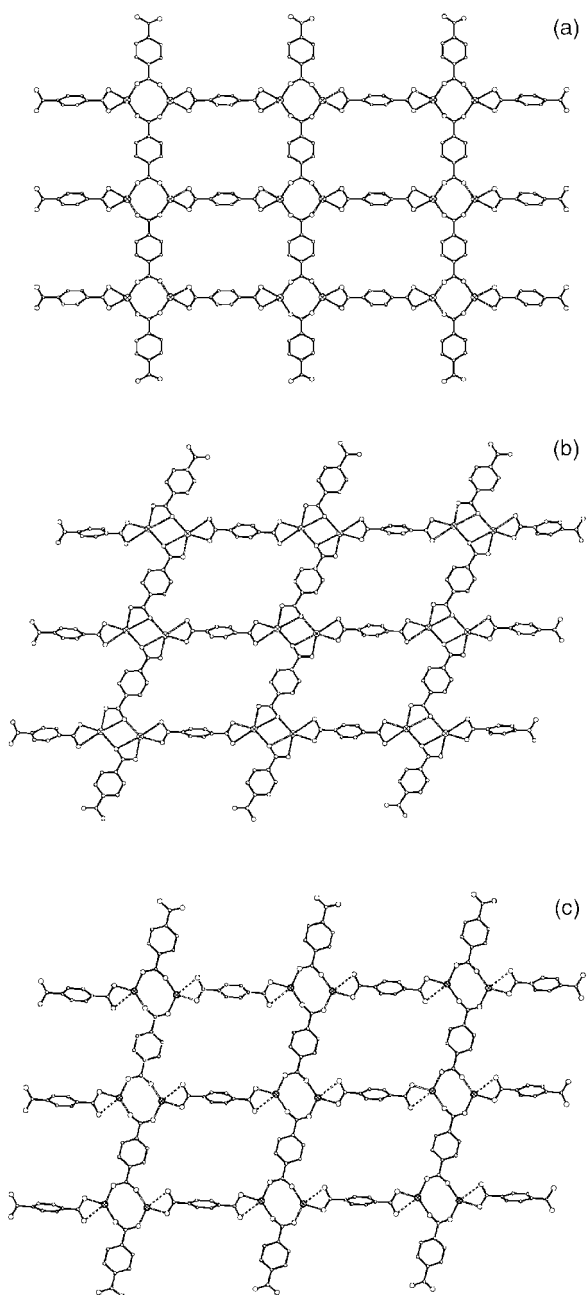
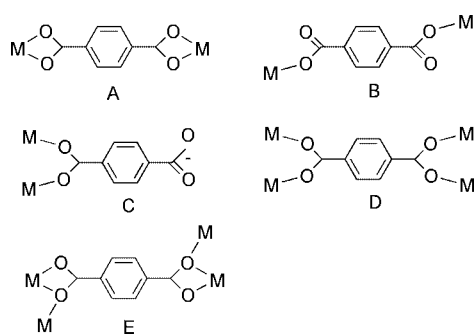


Fig. 2 Perspective views of the two-dimensional sheets of $[M(tp)_2]$ in complexes **1** ($M = Co$) (a), **2** ($M = Cd$) (b) and **3** ($M = Zn$) (c).



Scheme 1 The co-ordination modes of tp^{2-} : (A) chelating bis-bidentate (ref. 6 and this work); (B) bis-monodentate; (C) mono-bidentate (*syn-syn*);^{12,13} (D) bridging bis-bidentate (refs. 14–17, this work); (E) chelating/bridging bis-bidentate (ref. 18, this work).

link neighbouring two-dimensional sheets to generate an infinite three-dimensional co-ordination network featuring cuboidal $[Co_{16}(tp)_8(4,4'-bipy)_8]$ structural units, as shown in

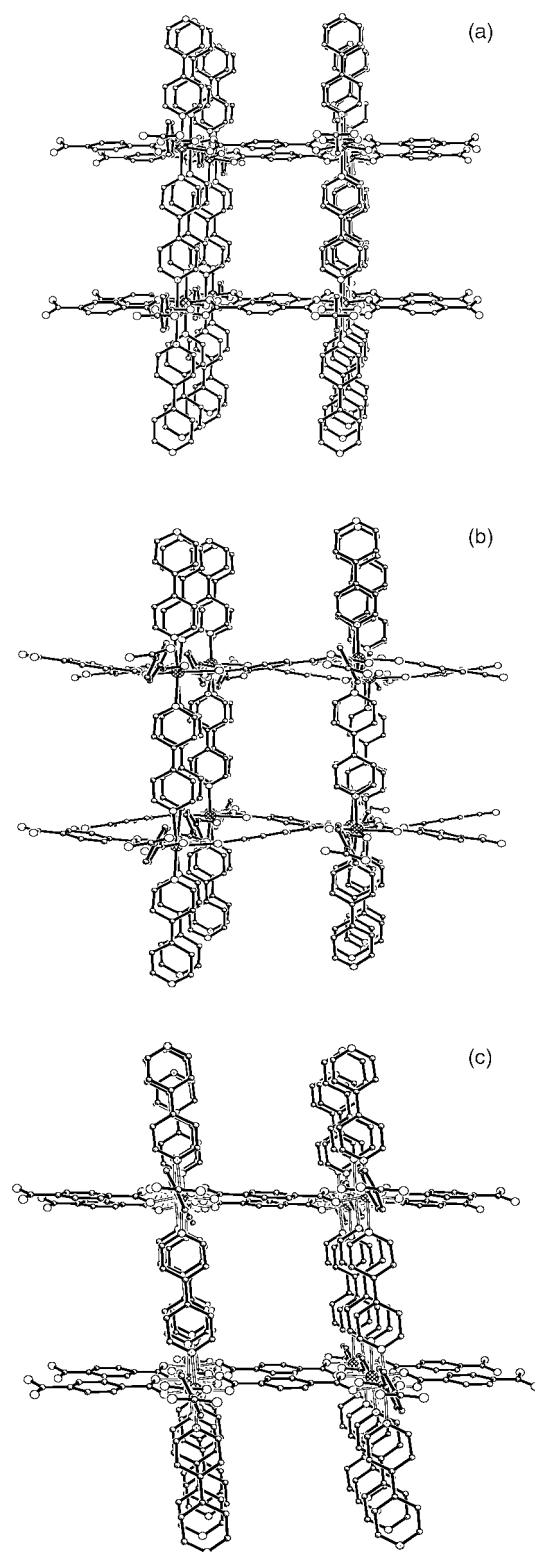


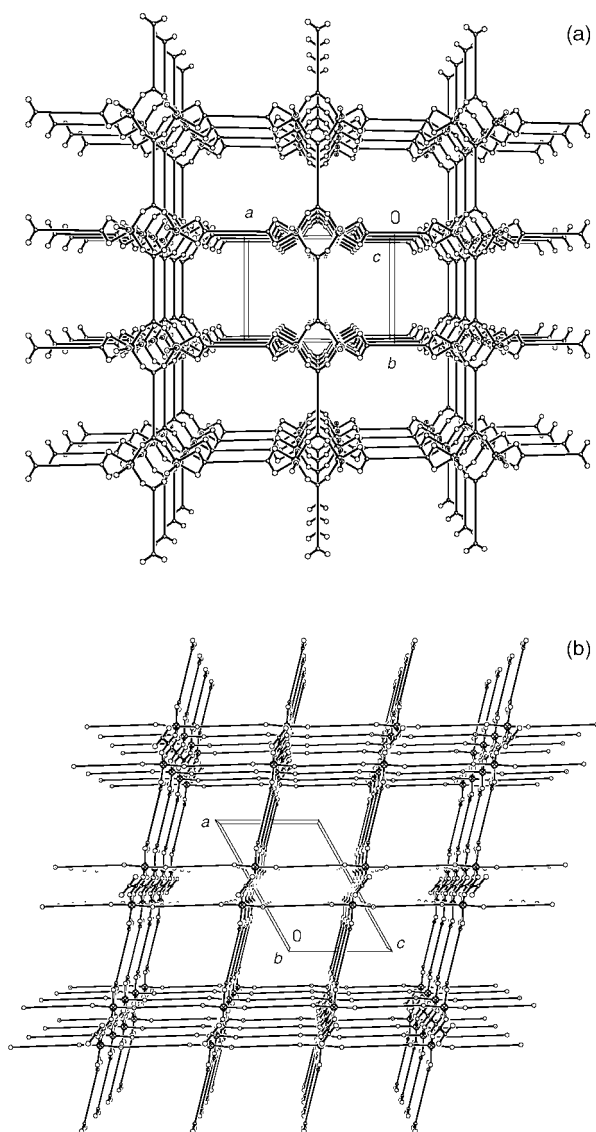
Fig. 3 Perspective views of the three-dimensional frameworks of complexes **1** (a), **2** (b) and **3** (c).

Figs. 3(a) and 4. It is noteworthy that the building block of the three-dimensional co-ordination network in complex **1** is unprecedented. In the cuboid each apex is occupied by a pair of Co atoms which are surrounded by two chelating bis-bidentate ends of *tp*, two bridging bis-bidentate ends of *tp* and two 4,4'-bipyridyl N atoms. Another end of the ligand bridges the cubes into a three-dimensional network.

In complex **2** the local co-ordination environment around the Cd atom can best be described as greatly distorted pentagonal

Table 1 Crystal data and structure refinement of complexes 1–3

	1	2	3
Formula	C ₁₈ H ₁₂ CoN ₂ O ₄	C ₁₈ H ₁₂ CdN ₂ O ₄	C ₁₈ H ₁₂ N ₂ O ₄ Zn
<i>M</i>	379.23	432.70	385.67
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/m</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	16.623(3)	16.108(3)	9.187(2)
<i>b</i> /Å	10.299(2)	11.675(2)	10.276(2)
<i>c</i> /Å	11.368(2)	20.171(4)	10.976(2)
<i>a</i> °			67.89(3)
<i>β</i> °	119.23(3)	111.99(3)	68.19(3)
<i>γ</i> °			65.69(3)
<i>V</i> /Å ³	1698.4(5)	3517.4(11)	845.6(3)
<i>Z</i>	4	8	2
<i>D_c</i> /g cm ⁻³	1.483	1.634	1.515
<i>μ</i> (Mo-Kα)/mm ⁻¹	1.035	1.265	1.477
No. unique data	5166	12474	6923
No. data with <i>I</i> > 2σ(<i>I</i>)	1968	5064	4698
<i>R</i> 1, <i>wR</i> 2	0.0337, 0.0942	0.0260, 0.0707	0.0463, 0.1282

**Fig. 4** Infinite three-dimensional co-ordination framework of complex 1 viewed along the *c* (a) and *b* axes (b).

bipyramid since the chelating/bridging bis-bidentate tp ligands take the place of the bridging bis-bidentate ones in 1, as shown in Fig. 1(b) and Scheme 1(E). The intraduclear Cd...Cd separation is 3.908(1) Å. The Cd(1)–O distances [2.287(2)–

2.653(2) Å] associated with the chelating/bridging bis-bidentate tp ligands are similar to those of [Cd(tp)(py)].^{18b} The two oxygen atoms from the chelating bidentate ends of the tp ligand asymmetrically co-ordinate with the Cd atom [Cd(1)–O(1) 2.608(2) and Cd(1)–O(2) 2.263(2) Å], the distortion of the chelation may be attributed to the seven-co-ordination in contrast to the six-co-ordination in complex 1. The five Cd–O bond lengths are quite similar to documented Cd–O(carboxy) distances [2.251–2.879 Å].²⁷ The axial Cd–N distances [2.294(2) and 2.342(2) Å] are similar to those found in related Cd–4,4'-bipy co-ordination polymers [2.325(3)–2.344(3) Å].^{20b,c,j,28} The two pyridyl rings of the 4,4'-bipy ligand in complex 2 are twisted by 33.5°, in contrast to those in 1 in which they are nearly coplanar. The binuclear subunit is inter-connected through tp ligands that bridge the Cd₂ centers to generate a parallelogram-like sheet with dimensions of 10.08 × 11.68 Å, as shown in Fig. 2(b), which is slightly different from that of complex 1. The distortion from a rectangular sheet in 1 to the parallelogram-like sheet in 2 is also ascribed to different co-ordination numbers, and this two-dimensional network is covalently linked by the 4,4'-bipy ligands to form an infinite three-dimensional co-ordination network with approximately prismatic [Cd₁₆(tp)₈(4,4'-bipy)₈] structural units (Fig. 3(b)), similar to that of 1.

Similarly to complexes 1 and 2, 3 is made up of an infinite three-dimensional co-ordination framework. The co-ordination environment is essentially identical to that of 1 with the exception that bis-monodentate tp ligands in 3 take the place of chelating bis-bidentate tp ligands in 1, as shown in Fig. 1(c) and Scheme 1(B). The Zn atom is in a distorted trigonal bipyramidal geometry. However, the Zn–O(2) distance of 2.617(2) Å suggests a non-negligible interaction with the unco-ordinated oxygen of the bis-monodentate tp ligand, which may be described as a semi-chelating co-ordination mode.²⁹ Hence, the Zn atom may be also regarded as in an octahedral geometry. It is interesting that the analogues with Co, Zn and Cd described here differ considerably in their co-ordination environments, in contrast to other reported series of interpenetrating and non-interpenetrating co-ordination polymers with Co, Zn, and Cd, which with the same ligand were found fully isostructural.³⁰ The Zn...Zn separation within the binuclear subunit is 4.022(2) Å. The Zn(1)–O distances [1.998(2) and 2.007(2) Å] of zinc with the bridging bis-bidentate tp ligands are quite similar to those of [Zn₃(tp)₃]·6MeOH.¹⁵ The axial Zn–N distances [2.154(2)–2.186(3) Å] are similar to those found in related Zn^{II}–4,4'-bipy co-ordination polymers.^{20b,c} The two pyridyl rings of the 4,4'-bipy ligand in complex 3 are virtually coplanar. The binuclear subunits are inter-connected through tp ligands and Zn₂ centers to generate a parallelogram-

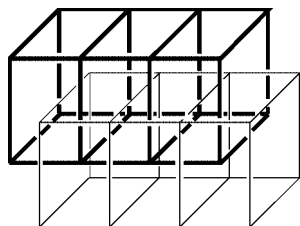
Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–3**

Complex 1			
Co(1)–N(1)	2.143(2)	Co(1)–O(2)	2.183(2)
Co(1)–N(2b)	2.153(2)	O(1)–C(7)	1.255(2)
Co(1)–O(1)	2.005(1)	O(2)–C(10)	1.249(2)
O(1a)–Co(1)–O(1)	114.89(9)	N(1)–Co(1)–O(2)	89.53(8)
O(1a)–Co(1)–N(1)	93.27(6)	N(2b)–Co(1)–O(2)	86.88(8)
O(1)–Co(1)–N(1)	93.27(6)	O(2a)–Co(1)–O(2)	59.90(9)
O(1a)–Co(1)–N(2b)	88.95(6)	N(2b)–Co(1)–O(2a)	86.88(8)
O(1)–Co(1)–N(2b)	88.95(6)	O(1a)–Co(1)–O(2)	92.48(6)
N(1)–Co(1)–N(2b)	175.86(9)	O(1)–Co(1)–O(2)	152.23(6)
O(1a)–Co(1)–O(2a)	152.23(6)	O(1c)–C(7)–O(1)	126.0(3)
O(1)–Co(1)–O(2a)	92.48(6)	O(2)–C(10)–O(2a)	121.4(3)
N(1)–Co(1)–O(2a)	89.53(8)		
Complex 2			
Cd(1)–N(1)	2.294(2)	Cd(1)–O(4a)	2.287(2)
Cd(1)–N(2b)	2.342(2)	O(1)–C(11)	1.235(3)
Cd(1)–O(1)	2.608(2)	O(2)–C(11)	1.241(3)
Cd(1)–O(2)	2.263(2)	O(3)–C(15)	1.244(3)
Cd(1)–O(3)	2.331(2)	C(15)–O(4)	1.254(3)
O(2)–Cd(1)–O(4a)	148.42(7)	O(3)–Cd(1)–N(2b)	91.41(6)
O(2)–Cd(1)–N(1)	99.11(7)	O(2)–Cd(1)–O(1)	52.52(7)
O(4a)–Cd(1)–N(1)	86.03(6)	O(4a)–Cd(1)–O(1)	97.78(7)
O(2)–Cd(1)–O(3)	84.15(7)	N(1)–Cd(1)–O(1)	83.51(6)
O(4a)–Cd(1)–O(3)	126.58(7)	O(3)–Cd(1)–O(1)	135.57(6)
N(1)–Cd(1)–O(3)	95.83(6)	N(2b)–Cd(1)–O(1)	93.45(7)
O(2)–Cd(1)–N(2b)	84.61(7)	O(1)–C(11)–O(2)	123.1(2)
O(4a)–Cd(1)–N(2b)	87.21(6)	O(3)–C(15)–O(4)	121.2(2)
N(1)–Cd(1)–N(2b)	172.15(7)		
Complex 3			
Zn(1)–O(1)	2.025(2)	Zn(1)–N(2b)	2.186(3)
Zn(1)–O(3)	2.007(2)	O(1)–C(1)	1.253(4)
Zn(1)–O(4a)	1.998(2)	C(1)–O(2)	1.216(4)
Zn(1)–O(2)	2.617(2)	O(3)–C(5)	1.257(3)
Zn(1)–N(1)	2.154(2)	O(4)–C(5)	1.250(3)
O(4a)–Zn(1)–O(3)	120.11(9)	O(4a)–Zn(1)–N(2b)	86.76(10)
O(4a)–Zn(1)–O(1)	139.75(9)	O(3)–Zn(1)–N(2b)	89.40(10)
O(3)–Zn(1)–O(1)	99.33(10)	O(1)–Zn(1)–N(2b)	85.87(10)
O(4a)–Zn(1)–N(1)	91.07(10)	N(1)–Zn(1)–N(2b)	175.72(9)
O(3)–Zn(1)–N(1)	94.88(10)	O(4)–C(5)–O(3)	125.4(2)
O(1)–Zn(1)–N(1)	93.44(10)	O(2)–C(1)–O(1)	123.1(3)

Symmetry codes: (a) $x, -y + 1, z$; (b) $x, y, z - 1$; (c) $-x + 2, y, -z + 2$ for **1**; (a) $-x, y, -z + \frac{1}{2}$; (b) $x, y - 1, z$; (c) $x, y + 1, z$; (d) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (e) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ for **2**; (a) $-x, -y + 1, -z$; (b) $x - 1, y, z + 1$ for **3**.

like sheet with dimensions of 10.28×10.98 Å (Fig. 2(c)), which is similar to that of complex **2**, and is linked by the 4,4'-bipy ligands to form an infinite three-dimensional co-ordination framework with prismatic $[Zn_{16}(tp)_8(4,4'\text{-bipy})_8]$ structural units (Fig. 3(c)).

Finally, it should be noted that the actual crystal structures of complexes **1**, **2** and **3** are twofold-interpenetrating three-dimensional co-ordination networks, as depicted in Scheme 2.

**Scheme 2** The twofold interpenetration model for complexes **1**, **2** or **3**.

This is in accord with the fact that tetrahedral, trigonal and octahedral metal templates have a high tendency to form interpenetrated or self-inclusion compounds, if the cavity generated in this way is more than 50% of the crystal by volume.³¹

Conclusion

Three new co-ordination polymers based on mixed O- and N-donor ligands have been hydrothermally synthesized and structurally characterized. The complexes are all made up of three-dimensional co-ordination frameworks with similar cuboid-like $[M_{16}(tp)_8(4,4'\text{-bipy})_8]$ [$M = Co^{II}, Cd^{II}$ or Zn^{II}] as building blocks. Twofold interpenetration of the three-dimensional co-ordination networks in complexes **1–3** results in highly stable crystal structures.

Acknowledgements

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