

Self-assembly of novel co-ordination polymers containing polycatenated molecular ladders and intertwined two-dimensional tilings

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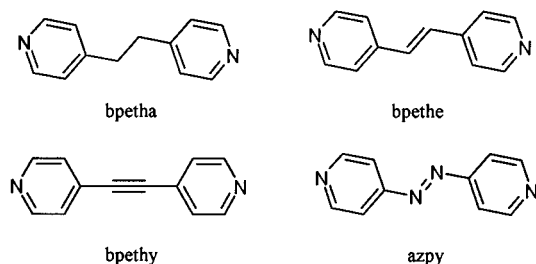
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Four novel co-ordination polymers have been obtained from the reactions of $M^{\text{II}}(\text{NO}_3)_2$ salts ($M^{\text{II}} = \text{Zn, Co or Cd}$) and the bidentate spacer ligands 1,2-bis(4-pyridyl)ethyne (bpethy) and *trans*-4,4'-azobis(pyridine) (azpy), all exhibiting the same metal-to-ligand molar ratio of 2:3. Crystal structure analyses, however, have revealed two quite different polymeric motifs, in spite of the presence of similar co-ordination geometries of the metal ions, that are bound to three pyridyl groups, with a T-shaped disposition, and to the oxygen atoms of two η^2 -nitrates, thus resulting in a distorted pentagonal-bipyramidal seven-co-ordination. The species $[\text{M}_2(\text{bpethy})_3(\text{NO}_3)_4]$ ($M = \text{Zn or Co}$) consist of ladder-like polymers that interpenetrate in an unprecedented fashion to produce an overall three-dimensional array. On the other hand, the species $[\text{Cd}_2(\text{bpethy})_3(\text{NO}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ and $[\text{Cd}_2(\text{azpy})_3(\text{NO}_3)_4]$ contain undulated two-dimensional layers with an unprecedented tiled pattern, that give threefold interpenetration in a parallel fashion.

Introduction

The recent studies on the crystal engineering of networked co-ordination polymers,¹ of potential interest as zeolite-like materials,² have afforded many noteworthy two- and three-dimensional frameworks.³ However, the use of new suitably tailored ligands can allow the characterization of networks unprecedented in inorganic chemistry, as well as of novel intertwining phenomena. A particularly promising class of ligands is represented by molecules containing two 4-pyridyl donor units interconnected by chains or groups of different types. The most simple of these ligands is 4,4'-bipyridyl, that has been used to produce a variety of fascinating architectures.⁴ Longer bis(4-pyridyl) spacers have given very interesting structural motifs in more recent times, including double helices,⁵ double sheets,⁶ simple⁶ and interpenetrated ladders,^{7,8} intertwined brick-wall frameworks,^{7a} interpenetrated diamondoid nets⁹ and other remarkable species.¹⁰ We are currently studying the self-assembly of different metal cations with 1,2-bis(4-pyridyl)ethane (bpetha), 1,2-bis(4-pyridyl)ethene (bpethe), 1,2-bis(4-pyridyl)ethyne (bpethy) and *trans*-4,4'-azobis(pyridine) (azpy) and have reported on some interesting polymers obtained with these ligands, including a complex $\text{Cu}^{\text{II}}(\text{bpethy})_2$ species exhibiting a triply interpenetrated chiral network of a novel topology,¹¹ $[\text{Ni}(\text{azpy})_2(\text{NO}_3)_2][\text{Ni}_2(\text{azpy})_3(\text{NO}_3)_4] \cdot 4\text{CH}_2\text{Cl}_2$, that represents the first example of intertwining of two different types of two-dimensional frames,¹² and $[\text{Ag}_2(\text{bpethy})_3][\text{BF}_4]_2$, containing infinite molecular ladders with sidearms that are threaded into adjacent ladders to produce a new type of supramolecular entanglement.¹³

We report here the characterization of four new co-



ordination polymers from the self-assembly of two of the above ligands and some metal nitrates, namely $[\text{M}_2(\text{bpethy})_3(\text{NO}_3)_4]$ ($M = \text{Zn, 1 or Co, 2}$), $[\text{Cd}_2(\text{bpethy})_3(\text{NO}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ **3** and $[\text{Cd}_2(\text{azpy})_3(\text{NO}_3)_4]$ **4**. In spite of the same formulation for the polymeric frameworks, the family presents two quite different types of structural motifs, *i.e.* polycatenated polymeric ladders of a new type in **1** and **2** (structural type A), and threefold interweaved two-dimensional layers with an unprecedented pattern in **3** and **4** (structural type B).

Results and discussion

We have treated the nitrate salts of Zn^{2+} , Co^{2+} and Cd^{2+} with bpethy in molar ratio 1:2 at room temperature in different solvent systems. Polycrystalline precipitates formed in high yields upon stirring for one hour, whose analytical data indicated the presence of a metal-to-ligand molar ratio of 2:3 in all cases, *i.e.* compounds of formulation $[\text{M}_2(\text{bpethy})_3(\text{NO}_3)_4]$. Single crystals of compounds **1–3** were then obtained within some days by slow diffusion methods, on carefully layering a solution of the ligand over a solution of the metal salt. The pairs of solvents employed for the metal salt and for the ligand, respectively, in the different cases were: water–ethanol (**1**), acetone–ethanol (**2**), and ethanol– CH_2Cl_2 (**3**). In some of these reactions minor amounts of unstable unidentified species were also obtained. Single crystal X-ray analyses have shown (see below) that compounds **1** and **2** present a type A structure, while **3** has a type B one.

In order to get a better insight into the nature of the bulk precipitates, we have examined the polycrystalline samples by X-ray powder diffraction methods. The diffraction patterns for the Zn^{2+} species (from acetone–ethanol) revealed the presence of two-component mixtures of type A and B structures (dominated by B), by comparison with the powder spectra calculated from the single crystal data of **1** and **3**.[†] In the case of cobalt we have observed that the samples obtained by addition of the metal salt solution to the ligand solution showed a pattern cor-

[†] The powder spectra for the $[\text{M}_2(\text{bpethy})_3(\text{NO}_3)_4]$ species ($M = \text{Zn or Co}$) with type B structure were calculated using the atomic coordinates of compound **3** and relaxing the unit cell parameters.

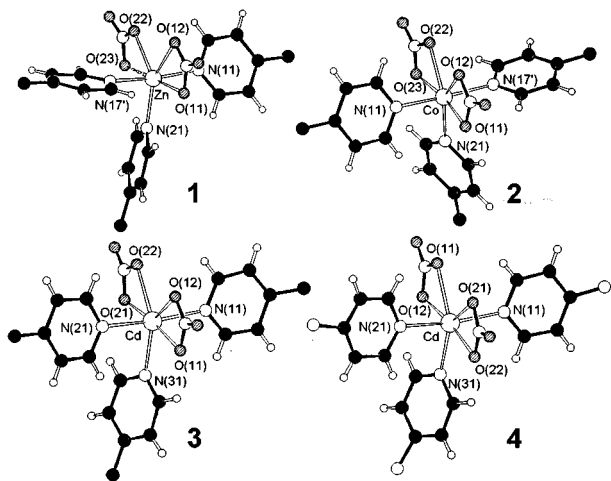


Fig. 1 The co-ordination spheres for the compounds 1–4, with partial atom labelling.

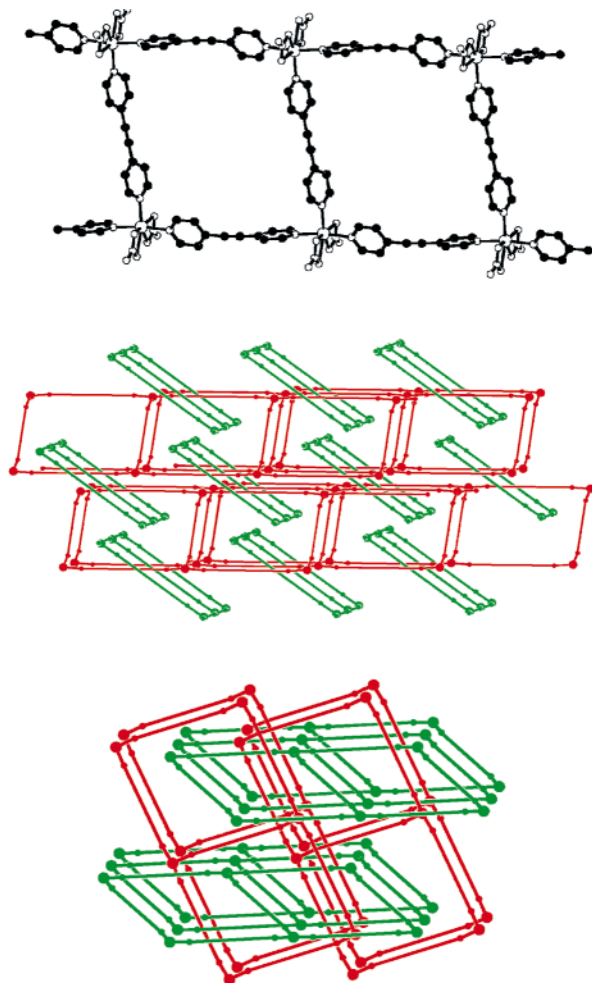
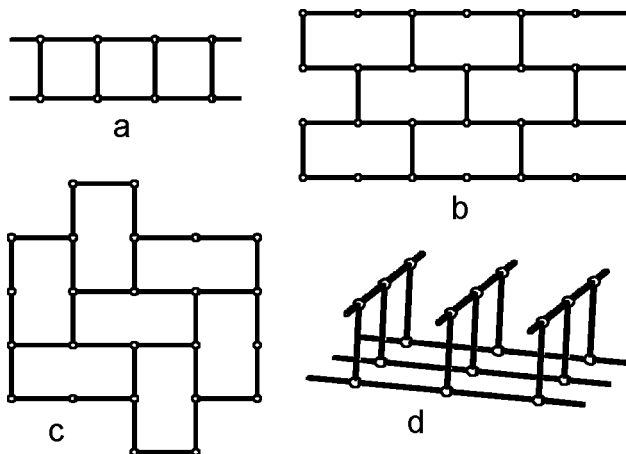


Fig. 2 A SCHAKAL¹⁶ view of a single molecular ladder in compound 1 (top) and two schematic views of the polycatenation of the two sets of ladders in the same species (middle and bottom).

responding to pure compound 2 (type A structure). On the other hand, samples obtained with the inverse mixing of the ligand solution to that of the metal salt gave spectra corresponding to *ca.* 20% of type A structure and 80% of type B structure. Powder spectra of the cadmium samples, whatever the order of the mixing of the two solutions, always indicated the presence of pure compound 3 (type B structure). Though the presence of species with type B structure was observed in the crude zinc and cobalt products, we were unable to isolate the corresponding single crystals.



Scheme 1

The analogous reactions of azpy with zinc and cadmium nitrates were also attempted. Compound 4 (type B structure) was recovered in high yield by treating cadmium nitrate dissolved in acetone with the ligand in CH_2Cl_2 (molar ratio 1:2). Single crystals were obtained in the same way as for compounds 1–3 from acetone– CH_2Cl_2 , while the nature of the bulk product was confirmed by X-ray powder diffraction. On the other hand, zinc nitrate produces a one-dimensional polymeric species of different stoichiometry, namely $[\text{Zn}(\text{azpy})(\text{NO}_3)_2]$, containing simple zigzag chains. The crystals are triclinic, space group $P\bar{1}$ (no. 2), with $a = 5.741(2)$, $b = 8.318(2)$, $c = 15.260(4)$ Å, $\alpha = 75.86(1)$, $\beta = 88.89(1)$, $\gamma = 89.85(1)^\circ$, $U = 706.5(4)$ Å³.¹⁴

The T-shaped metal centres

The molecular structures of the products 1–4 show similar co-ordination geometries at the metals. Each metal ion is bound to three pyridyl groups that display a T-shaped disposition and the metal co-ordination sphere is completed by two η^2 -nitrates, thus resulting in a MN_3O_4 quite distorted pentagonal-bipyramidal seven-co-ordination (see Fig. 1). The nitrate groups are almost symmetrically chelating in all compounds but 1, in which both anions give significantly asymmetric Zn–O bond interactions (difference long – short bond length 0.18 and 0.30 Å for the two nitrates). Selected bond distances and angles are listed in Table 1. The T-shaped geometry is rather common in co-ordination polymers obtained by the self-assembly of $\text{M}(\text{NO}_3)_2$ salts and *exo*-bidentate spacer ligands with a metal to ligand ratio of 2:3. These centres are able to generate one-dimensional,^{6–8} two-dimensional,^{7a,12} and double layered^{2b,6,10b,c} polymeric motifs that are illustrated in Scheme 1. With the flexible ligand bpehta other polymeric structural types are also possible.¹⁵

The polycatenated molecular ladders of compounds 1 and 2 (type A structure)

In the isomorphous compounds 1 and 2 the T-shaped metal centres form infinite molecular ladders, illustrated in Fig. 2 (top).[‡] The $\text{M}\cdots\text{M}$ contacts are in the range 13.91–13.95 Å within the siderails and 13.89–13.97 Å within the rungs of the ladders. Simple molecular ladders are relatively common structural motifs in co-ordination polymer chemistry,^{4f,6,17} and examples of ladders bearing additional ligands as sidearms have also been characterized.^{13,18} However, the peculiar feature of 1 and 2 consists in the intertwining of the ladders, that gives an overall three-dimensional architecture, schematically illustrated in Fig. 2 (middle and bottom). This arises from the fact

[‡] The same structure was also observed for the analogous cobalt polymer $[\text{Co}_2(\text{bpetho})_3(\text{NO}_3)_4]$, containing the 1,2-bis(4-pyridyl)ethane ligand, but the quality of the X-ray data was rather poor because of the marked crystal decay.

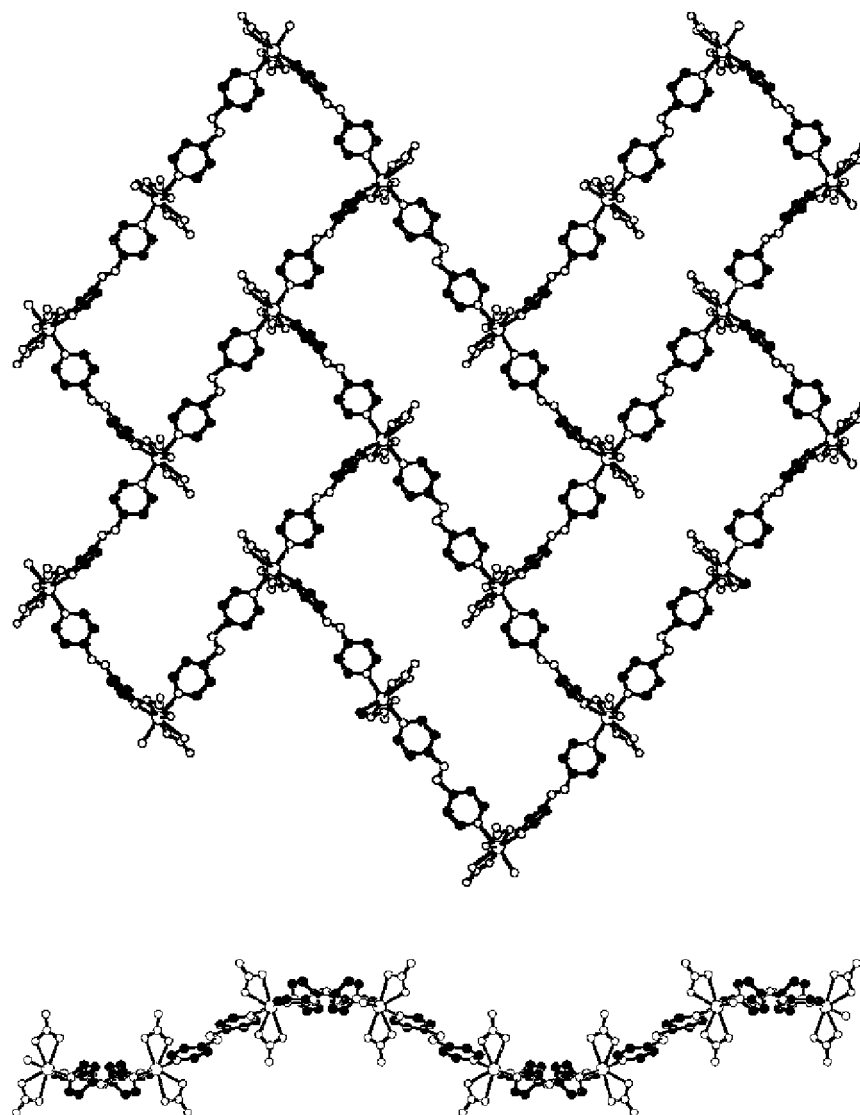
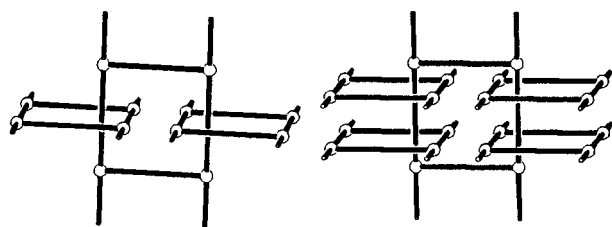


Fig. 3 A tiled single layer of the polymeric species 4 (top) and a side view of the same layer down [1 0 1] (bottom).

that there are two distinct sets of ladders running in two different directions (*i.e.* [1 1 2] and [1 -1 2]) rotated by *ca.* 76.1°, and that the ladders of one set are catenated by those of the other set and *vice versa*. Each square mesh of a ladder is interlocked with two squares of two adjacent ladders of the other set; thus polycatenation of a one-dimensional motif increases the dimensionality of the whole system. Only one previous example of this phenomenon has been reported,^{7a} but, due to the longer spacer ligands employed in that case [*i.e.* 1,4-bis(4-methylene-pyridyl)benzene], each square of a ladder is catenated by four other ladders, instead of two. A comparison of the two catenation modes is illustrated in Scheme 2. A polycatenation of



Scheme 2

different type was also observed in a species consisting of undulated ladders, based on tetrahedral copper(I) centers, that interpenetrate to produce an overall two-dimensional array.⁸

The threefold interpenetrated molecular 'tiled floors' of compounds 3 and 4 (type B structure)

The second polymeric motif produced by the T-shaped metal centres has been evidenced in the isostructural cadmium polymers 3 and 4. These two structures, though based on different ligands, are quite similar and consist of two-dimensional layers of three-connected centres, with rectangular tile-like motifs disposed on adjacent rows in a herring-bone fashion (see Fig. 3, top), to give a molecular 'tiled floor'. The Cd...Cd contacts are somewhat longer in 3 (14.04–14.20 Å) than in 4 (13.46–13.62 Å), in accord with the different N-to-N distance in the two ligands (mean 9.58 Å in bpethy *vs.* mean 9.01 Å in azpy). Three-connected polymeric layers commonly display more or less distorted hexagonal meshes. The tiling described here, generated by the peculiar geometry at the metal centres, is unprecedented in two-dimensional polymers and represents a structural motif alternative to the brick-wall patterns (see Scheme 1, b and c) previously reported,^{7a,12} though it has the same (6,3) topology. The layers are undulated, as illustrated in Fig. 3 (bottom), in contrast with the almost planar disposition of the brick-wall frames found in [Ni(azpy)₂(NO₃)₂][Ni₂(azpy)₃(NO₃)₄]·4CH₂Cl₂.¹² Three equivalent such layers interpenetrate in a parallel fashion, as schematically shown in Fig. 4, to give an overall two-dimensional entangled array.

Structures like these, beside their aesthetic appeal, represent useful basic contributions for the development of the area of

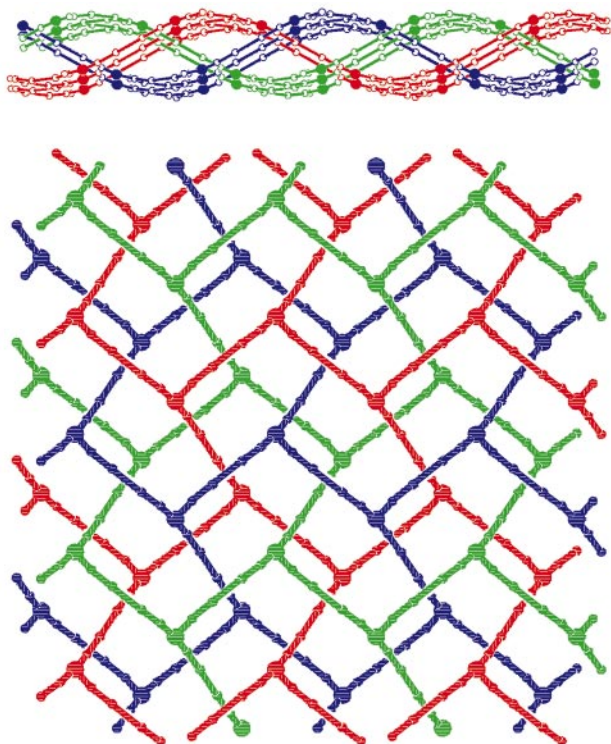


Fig. 4 Two schematic views of the interpenetration of the three equivalent layers in compounds 3 and 4.

crystal engineering of networked polymers. For example, the formation of T-shaped metal centres by using the nitrates as counter ions is now a well established feature, that allows a certain control of the networking process. On the other hand, our finding of two different structural motifs for compounds assembled with similar components in the same ratio (a sort of 'network isomerism') and even for species of equal composition (polymorphism) confirms that these processes are driven by subtle kinetic and/or thermodynamic factors that still remain difficult to rationalize. We can only outline that cadmium, in contrast to the first transition metals, seems to prefer type B structures.

Experimental

General

All the reagents and the solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. The IR spectra were collected on a Perkin-Elmer FT-IR Paragon 1000 spectrometer on Nujol mulls. X-Ray powder diffraction spectra were obtained on a Rigaku D/Max horizontal-scan diffractometer. Elemental analyses were carried out at the Microanalysis Laboratory of this University.

Literature methods were used to prepare 1,2-bis(4-pyridyl)ethyne (bpethy)¹⁹ and *trans*-4,4'-azobis(pyridine) (azpy).²⁰

Syntheses

Reactions of bpethy with zinc nitrate and isolation of compound 1. The compound $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.038 g, 0.128 mmol) dissolved in acetone (4 mL) was added to a solution of bpethy (0.046 g, 0.256 mmol) in ethanol (4 mL) and left to stir at room temperature for 1 h. A white precipitate formed which was recovered by filtration, washed with ethanol and dried in the air (yield 80%). The crude powder was subjected to X-ray powder diffraction (see above). This product, as well as all the other ones reported below, is thermally stable and does not change on

raising the temperature to 230 °C. Samples of these compounds were left in the oven at 100 °C for 1 h in order to remove all the residual solvent before elemental analyses. Elemental analyses for this species were in agreement with a formulation $[\text{Zn}_2(\text{bpethy})_3(\text{NO}_3)_4]$. (Calc. for $\text{C}_{18}\text{H}_{12}\text{N}_5\text{O}_6\text{Zn}$: C, 47.03; H, 2.63; N, 15.23. Found: C, 47.51; H, 2.82; N, 14.99%). Main IR bands (cm^{-1}): 1607s, 1462vs, 1298s, 1217m, 1018m, 839m and 722w. Single crystals of **1** were obtained, together with unidentified products, after many days by slow evaporation of a mixture obtained on layering over a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.021 g, 0.070 mmol) dissolved in water (4 mL) an ethanolic solution (4 mL) of bpethy (0.025 g, 0.139 mmol).

Compound 2. The compound $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.042 g, 0.144 mmol) dissolved in acetone (4 mL) was added to a solution of bpethy (0.052 g, 0.288 mmol) in ethanol (4 mL) and left stirring at room temperature for 1 h. A deep pink precipitate was obtained, that was filtered off, washed with ethanol and dried in the air (yield *ca.* 90%). X-Ray powder diffraction methods were used to confirm the nature of the bulk product. (Calc. for $\text{C}_{18}\text{H}_{12}\text{CoN}_5\text{O}_6$: C, 47.69; H, 2.67; N, 15.45. Found: C, 47.87; H, 2.80; N, 15.05%). Main IR bands (cm^{-1}): 1606s, 1462vs, 1298s, 1213m, 1015m, 838m and 722w. Single crystals of **2** were grown within a few days by layering over a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.020 g, 0.068 mmol) dissolved in acetone (4 mL) a solution of bpethy (0.025 g, 0.138 mmol) in EtOH (4 mL).

Compound 3. The compound $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.022 g, 0.072 mmol) in EtOH (4 mL) was added to a solution of bpethy (0.026 g, 0.144 mmol) in CH_2Cl_2 (4 mL) and left stirring at room temperature for 1 h. A white-cream precipitate was obtained, that was filtered off, washed with CH_2Cl_2 and dried in the air (yield *ca.* 80%). Elemental analyses are in agreement with the formulation $[\text{Cd}_2(\text{bpethy})_3(\text{NO}_3)_4]$ (Calc. for $\text{C}_{18}\text{H}_{12}\text{CdN}_5\text{O}_6$: C, 42.66; H, 2.39; N, 13.82. Found: C, 42.85; H, 2.22; N, 13.63%). Main IR bands (cm^{-1}): 1607s, 1460vs, 1293s, 1218m, 1017m, 833m and 722w. Large cream single crystals of **3** were obtained within a few days by layering over a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.020 g, 0.065 mmol) dissolved in ethanol (4 mL) a solution of bpethy (0.025 g, 0.138 mmol) in CH_2Cl_2 (4 mL).

Compound 4. Addition of the ligand azpy (0.054 g, 0.292 mmol) in CH_2Cl_2 (5 mL) to a stirred solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.045 g, 0.146 mmol) in acetone (5 mL) afforded a red precipitate. The mixture was left stirring at room temperature for about 1 h, then the product was filtered off, washed with ethanol, and dried in the air. Yield *ca.* 90%. (Calc. for $\text{C}_{15}\text{H}_{12}\text{CdN}_8\text{O}_6$: C, 35.14; H, 2.36; N, 21.86. Found: C, 35.45; H, 2.40; N, 21.01%). Main IR bands (cm^{-1}): 1601s, 1461vs, 1287s, 1018m, 843m and 722w. Single crystals of **4** were grown within some days by layering over a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.013 g, 0.042 mmol) dissolved in acetone (4 mL) a solution of azpy (0.018 g, 0.098 mmol) in CH_2Cl_2 (3 mL).

Crystallography

Crystal data for compounds **1–4** are reported in Table 2. The data collections were performed at 293 K on an Enraf Nonius CAD4 diffractometer for **1** and **3** and a Bruker SMART CCD area-detector for **2** and **4**, using Mo-K α radiation ($\lambda = 0.71073$ Å), by the ω -scan method, within the limits $3 < \theta < 24$ (**1**), $2 < \theta < 30$ (**2**), $3 < \theta < 25$ (**3**) and $2 < \theta < 31^\circ$ (**4**). Empirical absorption corrections (ψ scan for **1,3** and SADABS²¹ for **2,4**) were applied in all cases. The structures were solved by direct methods (SIR 97)²² and refined by full-matrix least squares on F^2 (SHELXL 97).²³ Anisotropic thermal factors were assigned to all the non-hydrogen atoms, except in **3** where the statistically disordered solvated dichloromethane molecules were treated isotropically. All the diagrams were drawn using the SCHAKAL 97 program.¹⁶

Table 1 Selected bond distances (Å) and angles (°) in compounds 1–4

Compound 1					
Zn–N(11)	2.147(5)	N(11)–Zn–N(17')	171.9(2)	N(21)–Zn–O(11)	91.6(2)
Zn–N(17')	2.148(5)	N(11)–Zn–N(21)	97.0(2)	N(21)–Zn–O(23)	84.4(2)
Zn–N(21)	2.136(6)	N(17')–Zn–N(21)	90.6(2)	O(11)–Zn–O(12)	54.6(2)
Zn–O(11)	2.197(5)	N(11)–Zn–O	86.1(2)–89.5(2)	O(22)–Zn–O(23)	50.6(2)
Zn–O(12)	2.385(6)	N(17')–Zn–O	86.0(2)–97.5(2)	O(12)–Zn–O(22)	79.8(2)
Zn–O(22)	2.207(7)				
Zn–O(23)	2.508(8)				
Compound 2					
Co–N(11)	2.148(2)	N(11)–Co–N(17')	173.7(1)	N(21)–Co–O(11)	89.1(1)
Co–N(17')	2.158(2)	N(11)–Co–N(21)	96.3(1)	N(21)–Co–O(23)	84.0(1)
Co–N(21)	2.167(2)	N(17')–Co–N(21)	89.2(1)	O(11)–Co–O(12)	56.9(1)
Co–O(11)	2.185(2)	N(11)–Co–O	86.2(1)–90.3(1)	O(22)–Co–O(23)	53.6(1)
Co–O(12)	2.257(3)	N(17')–Co–O	86.7(1)–95.2(1)	O(12)–Co–O(22)	77.1(1)
Co–O(22)	2.275(3)				
Co–O(23)	2.277(3)				
Compound 3					
Cd–N(11)	2.298(9)	N(11)–Cd–N(21)	169.6(4)	N(31)–Cd–O(11)	86.2(4)
Cd–N(21)	2.309(9)	N(11)–Cd–N(31)	97.8(4)	N(31)–Cd–O(21)	85.9(4)
Cd–N(31)	2.331(10)	N(21)–Cd–N(31)	91.0(4)	O(11)–Cd–O(12)	51.6(4)
Cd–O(11)	2.435(11)	N(11)–Cd–O	84.8(4)–92.0(4)	O(21)–Cd–O(22)	51.9(4)
Cd–O(12)	2.432(9)	N(21)–Cd–O	84.9(4)–94.2(4)	O(12)–Cd–O(22)	84.4(4)
Cd–O(21)	2.421(11)				
Cd–O(22)	2.365(11)				
Compound 4					
Cd–N(11)	2.293(6)	N(11)–Cd–N(21)	166.3(2)	N(31)–Cd–O(12)	85.1(2)
Cd–N(21)	2.310(5)	N(11)–Cd–N(31)	98.9(2)	N(31)–Cd–O(22)	86.8(2)
Cd–N(31)	2.326(5)	N(21)–Cd–N(31)	93.4(2)	O(11)–Cd–O(12)	52.7(2)
Cd–O(11)	2.418(6)	N(11)–Cd–O	85.2(2)–92.8(2)	O(21)–Cd–O(22)	52.0(2)
Cd–O(12)	2.443(6)	N(21)–Cd–O	81.6(2)–94.2(2)	O(11)–Cd–O(21)	83.2(2)
Cd–O(21)	2.472(6)				
Cd–O(22)	2.426(6)				

Table 2 Crystal data and structure refinement parameters for compounds 1–4

	1	2	3	4
Formula	C ₃₆ H ₂₄ N ₁₀ O ₁₂ Zn ₂	C ₃₆ H ₂₄ Co ₂ N ₁₀ O ₁₂	C ₃₇ H ₂₆ Cd ₂ Cl ₂ N ₁₀ O ₁₂	C ₃₀ H ₂₄ Cd ₂ N ₁₆ O ₁₂
<i>M</i>	919.39	906.51	1098.38	1025.45
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i> (15)	<i>C2/c</i> (15)	<i>C2/c</i> (15)	<i>C2/c</i> (15)
<i>a</i> /Å	20.414(3)	20.383(2)	20.682(9)	21.044(3)
<i>b</i> /Å	17.153(4)	17.247(2)	11.244(3)	10.811(2)
<i>c</i> /Å	14.177(2)	14.203(1)	20.821(9)	20.849(3)
β /°	129.80(1)	129.85(2)	112.80(4)	117.31(1)
<i>U</i> /Å ³	3813.9(12)	3833.2(6)	4464(3)	4214.6(12)
<i>Z</i>	4	4	4	4
<i>D_c</i> /g cm ⁻³	1.601	1.571	1.634	1.616
μ /mm ⁻¹	1.336	0.943	1.142	1.084
Reflections collected	3202	13632	4120	31013
Unique reflections, <i>R</i> _{int}	2961, 0.055	4711, 0.038	3903, 0.000	6701, 0.076
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1917	3238	2189	3990
Final <i>R</i> 1, <i>wR</i> 2 (observed data)	0.0572, 0.1043	0.0381, 0.0972	0.0720, 0.1780	0.0636, 0.1795

CCDC reference number 186/1429.

See <http://www.rsc.org/suppdata/dt/1999/1799/> for crystallographic files in .cif format.

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