Using long bis(4-pyridyl) ligands designed for the self-assembly of coordination frameworks and architectures

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Five long bis(4-pyridyl) ligands with different tether groups, namely 1,4-phenylenebis(4-pyridylmethanone) (L^1), bis(4-pyridyl)terephthalate (L^2), 1,5-bis(pyridin-4-ylmethoxy)naphthalene (L^3), 1,4-bis[2-(4-pyridyl)ethenyl]benzene (L^4) and 4,4′-bis(pyridin-4-ylmethoxy)biphenyl (L^5), have been synthesized and employed for the self-assembly of coordination polymers and architectures, with the aim of obtaining structural motifs characterized by long metal–metal separations. Six coordination products (compounds **1**–**6**) have been obtained by reacting the ligands with cobalt(II) nitrate in all cases but one, in which zinc(II) triflate was used. The crystal structures show a variety of structural motifs. $[Co(L^2)(NO_3)_2(MeCN)]·MeCN$ (**2**) and $[Co(L^5)(NO_3)_2]$ (**5**) contain one-dimensional polymeric chains (linear, with a period of 19.64 Å in **2**; zigzag, with a period of 38.65 Å in **5**). $[Zn(L^1)(H_2O)_4](CF_3SO_3)_2·(L^1)_2·H_2O$ (**1**) and $[Co(L^4)_2(H_2O)_4](NO_3)_2·(L^4)_4·(H_2O)_8$ (**4**) exhibit extended three-dimensional and two-dimensional arrays, respectively, sustained both by coordinative and hydrogen bonds. Compound **3**, $[Co(L^3)_2(NO_3)_2]·(CH_2Cl_2)_2$, consists of two-dimensional layers of large rhombic meshes (diagonals of the rhombus 15.43 and 35.74 Å), while compound **6**, $[Co_2(L^5)_4(NO_3)_4]·(Me_2CO)_2$, contains discrete dinuclear molecules, consisting of large rings with appendages, which exhibit an exceptionally long dimension of 62.84 Å and form columnar supramolecular arrays.

Introduction

The use of bridging multidentate ligands and suitable metal centres to construct predictable metal-based multidimensional infinite networks,[1] as well as supramolecular architectures,[2] represents an area of coordination chemistry that has received ever-increasing attention over recent years due to the interest in the potential properties of these species as new materials. Applications can be envisaged in fields such as molecular recognition, host–guest chemistry, ion exchange, catalysis, electrical conductivity, magnetism and optics.[1d,3] Ligand design, together with the coordination properties of the transition metal centres, can be used, in principle, to achieve control over the structure of the network and, thus, to modify the properties of these compounds. Among the ligands employed in these processes, an important class is represented by aromatic molecules containing two (or more) pyridyl donor units interconnected by chains or tether groups of different types, which can afford a variety of lengths, linear or non-linear geometries, and conformationally rigid or non-rigid molecular skeletons. With the most simple of these ligands, *i.e.* 4,4′-bipyridyl, a variety of architectures have been obtained over the past few years.[4] The use of longer bis(pyridyl) spacers has afforded very interesting structural motifs, such as double helices,[5] multiple sheets,[6] interpenetrated ladders,[7] interpenetrated diamondoid nets[8] and other noteworthy species,[9] as a consequence of the different metal centres and counterions, and the nature of the groups joining the pyridyl donor moieties. Though most of these interesting species have been discovered by systematic variation of the metals and ligands, the synthetic strategies certainly imply careful design of the ligand geometry and properties.

We planned to investigate the networking ability of new bis(4-pyridyl) ligands with long tether groups. Some examples of particularly long ligands of this class, previously employed in the self-assembly of coordination polymers or for the construction of molecular rings and cages, leading to particularly long M · · · M separations, are shown in Scheme 1.[10–16]

ref. 10

ref. 11

ref. 12

ref. 13

ref. 14

ref. 15

ref. 16
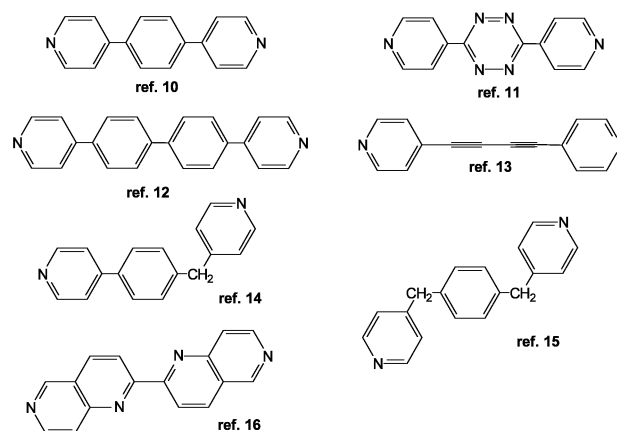
Scheme 1

We report here our exploratory studies on the behaviour of the five ligands illustrated in Scheme 2 towards metal centres, leading to the isolation and characterization of six new metal complexes. The metal salt employed was cobalt(II) nitrate in all but one case, in which we have used zinc(II) triflate. The ligands reported here are among the longest spacers ever employed in the area of coordination compounds. They are all novel, except for L^4, whose synthesis was previously reported.[17] Attempts to react L^4 with an iron salt were made by Batten *et al.*,[8d] but only the salt of the protonated ligand was isolated in that case.

Table 1 Formulae and structure types of the coordination compounds **1–6**

Compound	Formula	Structural type
1	$[Zn(L^1)(H_2O)_4](CF_3SO_3)_2 \cdot (L^1)_2 \cdot H_2O$	3D net; α-polonium topology, coordinative bonds + H-bonds
2	$[Co(L^2)(NO_3)_2(MeCN)] \cdot MeCN$	1D linear chains; coordinative bonds
3	$[Co(L^3)_2(NO_3)_2] \cdot (CH_2Cl_2)_2$	2D layers; (4,4) topology, coordinative bonds
4	$[Co(L^4)_2(H_2O)_4](NO_3)_2 \cdot (L^4)_4 \cdot (H_2O)_8$	2D complex layers; new topology, coordinative bonds + H-bonds
5	$[Co(L^5)(NO_3)_2]$	1D zigzag chains; coordinative bonds
6	$[Co_2(L^5)_4(NO_3)_4] \cdot (Me_2CO)_2$	0D molecular rings with appendages
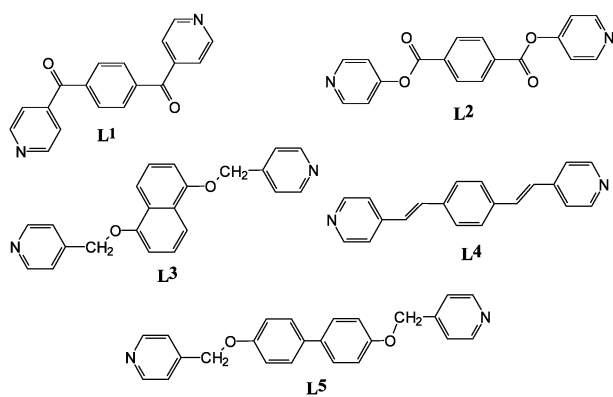
Scheme 2

Results and discussion

The reactions of the spacers L^1–L^5 with $Co(NO_3)_2 \cdot 6H_2O$ were carried out in different solvent systems using various molar ratios of the reagents from 1 : 1 to 2 : 1. Crystalline products were isolated with all the ligands, except for L^1. We have also observed the formation of different products with L^5 upon variation of the solvents. The L^1 ligand was further reacted under similar conditions with $Zn(CF_3SO_3)_2$, giving another species that was also characterized. Single crystals of all the products, compounds **1–6** (listed in Table 1), were grown in a few days by slow diffusion methods and characterized by single crystal X-ray analysis. In Scheme 2 and Table 1, the ligands are numbered according to their increasing lengths.

Two of these species (**2** and **5**) are simple one-dimensional polymeric chains but the others exhibit more interesting structural features that are described below, including two extended arrays sustained both by coordinative and hydrogen bonds (**1** and **4**). Relevant bond parameters for all the compounds are given in Tables 2–7.

Structure of $[Zn(L^1)(H_2O)_4](CF_3SO_3)_2 \cdot (L^1)_2 \cdot H_2O$ (1)

The crystal structure of compound **1** contains –L^1–Zn–L^1–Zn– polymeric linear chains all running in the [1 0 1] direction, with a Zn ··· Zn separation of 16.603(4) Å. In the L^1 ligands, the N-to-N distances are in the range 12.628(4)–12.725(5) Å (Table 2). The metal ions, lying on inversion centres, exhibit octahedral geometry, with the four equatorial positions occupied by coordinated water molecules. A single chain is shown in Fig. 1. There are two uncoordinated L^1 ligands per metal atom (with the *anti* conformation, as for the coordinated one) that are involved in hydrogen bond bridges of the type Zn–OH_2–

(L^1)–H_2O–Zn, with water molecules coordinated to different metal centres (N ··· O hydrogen bond lengths in the range 2.750(4)–2.790(4) Å). Each $Zn(H_2O)_4$ unit is connected *via* these bridges to four other such units: the resulting hydrogen-bonded sublattice is comprised of two-dimensional layers of rhombic mesh, with edges of 18.608(4) and 18.853(4) Å. The overall architecture is a three-dimensional network of 6-connected nodes with the α-polonium topology.[18] Indeed, the individual cells are highly stretched along a body diagonal (the three diagonals have lengths of 14.30 × 27.11 × 45.76 Å), resulting in a 'rhombohedral' geometry (α-Hg-type cell),[18] as shown in Fig. 2. The triflate anions and the solvated water
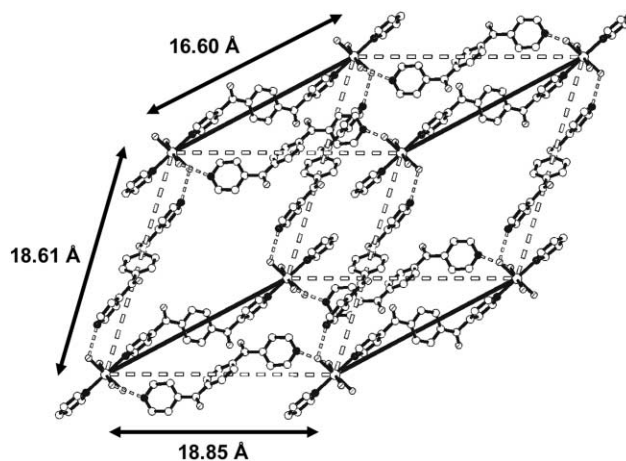
Fig. 2 A single cell (α-Hg-type) of the non-interpenetrated three-dimensional network in compound **1**. The four parallel edges bridged by the metal-coordinated ligands are evidenced by full lines, while the hydrogen bond bridged edges are represented by dashed lines. The view is approximately down the shortest cell diagonal, with a length of 14.30 Å.

molecules occupy the large channels extending in the direction of the *b* axis. The system of hydrogen bonds thus increases the dimensionality from 1D to 3D, and the overall network is schematically shown in Fig. 3. Similar hydrogen bond bridges involving coordinated H_2O molecules and a shorter spacer ligand, 4,4′-bipy, were previously found to connect polymeric
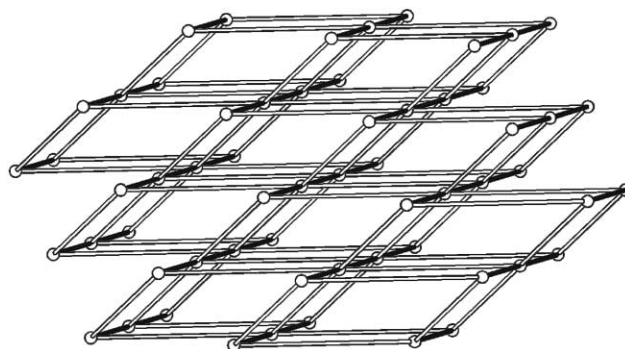
Fig. 3 A schematic view illustrating the topology of the three-dimensional network in **1**.

Fig. 1 A one-dimensional polymeric chain in compound **1**.

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

Zn–O(1W)	2.104(2)	Zn–O(2W)	2.117(2)
Zn–N(21)	2.154(2)		
O(1W)–Zn–O(2W)	88.83(9)	O(1W)–Zn–O(2W)[a]	91.17(9)
O(1W)–Zn–N(21)	88.15(8)	O(1W)–Zn–N(21)[a]	91.85(8)
O(2W)–Zn–N(21)	92.55(8)	O(2W)–Zn–N(21)[a]	87.45(8)

[a] Symmetry operation: $-x, -y + 1, -z$.

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

Co–N(71)	2.11(1)	Co–O(21)	2.20(1)
Co–N(1)	2.13(1)	Co–O(22)	2.21(1)
Co–N(20)	2.13(1)	Co–O(11)	2.21(1)
Co–O(12)	2.35(1)		
N(71)–Co–N(1)	91.8(5)	N(71)–Co–N(20)[a]	93.9(5)
N(1)–Co–N(20)[a]	173.7(5)	N(71)–Co–O(21)	85.2(5)
N(1)–Co–O(21)	88.5(5)	N(20)[a]–Co–O(21)	89.4(4)
N(71)–Co–O(22)	142.5(5)	N(1)–Co–O(22)	85.8(4)
N(20)[a]–Co–O(22)	88.1(4)	O(21)–Co–O(22)	57.3(4)
N(71)–Co–O(11)	80.9(5)	N(1)–Co–O(11)	94.7(5)
N(20)[a]–Co–O(11)	88.8(4)	N(71)–Co–O(12)	137.7(5)
O(21)–Co–O(11)	165.8(5)	O(22)–Co–O(11)	136.7(5)
N(1)–Co–O(12)	89.6(4)	N(20)[a]–Co–O(12)	87.9(4)
O(21)–Co–O(12)	137.1(5)	O(22)–Co–O(12)	79.8(5)
O(11)–Co–O(12)	56.9(5)		

[a] Symmetry operation: $x + 1, y + 2, z + 1$.

Table 4 Selected bond distances (Å) and angles (°) for compound **3**

Co–O(11)	2.082(3)	Co–N(11)	2.225(3)
Co–N(7)	2.201(3)		
O(11)–Co–N(7)	86.1(1)	O(11)–Co–N(7)[a]	93.9(1)
O(11)–Co–N(11)	91.4(1)	O(11)–Co–N(11)[a]	88.6(1)
N(7)–Co–N(11)	87.7(1)	N(7)–Co–N(11)[a]	92.3(1)

[a] Symmetry operation: $-x + 1, -y, -z + 1$.

Table 5 Selected bond distances (Å) and angles (°) for compound **4**

Co–O(1w)	2.112(2)	Co–O(2w)	2.135(2)
Co–O(3w)	2.103(2)	Co–O(4w)	2.109(2)
Co–N(1)	2.125(2)	Co–N(3)	2.132(2)
O(3)–Co–O(4)	179.62(8)	O(3)–Co–O(1)	92.63(8)
O(4)–Co–O(1)	87.42(8)	O(3)–Co–N(1)	92.07(9)
O(4)–Co–N(1)	88.31(8)	O(1)–Co–N(1)	89.67(8)
O(3)–Co–N(3)	87.67(8)	O(4)–Co–N(3)	91.95(8)
O(1)–Co–N(3)	91.00(8)	O(3)–Co–O(2)	87.44(8)
N(1)–Co–N(3)	179.29(9)	O(4)–Co–O(2)	92.51(8)
O(1)–Co–O(2)	178.76(7)	N(1)–Co–O(2)	89.09(8)
N(3)–Co–O(2)	90.24(8)		

Table 6 Selected bond distances (Å) and angles (°) for compound **5**

Co–N(3)	2.034(9)	Co–N(4)	2.066(10)
Co–O(13)	2.047(8)	Co–O(12)	2.273(9)
Co–O(22)	2.149(10)	Co–O(23)	2.199(11)
N(3)–Co–O(13)	97.7(4)	N(3)–Co–N(4)	100.6(4)
O(13)–Co–N(4)	107.7(4)	O(13)–Co–O(22)	94.6(4)
N(3)–Co–O(22)	97.1(4)	N(4)–Co–O(22)	149.2(4)
N(3)–Co–O(23)	92.0(4)	N(4)–Co–O(23)	94.4(4)
O(13)–Co–O(23)	153.7(4)	O(22)–Co–O(23)	59.8(4)
N(3)–Co–O(12)	155.8(4)	N(4)–Co–O(12)	91.0(4)
O(13)–Co–O(12)	58.3(3)	O(22)–Co–O(12)	82.8(4)
O(23)–Co–O(12)	108.4(4)		

chains into layers.[19] We have also reported that [Zn(4,4′-bipy)-(H$_2$O)$_4$](NO$_3$)$_2$·(4,4′-bipy) contains a two-fold interpenetrated network with the same α-polonium topology found here, but sustained by three different types of interactions: Zn–(4,4′-bipy)–Zn coordinative bonds, and Zn–OH$_2$–(4,4′-bipy)–H$_2$O–Zn and Zn–OH$_2$–(nitrate)–H$_2$O–Zn hydrogen bond bridges.[19a]

Table 7 Selected bond distances (Å) and angles (°) for compound **6**

|			
Co–N(9)	2.129(3)	Co–N(45)	2.140(3)
Co–N(48)[a]	2.150(3)	Co–O(37)	2.157(3)
Co–O(25)	2.257(3)	Co–O(50)	2.318(3)
Co–O(42)	2.342(3)		
N(9)–Co(1)–N(45)	94.5(1)	N(9)–Co(1)–N(48)[a]	87.8(1)
N(45)–Co(1)–N(48)[a]	177.5(1)	N(9)–Co(1)–O(37)	141.6(1)
N(45)–Co(1)–O(37)	84.6(1)	N(9)–Co(1)–O(25)	137.2(1)
O(37)–Co(1)–N(48)[a]	94.3(1)	O(25)–Co(1)–N(48)[a]	84.5(1)
N(45)–Co(1)–O(25)	93.1(1)	N(9)–Co(1)–O(50)	85.3(1)
O(37)–Co(1)–O(25)	81.0(1)	O(50)–Co(1)–N(48)[a]	94.2(1)
N(45)–Co(1)–O(50)	87.0(1)	N(9)–Co(1)–O(42)	84.7(1)
O(37)–Co(1)–O(50)	56.3(1)	O(25)–Co(1)–O(50)	137.2(1)
N(45)–Co(1)–O(42)	86.8(1)	O(42)–Co(1)–N(48)[a]	92.4(1)
O(37)–Co(1)–O(42)	133.4(1)	O(25)–Co(1)–O(42)	53.8(1)
O(50)–Co(1)–O(42)	167.8(1)		

[a] Symmetry operation: $-x, -y, -z$.

As already pointed out in that case, structural control of systems involving hydrogen bonding of metal-coordinated water molecules is quite difficult and, therefore, such interactions seem to be of limited relevance in crystal engineering. The α-polonium topology is rather common in these systems. For instance, the recently reported species [Mn(bpe)(H$_2$O)$_4$](ClO$_4$)$_2$·(bpe)$_4$·H$_2$O [bpe = 1,2-bis(4-pyridyl)ethane] contains a similar array linked by both coordinative and hydrogen bonds. However, in spite of the presence of shorter spacer ligands with respect to L^1, it contains two interpenetrated α-polonium networks (which are not translationally equivalent).[20]

In all the L^1 molecules of **1**, the planes of the pyridyl rings are rotated with respect to the plane of the central ring [with dihedral angles in the range 49.6(2)–56.8(2)°].

### Structure of [Co(L^2)(NO$_3$)$_2$(MeCN)]·MeCN (2)

The structure of this species simply consists of one-dimensional linear chains, all running in the [1 2 1] direction, with a Co · · · Co separation of 19.637(4) Å, coincident with the period of the polymer (see Fig. 4, Table 3). The shortest inter-
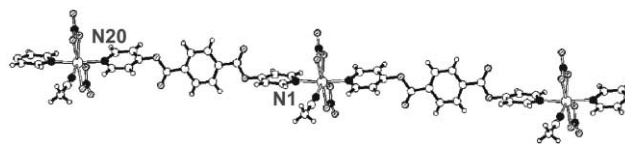
Fig. 4 Two steps of the polymeric chain in compound **2**. The heptacoordination of the metal ions is illustrated.

chain Co · · · Co distances are much smaller [6.239(3) Å] than the intrachain distance. Within the L^2 ligands [N-to-N 15.40(2) Å, *anti* conformation], the planes of the two pyridyl groups are rotated with respect to the plane of the central aromatic ring [dihedral angles of 85.8(9) and 68.1(8)°]. The coordination of the cobalt atoms is distorted pentagonal bipyramidal, with the two pyridyl groups axially disposed and two chelate nitrate anions and a linearly bound MeCN in equatorial positions. Solvated MeCN molecules are located in the interchain regions, almost parallel to the chains.

Structure of [Co(L^3)$_2$(NO$_3$)$_2$]·(CH$_2$Cl$_2$)$_2$ (3)

Compound **3** contains 2D polymeric (4,4)-layers of large rhombic meshes (68-membered rings), with Co · · · Co edges of 19.486(6) Å, illustrated in Fig. 5 (Table 4). The two diagonals of the rhombus are quite different, 15.53 *vs.* 35.74 Å. The cobalt atoms, located on inversion centres, are octahedrally coordinated by four pyridyl groups in the equatorial plane and by two oxygen atoms of two η^1-nitrate anions in axial positions. In the L^3 ligand, the N-to-N distance is 15.455(7) Å The layers stack along the [−2 0 1] direction, with an average separation of
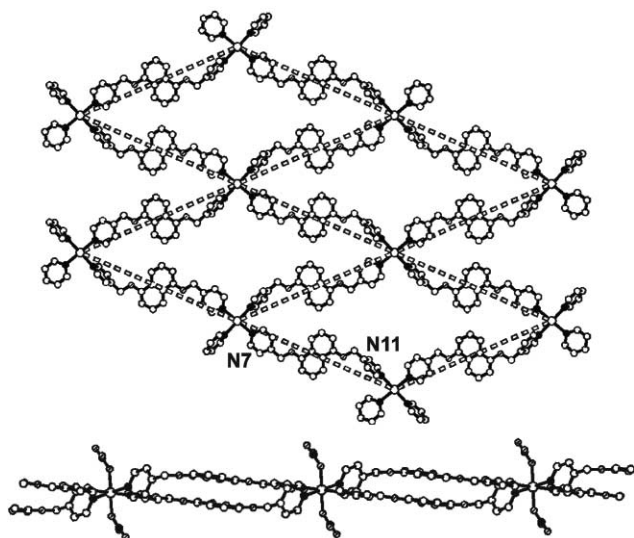
Fig. 5 Two views of a layer in compound **3**. The large rhombic meshes are evidenced in the top view. The (bottom) side view shows that the bridging ligands are not all coplanar.

4.16 Å. There are interplanar π–π interactions involving the aromatic rings of the L^3 ligands (pyridyl rings with the central napthalene unit on an adjacent layer, distance 3.75 Å, offset 1.18 Å).[21] Weak C–H ··· π (centroids of the aromatic rings) interactions are also present,[22] with lengths of 2.65 Å. Channels are observed running along the *a* axis and containing solvated CH_2Cl_2 molecules.

The ligands exhibit a *trans* conformation; one of the pyridyl groups is almost coplanar with the naphtalene unit [dihedral angle 4.6(1)°], while the other one is rotated to an almost perpendicular position [dihedral angle 78.3(1)°].

Structure of $[Co(L^4)_2(H_2O)_4](NO_3)_2 \cdot (L^4)_4 \cdot (H_2O)_8$ (4)

The crystal structure of compound **4** consists of different components, *i.e.* mononuclear $[Co(L^4)_2(H_2O)_4]^{2+}$ complexes, free nitrate anions, uncoordinated ligands and solvated water molecules. The metal complexes are octahedral and display two axial L^4 ligands, acting as monodentate donors, and four coordinated water molecules in equatorial sites. This complex cation exhibits one exceptionally long dimension, with an N ··· N distance between the two uncoordinated ends of 36.37 Å (Fig. 6, top; Table 5). The L^4 ligands (in *trans*, *trans*
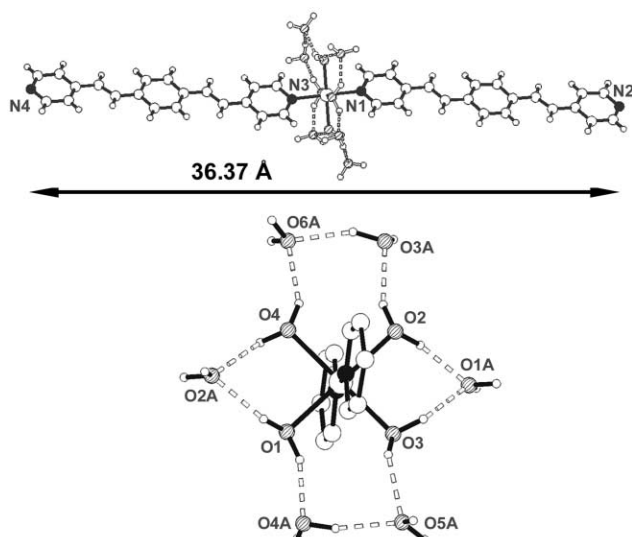
Fig. 6 A view of the mononuclear complex of compound **4** (top), and of the coordination at the metal ion (bottom), showing the hydrogen bond pattern involving the four coordinated water molecules and the six waters of the 'second sphere'.

geometry) contain coplanar aromatic rings. The ligand is the most rigid among those described herein, and the N-to-N distances are in the range 16.084(7)–16.137(8) Å. It is noteworthy that the four coordinated water molecules are surrounded by a 'second sphere' of six water molecules joined *via* hydrogen bonds to the coordinated ones and lying approximately in the same equatorial plane of the complex (Fig. 6, bottom). The O ··· O hydrogen bond lengths are in the range 2.671(3)–2.865(3) Å. These $[Co(H_2O)_4](H_2O)_6^{2+}$ units, by means of the coordinated and uncoordinated ligands, give rise in a complex way to extended two-dimensional layers *via* hydrogen bond bridges. Each cobalt unit is multiply connected to four different metal centres. The coordinated L^4 ligands form hydrogen bonds involving their uncoordinated-N ends and water molecules of the second sphere of a different cobalt unit. Indeed, the six water molecules of the second sphere posses ten hydrogen atoms suitable for hydrogen bonding (6 by one side and 4 by the other side of the equatorial plane, see Fig. 6, bottom) that are all involved in such interactions [9 O–H ··· N(L^4), with N ··· O distances in the range 2.725(3)–2.870(3) Å, and one O–H ··· O(NO_3), with a O ··· O distance of 2.850(3) Å]. Three uncoordinated ligand molecules give H_2O–L^4–H_2O bridges while the fourth one is hydrogen bonded at one end only. Since all the L^4 molecules show an almost parallel orientation, they form columnar blocks surrounding the cobalt atoms (see Fig. 7). The stacking of the complex hydrogen bonded
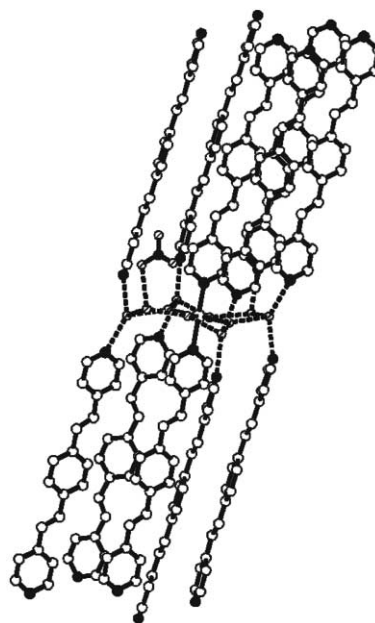
Fig. 7 A view of the columnar block of twelve almost parallel ligands organized around each metal centre by coordinative and hydrogen bond interactions in compound **4**.

layers leaves regions occupied by the nitrate anions and the free water molecules. The topology of a single layer is schematically illustrated in Fig. 8.

Structure of $[Co(L^5)(NO_3)_2]$ (5)

This compound consists of one-dimensional zigzag chains, all running in the [1 4 −1] direction, with Co ··· Co separations of 23.78(1) and 23.63(1) Å, and a polymer period of 38.65 Å (Fig. 9, Table 6). The zigzag geometry of **5** contrasts with the linear nature of **2** and arises because of the different coordination geometry at the metal centres. The Co(II) coordination in **5** is an unusual six-coordinate geometry that can be described as highly distorted octahedral, with two *cis* pyridyl groups and two chelate nitrate anions, as shown in Fig. 9. Particularly interesting is the supramolecular organization of these chains. There are two independent alternating L^5 ligands, both
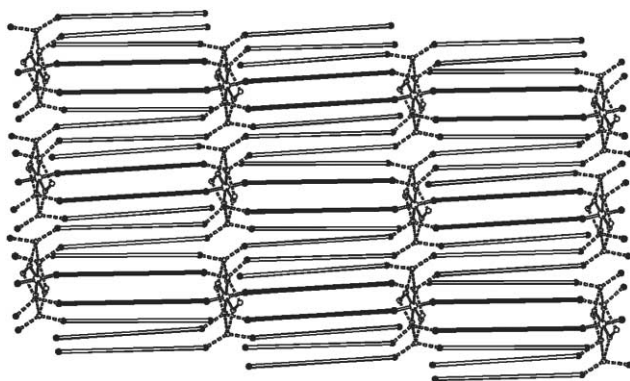
Fig. 8 A schematic view of the topology of a two-dimensional layer in compound **4**.
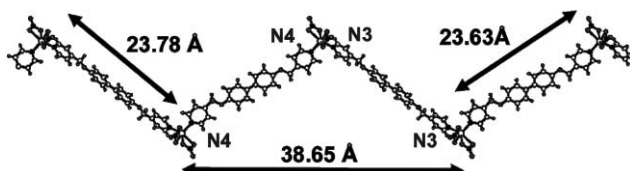

Fig. 9 A view of a single zigzag chain in compound **5**, showing the different orientation of the molecular planes for adjacent ligands.

displaying a *trans* conformation and an almost coplanar disposition of all their aromatic rings. In these ligands, the N-to-N distances are 19.65(2) and 19.78(2) Å. The average L^5 plane in one ligand is almost perpendicular, while in the second one it is almost parallel to the plane of the zigzag chain [with dihedral angles of 81.5(2) and 4.3(2)°, respectively, the dihedral angle between the two L^5 ligands is 84.3(2)°]. Two-dimensional layers are formed *via* π–π stacking interactions[21] involving the former ligands (interplanar distance of 3.45 Å), as shown in Fig. 10.
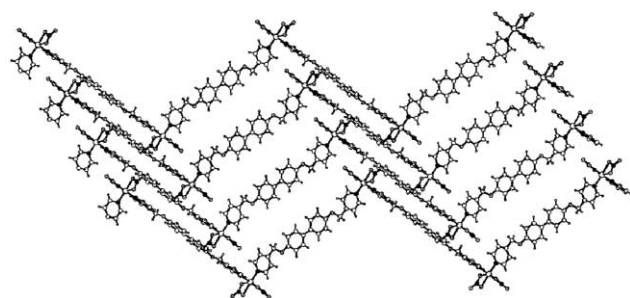

Fig. 10 A view of a two-dimensional layer in **5** formed *via* π–π stacking interactions involving one type of ligand (see text).

Moreover, these layers superimpose in the third dimension in such a way as to give interactions among the stacked ligands of the second type (interplanar distance of 3.75 Å).

Structure of $[Co_2(L^5)_4(NO_3)_4]\cdot(Me_2CO)_2$ (6)

Compound **6** was obtained using the same L^5 ligand as for **5** in a different solvent system. It contains distinct dinuclear molecules. In these species, two cobalt atoms are bridged by two ligands to give a 42-membered molecular ring and each metal bears another terminally bonded L^5 ligand, as shown in Fig. 11 (Table 7). The Co···Co distance within the rings is 19.972(2) Å. The two ligands display different conformations: a *cis*-type in the rings and a *trans*-type outside, with N-to-N distances of 17.076(4) and 19.688(4) Å, respectively. The coordination geometry of the cobalt atoms is pentagonal bipyramidal, with two chelate nitrates and a pyridyl group in equatorial positions, and two pyridyl groups in the axial sites. The overall complex is very long, with an N-to-N distance between the two external free N atoms of 62.84 Å (potentially, a new exceptionally long
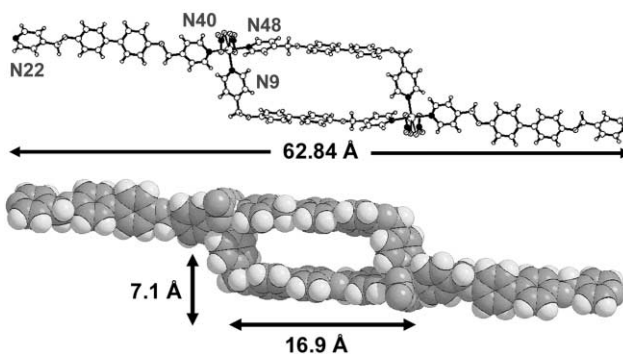

Fig. 11 The discrete molecular motif of compound **6**, consisting of a ring with lateral dangling ligands.

spacer ligand!). The central ring looks like a rectangular box (Fig. 11 bottom) of approximate dimensions 7.1 × 16.9 Å. The dinuclear complexes are organised into one-dimensional parallel columnar arrays through interdigitation of each motif with the dangling ligands of the two adjacent units, as shown in Fig. 12. The solvated acetone molecules lie in the interchain regions.

Fig. 12 The columnar array formed by the interdigitated dinuclear complexes in **6**.

Conclusions

We have described here some new long bidentate ligands and reported on our attempts to obtain coordination networks from their reactions with metal centres. With the exception of the Zn species (**1**), the other products (**2**–**6**) have been assembled using the same metal centres and spacer ligands of various lengths, but all containing two 4-pyridyl units as donor groups. In spite of the similarity of the building blocks employed, the products display quite different structures. The isolated coordination compounds include one or two-dimensional polymeric species sustained only by coordinative bonds (**2**, **3** and **5**), two or three-dimensional arrays connected both by coordinative and hydrogen bonds (**4** and **1**, respectively) or large finite molecules (**6**). The variety of the observed structural motifs confirms that any rationalization of the resulting topologies is still a difficult goal. Many factors play a fundamental role in the formation of the final product, *e.g.* the reagent ratio and the solvent system (see the cases of compounds **5** and **6**). Additional factors responsible for the diversity in these species are: (i) the possible presence of solvent molecules (mainly H_2O) in the metal coordination sphere; (ii) the versatility of the metal coordination geometry (six or seven-coordinate); (iii) the conformational flexibility of some ligands (as L^3 and L^5).

The peculiar structural features in these species are the long metal–metal separations imposed by the spacers, and, when present (as in **3** and **6**), the large dimensions of the metal–ligand rings. This is indeed one of the desired structural properties in the crystal engineering of nanoporous materials. Therefore, though the structures of these species can be considered unexceptional, we think that the spacers described here can be useful tools for the assembly of new materials upon rational variation of the metal centres.

Experimental

The syntheses of the ligands were performed under an inert atmosphere of nitrogen, using standard Schlenk techniques. The coordination compounds were synthetized under aerobic

conditions. Solvents used for the preparation of the ligands were purified according to standard literature procedures and distilled under nitrogen prior to use. The L^4 ligand was prepared according to literature methods.[17] ^1H NMR spectra in $CDCl_3$ were collected with Bruker DRX300 and Bruker AC200 instruments. Infrared spectra were obtained using a Perkin-Elmer Paragon 1000 spectrometer from KBr pellets or Nujol mulls. XRPD analyses were performed on a Rigaku D/Max horizontal-scan diffractometer. Microanalyses were carried out at the University of Milan.

Preparation of the ligands

1,4-Phenylenebis(4-pyridylmethanone) (L^1). This ligand was prepared from 4-bromopyridine (30.4 mL of a 0.345 M ethereal solution) and 1,4-dicyanobenzene (0.672 g; 5.24 mmol) following a procedure described in the literature for the synthesis of di(4-pyridyl)ketone.[23] L^1 was purified and obtained as a yellow–cream solid after succesive precipitation with hexane from a dicloromethane solution. Yield 30% (0.450 g). Calc. for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72; found: C, 74.13; H, 4.22; N, 10.66%. IR (Nujol): 1652 cm^{-1} (ν CO). δ_H (300 MHz): 8.88 [4H, d, py], 7.97 [4H, s, bz], 7.61 [4H, complex d, py].

Bis(4-pyridyl)terephthalate (L^2). 4-Hydroxypyridine (1.424 g; 14.97 mmol) was suspended in CH_2Cl_2 (15 mL) and 1 mL of triethylamine (PM = 101.19; $d = 0.726$ g mL^{-1}) was added under stirring. To this suspension, a solution of terephthaloyl chloride (1.52 g; 7.486 mmol) in CH_2Cl_2 (10 mL) was added dropwise under stirring, followed finally by 2 mL more of triethylamine. After addition of N,N'-dimethylpropionamide (0.183 g; 0.2 eq.) dissolved in 6 mL of CH_2Cl_2, the reaction mixture was left to react for about 2 h and then filtered on a frit. The white precipitate was washed four times with water and dried over silica gel under vacuum for a night. Yield *ca.* 80% (1.9 g). Calc. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75; found: C, 67.91; H, 3.93; N, 8.58%. IR cm^{-1} (Nujol): 1732vs (ν CO). δ_H (300 MHz): 8.72 [4H, d, py], 7.28 [4H, d, py], 8.35 [4H, s, bz].

1,5-Bis(pyridyn-4-ylmethoxy)naphthalene (L^3). 1,5-Dihydroxynaphthalene (0.288 g, 1.8 mmol) was placed in a two-neck round-bottom flask, dissolved under stirring in 15 mL of anhydrous DMF and a 10% excess of potassium *tert*-butoxide (0.888 g, 8 mmol) with 5 mL more of DMF was added. The solution was left to stir at room temperature for 15 min and then 4-picolyl chloride hydrochloride (0.5904 g, 3.6 mmol) was added. The reaction mixture was left to react at the boiling temperature for about 3 h and then was allowed to cool to room temperature. Acetic acid was added to neutralize the mixture. Then, 50–60 mL both of water and ethyl acetate were added. The organic layer was separated, dried with anhydrous sodium sulfate and evaporated to dryness. The product was purified by column chromatography on silica using CH_2Cl_2 containing 2% methanol as the eluant. Pure L^3 was obtained by evaporation of a fraction collected after elution of some impurities, and isolated as a red–brown solid. Yield 84% (0.523 g). Calc. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18; found: C, 77.01; H, 5.51; N, 8.27%. δ_H (300 MHz): 8.68 [4H, d, py], 7.51 [4H, d, py], 8.01 [2H, d, naph], 7.42 [2H, t, naph], 6.89 [2H, d, naph], 5.31 [4H, s, CH$_2$].

4,4′-Bis(pyridin-4-ylmethoxy)biphenyl (L^5). This ligand was prepared following the same procedure described for L^3 by reacting 4,4′-biphenol (0.372 g, 2 mmol) and 4-picolyl chloride hydrochloride (0.650 g, 4 mmol). The ligand was purified by column chromatography on silica using CH_2Cl_2–ethyl acetate (3:2) containing a few drops of triethylamine as the eluant. Pure L^5 was obtained by evaporation of the second fraction as a light yellow solid. Yield 50% (0.368 g). Calc. for $C_{24}H_{20}N_2O_2$: C,

78.24; H, 5.47; N, 7.60; found: C, 78.55; H, 5.63; N, 7.53%. δ_H (300 MHz): 8.64 [4H, d, py], 7.51 [4H, d, py], 7.39 [4H, d, bipy], 7.02 [4H, d, bipy], 5.14 [4H, s, CH$_2$].

Synthesis of the metal complexes

Different metal-to-ligand molar ratios were used in the attempt to improve the yields of the products. The best results, both in terms of crystallinity and yields of the compounds were obtained according to the following procedures.

Compound 1. A solution of $Zn(CF_3SO_3)_2$ (21.2 mg; 0.058 mmol) in ethanol (6 mL) was layered on a solution of L^1 (16.7 mg; 0.058 mmol) in CH_2Cl_2 (5 mL). After slow evaporation of the solvents almost to dryness, elongated crystals of **1**, together with a small amount of a white powder, were formed. The crystals were mechanically separated and subjected to elemental analysis. Yield 35% (26.8 mg). Calc. for $C_{56}H_{46}F_6N_6O_{17}S_2Zn$: C, 51.01; H, 3.52; N, 6.38; found: C, 50.95; H, 3.22; N, 6.43%.

Compound 2. A solution of $Co(NO_3)_2\cdot6H_2O$ (6 mg; 0.021 mmol) in CH_3CN (4 mL) was layered on a solution of L^2 (6.4 mg; 0.020 mmol) in CH_3NO_2 (8 mL). Crystals of **2** grew at the interlayer within a few days, and were recovered by filtration, washed with CH_3CN and dried in air. Yield 50% (6 mg). Calc. for $C_{22}H_{18}CoN_6O_{10}$: C, 45.14; H, 3.10; N, 14.36; found: C, 45.50; H, 3.20; N, 14.14%.

Compound 3. A solution of $Co(NO_3)_2\cdot6H_2O$ (24.7 mg; 0.0849 mmol) in Me_2CO (6 mL) was layered on a solution of L^3 (54.4 mg; 0.170 mmol) in CH_2Cl_2 (6 mL). Pale pink crystals of **3** grew during concentration of the solution by slow evaporation. The crystals, along with some powdered material, were recovered by filtration, washed with acetone and dried in air. Yield 65% (54 mg). XRPD analysis showed that the bulk sample had the composition of pure **3**. Calc. for $C_{46}H_{40}Cl_4CoN_6O_{10}$: C, 53.24; H, 3.87; N, 8.10; found: C, 58.37; H, 4.14; N, 9.22%. The microanalysis accounts for partial loss of the solvated dichloromethane.

Compound 4. A solution of L^4 (40.0 mg; 0.141 mmol) in EtOH (6 mL) was layered on a solution of $Co(NO_3)_2\cdot6H_2O$ (25.6 mg; 0.088 mmol) in H_2O (3 mL). Pale yellow needle-shaped crystals of **4** were formed after slow evaporation of the solvent, and were recovered by filtration, washed with ethanol and dried in air. Yield 30% (55 mg). Calc. for $C_{120}H_{120}CoN_{14}O_{18}$: C, 68.46; H, 5.74; N, 9.32; found: C, 68.91; H, 5.43; N, 9.38%.

Compound 5. A solution of $Co(NO_3)_2\cdot6H_2O$ (12.2 mg; 0.042 mmol) in CH_3CN (5 mL) was layered on a solution of L^5 (31 mg; 0.084 mmol) in $CHCl_3$ (5 mL). Crystals of **5** grew over the period of several days within a pink powder, which formed during concentration of the solution by slow evaporation. The crystals and the powder were recovered by filtration, washed with $CHCl_3$ and dried in air. Yield 75% (17.4 mg). XRPD analysis showed that the sample had the composition of pure **5**. Calc. for $C_{24}H_{20}CoN_4O_8$: C, 52.28; H, 3.66; N, 10.16; found: C, 52.10; H, 3.53; N, 9.98%.

Compound 6. A solution of $Co(NO_3)_2$ $6H_2O$ (13.7 mg; 0.0472 mmol) in Me_2CO (10 mL) was layered on a solution of L^5 (34.8 mg; 0.0944 mmol) in CH_2Cl_2 (8 mL). Slow evaporation of the solvent yielded pale pink crystals of **6**, and were recovered by filtration, washed with acetone and dried in the air. Yield (15 mg) 45%. XRPD analysis showed that the sample had the composition of pure **6**. Calc. for $C_{51}H_{46}CoN_6O_{11}$: C, 62.64; H, 4.74; N, 8.60; found: C, 62.18; H, 4.63; N, 8.41%.

Table 8 Crystallographic data for compounds **1**–**6**

	1	2	3	4	5	6
Formula	$C_{56}H_{46}F_6N_6O_{17}S_2Zn$	$C_{22}H_{18}CoN_6O_{10}$	$C_{46}H_{40}Cl_4CoN_6O_{10}$	$C_{120}H_{120}CoN_{14}O_{18}$	$C_{24}H_{20}CoN_4O_8$	$C_{51}H_{46}CoN_6O_{11}$
M	1318.48	585.35	1037.57	2105.23	551.37	977.87
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	9.323(2)	11.359(2)	13.338(4)	12.554(5)	8.172(5)	11.320(1)
$b/\text{Å}$	11.113(2)	11.765(2)	15.531(5)	18.420(5)	8.482(5)	13.261(1)
$c/\text{Å}$	14.306(2)	11.928(2)	12.136(4)	23.888(5)	17.977(5)	16.001(1)
$\alpha/°$	93.26(1)	112.50(1)	90	89.02(1)	81.23(1)	92.38(1)
$\beta/°$	93.42(1)	93.74(1)	113.02(1)	87.26(1)	89.94(1)	99.64(1)
$\gamma/°$	97.11(1)	112.77(1)	90	87.11(1)	75.46(1)	98.53(1)
$U/\text{Å}^3$	1465.1(5)	1314.7(4)	2313.8(13)	5510(3)	1191.2(11)	2336.4(3)
Z	1	2	2	2	2	2
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.585	0.718	0.667	0.230	0.779	0.437
Refl. collected	19777	10202	25292	40207	10293	20146
Indep. refl., $R(\text{int})$	7249, 0.0353	3368, 0.0442	5068, 0.0669	18283, 0.0635	10293, 0.00	8183, 0.0349
Refl. observed $[F > 4\sigma(F)]$	5058	2702	3251	8014	4019	5503
$R1$ $[F > 4\sigma(F)]$	0.0587	0.1202	0.0696	0.0482	0.1138	0.0492
$wR2$ (all data)	0.1396	0.3533	0.2196	0.1183	0.3586	0.1342

Crystallography

Single crystal X-ray experiments for compounds **1**–**6** were performed on a Bruker SMART-CCD diffractometer, the data collections were performed at 293 K by the ω-scan method using Mo-Kα radiation ($\lambda = 0.71073$ Å). Other details of crystal data, data collection and processing are given in Table 8. Empirical absorption corrections (SADABS)[24] were applied in all cases. The structures were solved by direct methods (SIR97)[25] and refined by full-matrix least-squares on F^2 (SHELX-97).[26] All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C})$. All non-hydrogen atoms were refined with anisotropic displacement parameters. In compound **1**, the anion triflate was found to be disordered and was refined using two models with occupancies of 52 and 48%. The solvated water molecules were statistically disordered and were refined isotropically with half occupancy. In compound **3**, the coordinated nitrate anion was found to be disordered and was refined using two models with occupancies of 71 and 29%. Structures **2** and **5** were found to be non-merohedrally twinned and a suitable set of BASF parameters were used in the refinement, according to the procedure described in GEMINI.[27] All the diagrams were created using the SCHAKAL99 program.[28]

CCDC reference numbers 173813–173818.

See http://www.rsc.org/suppdata/dt/b1/b110189g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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