Polycatenane systems from Co(II) and *trans*-1,2-bis(4-pyridyl)ethene (bpe). Synthesis and structure of $Co(bpe)_2(NCS)_2 \cdot CH_3OH$, $[Co(bpe)_2(H_2O)_2](ClO_4)_2 \cdot 2CH_3OH$ and $[Co(bpe)_2(H_2O)_2(CH_3OH)_2](ClO_4)_2 \cdot bpe \cdot H_2O$

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Three new compounds of formulae $Co(bpe)_2(NCS)_2 \cdot CH_3OH$, **1**, $[Co(bpe)_2(H_2O)_2](ClO_4)_2 \cdot 2CH_3OH$, **2** and $[Co(bpe)_2(H_2O)_2(CH_3OH)_2](ClO_4)_2 \cdot bpe \cdot H_2O$, **3**, [bpe = *trans*-1,2-bis(4-pyridyl)ethene] have been synthesised and characterised by single crystal X-ray diffraction. The metal environment in **1**–**3** is distorted octahedral. Compound **1** is a polycatenane. Its structure consists of parallel layers containing Co^{2+} ions linked by bpe ligands, the Co···Co distance through the bpe bridge being 13.65(3) Å. Each metal ion, in a layer, defines the edges of a rhombus. Two thiocyanate groups *trans*-coordinated to the metal atoms are perpendicular to the sheets. Each sheet has an infinite number of perpendicular sheets concatenated with it in such a way that a polycatenane structure results. The structure of **2** also contains parallel sheets composed of cobalt atoms and bpe molecules, but concatenation is absent and the thiocyanate groups are replaced by water molecules. In this case, the metal atoms define the edges of a square and the Co···Co distance through the bpe bridge is 13.78(3) Å. Uncoordinated perchlorate anions and methanol molecules are linked by means of hydrogen bonds to the water molecules and they connect alternate parallel layers, occupying the middle of the intermediate layers. The structure of **3** exhibits an almost planar arrangement of Co^{2+} ions forming rectangular rings through hydrogen bonds involving both coordinated and free bpe groups and coordinated water and methanol molecules. The Co···Co distances through the coordinated and uncoordinated bpe bridges are 14.6(1) and 16.8(1) Å, respectively. No concatenation of rings from different layers occurs in **3**.

The study of supramolecular systems whose structure is made up of metals coordinated by suitable organic ligands is a very active and expanding research field. The number and variety of coordination compounds, containing both covalent and hydrogen bonds and showing networks of different dimensionality, that have been extensively studied in the last decade are very impressive.[1,2] The interest in these systems is justified by the numerous applications that they may have: magnetic properties arising from the interaction between the spin carriers they contain,[3] low-dimensional conducting polymers,[4] models for metalloenzymes,[5] crystal bending effect,[6] *etc.* In particular, open framework structures are extensively studied due to their very specific pore size and zeolite-type properties, which enable them to be used for adsorption of molecules[7] and host–guest chemistry.[8]

Among the factors to be taken into account when preparing this type of compounds the metal coordination geometry, the structure of the organic ligands that are planned to be used as bridges between the metal centres and the nature of the solvent utilized are crucial. Concerning the organic spacer, particular attention has been devoted to pyrazine (pyz) and 4,4′-bipyridine (4,4′-bipy). These ligands, which contain a delocalized π system, can mediate electronic effects between the metal centres they bridge and have provided examples of one-,[9] two-[10] and three-dimensional[10d,11] frameworks. Structures containing holes of greater size can potentially be built by adopting ligands that differ from 4,4′-bipy by adding suitable groups between the pyridine rings. It is, nonetheless, necessary that any conformational freedom be prevented.[12] 1,2-*trans*-Bis(4-pyridyl)ethene (bpe), which contains an ethylene group between the two pyridine rings, has been successfully used for this purpose, and structures of different dimensionality have been prepared with this ligand and Fe(II),[13] Cu(I)[14a] and Cu(II),[14b] Mn(II),[15] Cd(II)[16] and Co(II).[17] An adamantoid structure has been obtained with Cu(I),[14a] whereas a polycatenane network is formed when the thiocyanate iron(II) salt is used.[13] The large cavities defined by the bridging bpe ligand account for the interpenetrated networks occurring in these systems. It has been shown that the compound dimensionality and the concatenation between the rings depend on the counterion and the metal : ligand molar ratio, besides the identity of the metal ion. When using manganese(II) thiocyanate solutions instead of iron(II), compounds composed of neutral chains of Mn^{2+} ions bridged by either mutually *trans* bpe molecules[15a] or alternating bpe and bis-μ-end-to-end thiocyanate groups,[15b] as well as the mononuclear complex of formula $Mn(bpe)_2(NCS)_2(H_2O)_2$,[15b] are obtained. The structures of the Mn(II)–bpe–NCS^- family show that uncoordinated bpe molecules are placed between the chains and linked by hydrogen bonds to the coordinated solvent molecules. Furthermore, the interaction of copper(II) sulfate with bpe afforded two different compounds.[14b] The first is a virtual three-dimensional compound, made up of interpenetrating cationic grids of $[Cu(bpe)_2]^{2+}$ linked by

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linear $[Cu(bpe)(H_2O)_2(SO_4)_2]^{2+}$ anionic chains, which fill the cavities between the same grids. The second, on the contrary, is composed of bpe-bridged Cu^{2+} chains of formula $[Cu(bpe)(H_2O)],^{2+}$ which are connected through sulfate anions in order to form a three-dimensional structure. A ladder-like chain is formed in the case of Cd(II), the ladder motif being constructed from three *trans*-bpe ligands coordinated to the metal centre, forming a T-shaped unit.[16] Finally, an interesting solvent-dependent interconversion of a molecular ladder into a mononuclear species was reported for the $Co(NO_3)_2$–bpe system.[17]

We report here the preparation and structural characterisation of three new bpe-containing Co(II) compounds of formulae $Co(bpe)_2(NCS)_2 \cdot CH_3OH$, **1**, $[Co(bpe)_2(H_2O)_2](ClO_4)_2 \cdot 2CH_3OH$, **2** and $[Co(bpe)_2(H_2O)_2(CH_3OH)_2](ClO_4)_2 \cdot bpe \cdot H_2O$, **3**, which are obtained by reacting bpe and cobalt(II) thiocyanate (**1**) or perchlorate (**2** and **3**) salts in methanol.

Experimental

Materials and syntheses

Cobalt(II) thiocyanate, cobalt(II) perchlorate hexahydrate and bpe were obtained from commercial sources and used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Università degli Studi della Calabria (Italy).

$Co(bpe)_2(NCS)_2 \cdot CH_3OH$, 1. Single crystals of **1** (orange needles) were obtained, together with a dark violet powder of formula $[Co(bpe)(NCS)_2]$, by slow diffusion using an H-tube glass vessel. The starting solutions were methanolic, containing $Co(NCS)_2$ (17.5 mg, 0.1 mmol) in one arm and bpe (18.2 mg, 0.1 mmol) in the other. With time, **1** dissolves and the amount of dark violet powder increases. When filtered off, the crystals of compound **1** are not air stable because of loss of solvent. (Found: C, 57.26; H, 3.75; N, 15.52; calc. for $C_{27}H_{24}CoN_6S_2O$ **1**: C, 57.88; H, 3.71; N, 15.58%).

$[Co(bpe)_2(H_2O)_2](ClO_4)_2 \cdot 2CH_3OH$, 2, and $[Co(bpe)_2(H_2O)_2(CH_3OH)_2](ClO_4)_2 \cdot bpe \cdot H_2O$, 3. Cubic dark pink crystals of **2** were obtained by slow evaporation at room temperature of a methanolic solution containing equimolar amounts of $Co(ClO_4)_2 \cdot 6H_2O$ (366 mg, 1 mmol) and bpe (182 mg, 1 mmol). Compound **3** was obtained in a similar way as orange crystal needles by using stoichiometric amounts of $Co(ClO_4)_2 \cdot 6H_2O$ (366 mg, 1 mmol) and bpe (547 mg, 3 mmol). Crystals of both **2** and **3** lose solvent when filtered off. (**2** Found: C, 43.35; H, 3.53; N, 8.45; calc. for $C_{26}H_{32}Cl_2CoN_4O_{12}$ **2**: C, 43.83; H, 3.56; N, 8.52%. **3** Found: C, 49.87; H, 4.39; N, 9.25; calc. for $C_{38}H_{44}Cl_2CoN_6O_{13}$ **3**: C, 49.42; H, 4.81; N, 9.11%).

IR spectra

Infrared spectra were recorded on a Jasco FT IR/430 spectrophotometer, from KBr pellets, in the range 4000–250 cm^{-1}. The C–N stretching vibration of the thiocyanate group appears as a single and strong peak at 2067 cm^{-1} for **1**, which is consistent with the occurrence of thiocyanate-N coordination in **1**.[9b,18] A strong absorption at 1610 cm^{-1} in **1** and **2** and a sharp strong intensity doublet at 1610 and 1590 cm^{-1} for **3** (tentatively assigned to a C–N stretching vibration of bpe) are in agreement with the presence of coordinated (**1–3**) and uncoordinated (**3**) bpe ligands. The C–N stretching vibration of free bpe appears at 1590 cm^{-1}.

Crystallography

Diffraction data were collected at room temperature (295 K) on a Siemens R3m/V automatic diffractometer using graphite monochromated Mo-Kα radiation. In order to avoid the loss of solvent, single crystals were sealed in a Lindemann tube and then used for intensity data collection. Information concerning crystallographic data collection and structure refinements is summarised in Table 1. Lorentz-polarisation corrections (semi-empirical Ψ scan absorption corrections only for **2**)[19] were applied to the intensity data.

Solutions and refinements were performed with the SHELXTL PLUS system.[20] The methanol molecule in **1** is disordered and, consequently, its atoms were not defined. The sulfur atom in **1** is affected by some disorder as indicated by the large values of the displacements in the directions normal to the Co–S bond. All non-hydrogen atoms, except bpe and water oxygen [O(2)] atoms in **2** and the non-coordinated water oxygen [O(7)] atom in **3**, were refined anisotropically. The water of crystallisation molecule in **3** was disordered and its oxygen atom was given a 0.5 population factor. All hydrogen atoms, except those of the water of crystallisation in **3** that were not defined, were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The final geometrical calculations were carried out with the PARST program.[21] The graphical manipulations were performed using the XP utility of the SHELXTL PLUS system.

Table 1 Summary of crystal data for $Co(bpe)_2(NCS)_2 \cdot CH_3OH$, **1**, $[Co(bpe)_2(H_2O)_2](ClO_4)_2 \cdot 2CH_3OH$, **2** and $[Co(bpe)_2(H_2O)_2(CH_3OH)_2](ClO_4)_2 \cdot bpe \cdot H_2O$, **3**

	1	2	3
Formula	$C_{27}H_{24}CoN_6S_2O$	$C_{26}H_{32}Cl_2CoN_4O_{12}$	$C_{38}H_{44}Cl_2CoN_6O_{13}$
Formula weight	571.5	722.4	922.6
Crystal system	Tetragonal	Tetragonal	Triclinic
Space group	*P*4/*ncc*	*I*4$_1$*cd*	$P\bar{1}$
a/Å	15.798(5)	19.490(5)	8.958(4)
b/Å			11.093(7)
c/Å	15.674(7)	16.508(7)	12.994(5)
α/°			105.73(5)
β/°			94.55(3)
γ/°			113.60(4)
U/Å^3	3912(2)	6271(3)	1112.8(9)
Z	4	8	1
μ(Mo-Kα)/cm^{-1}	5.67	7.85	5.72
Collect./indep. reflect.	2385/1549	4672/1443	3887/3493
Obs. reflect. [$I > n\sigma(I)$]	651 ($n = 1$)	824 ($n = 2$)	2305 ($n = 3$)
R^a	0.085	0.073	0.072
R'^b	0.093	0.071	0.080

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$.

CCDC reference numbers 164616–164618. See: http//www.rsc.org/suppdata/nj/b1/b102302k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Compound **1** is a polycatenane species whose structure is made up of perpendicular interpenetrated two-dimensional networks. It is isostructural with the parent compound $Fe(bpe)_2(NCS)_2 \cdot CH_3OH$[13] (**4**). Each network contains parallel sheets, composed of cobalt(II)–bpe rings, separated by 11.17(2) Å [11.3(1) Å in **4**]. The metal ions have a compressed octahedral environment (Fig. 1) with two *trans*-thiocyanato groups filling the axial positions and four pyridine nitrogen atoms from four bpe ligands building the equatorial plane [$Co–N_{NCS^-}$ = 2.03(1), $Co–N_{bpe}$ = 2.15(1) Å (Table 2); these distances are 2.06(1) and 2.20(1) Å in **4**]. The metal atom is displaced 0.103(1) Å out of the equatorial plane. The two pyridine rings are tilted by 13(1)° with respect to the ethylene group. The four pyridine units associated with each metal atom are arranged in a propeller fashion [the dihedral angle between their planes and the metal equatorial plane is 59.3(4)°]. Each sheet contains rhombus rings, in which four metal ions are joined to four bpe molecules (Fig. 2). The cobalt–cobalt separation through the bpe ligand is 13.65(3) Å whereas those through the diagonals of the rhombus are 22.34(1) and 15.67(1) Å [these distances are 13.66(1), 22.59(1) and 15.36(1) Å in **4**]. It is noteworthy that similar sheets are formed in the analogous $[Co(NCS)_2(4,4'\text{-bipy})_2] \cdot 2(CH_3CH_2)_2O$ compound (**5**), but square rings and no interpenetration are observed.[22] Adjacent sheets are shifted in such a way that the metal atoms of the first correspond to the ring centre of the second and *vice versa.* Consequently, the metal centres of the first sheet are vertically above those of the 3rd, 5th, 7th, *etc.* sheets, while vertically above the middle centers of the rhombuses of the 2nd, 4th, 6th, *etc.* sheets (Fig. 2). An equivalent stack of sheets is found in planes perpendicular to the first sheet, defining large square-shaped channels oriented in the [001] direction (Fig. 3). Most likely, the solvent molecules are located in these channels.

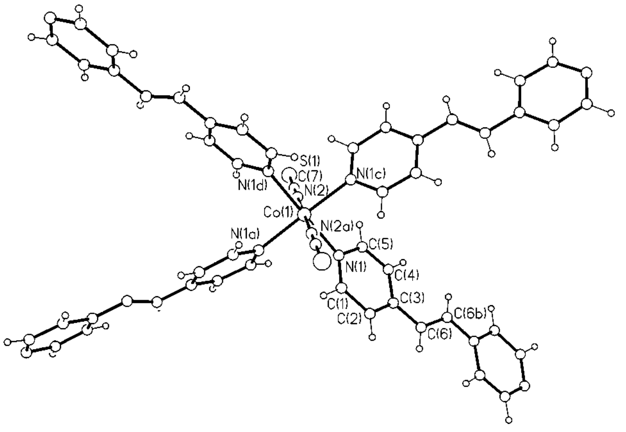

Fig. 1 A perspective view of the cobalt(II) environment in complex **1** along with the atom numbering.

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1** with esds in parentheses[a]

Co(1)–N(1)	2.15(1)	Co(1)–N(2)	2.032(1)
N(1)–Co(1)–N(1a)	90.4(6)	N(1)–Co(1)–N(1c)	89.8(6)
N(1)–Co(1)–N(1d)	176.3(7)	N(1)–Co(1)–N(2)	88.1(5)
N(1)–Co(1)–N(2a)	91.9(5)	N(2)–Co(1)–N(2a)	180.0(1)

[a] Symmetry codes: (a) $0.5 - x, 1.5 - y, z$; (b) $-x, 1 - y, -z$; (c) $-0.5 + y, 0.5 + x, 0.5 - z$; (d) $1 - y, 1 - x, 0.5 - z$.

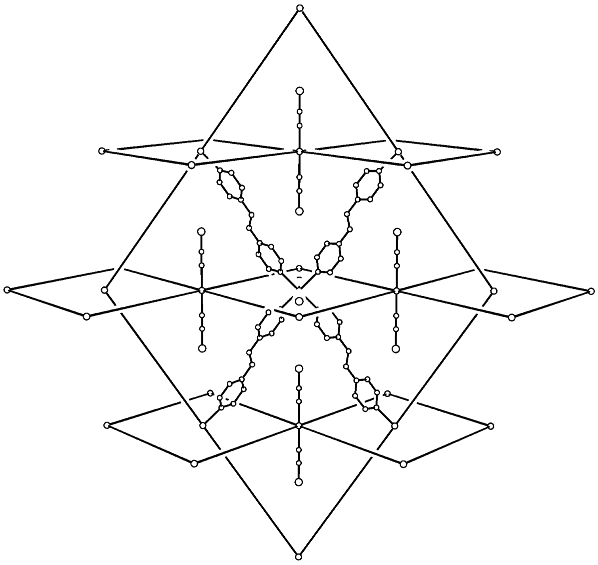

Fig. 2 A view of a fragment of the concatenated layers (oriented in the [110] direction) in complex **1**.

The structure of compound **2** consists of non-interpenetrating layers of cobalt(II) ions bridged by bpe molecules. Each layer contains square rings formed by four cobalt atoms and four bpe ligands. The Co···Co separation through bpe is 13.78(3) Å. Each cobalt atom shows a slightly elongated octahedral geometry (Fig. 4), being bonded to four nitrogen atoms from bpe, which constitute the equatorial plane, and two oxygens from water in the axial positions [average values for the Co–N and Co–O bond distances are 2.11(1) and 2.18(1) Å, respectively (Table 3)]. The cobalt atom is shifted by 0.143(1) Å from the equatorial plane. Both rings of the bpe ligand are planar but the ligand as a whole is not [they form angles of 12(1) and 21(1)° with the ethylene group]. The dihedral angles between the pyridine planes and the metal equatorial plane are 25.7(4) and 58.4(4)°. Adjacent layers are shifted so that the cobalt atoms of the first are placed above the ring centres of the second and *vice-versa* (Fig. 5). The distance between two adjacent layers is 4.18(1) Å. In compound **5**,

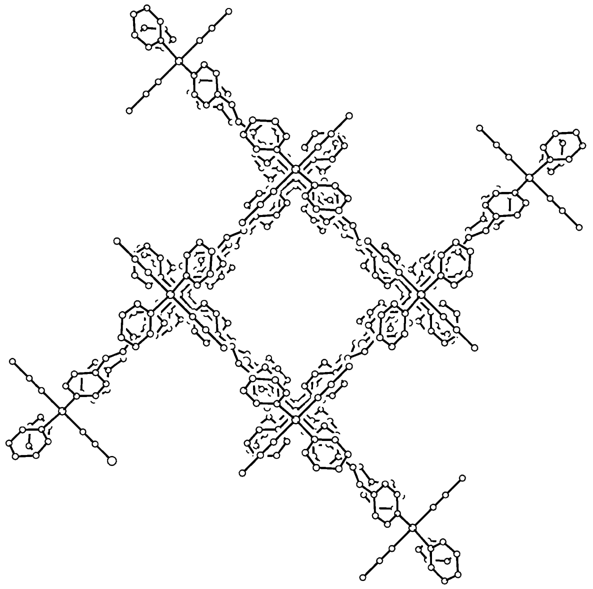

Fig. 3 Projection of the structure of complex **1** along the [110] direction showing the large channel arising from the interlocking layers.

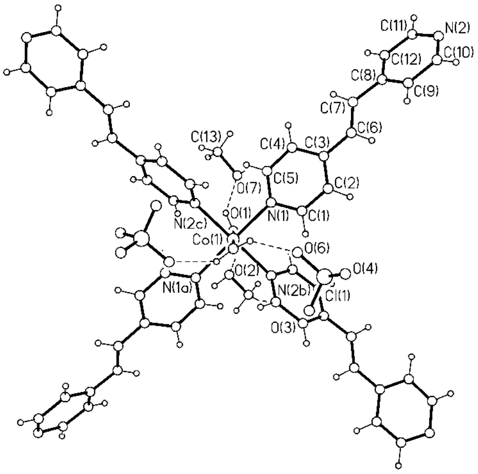

Fig. 4 A perspective view of the cobalt(II) environment in complex **2** along with the atom numbering. The hydrogen bonding involving coordinated water molecules and non-cordinated methanol and perchlorate groups is illustrated by broken lines.

which is composed of layers staggered relative to each other, as in compound **2**, this distance is 6.49 Å due to the presence of linked thiocyanate groups instead of water molecules. Parallel alternate layers (the 1st, 3rd, 5th, *etc.* or the 2nd, 4th, 6th, *etc.*] are joined together through hydrogen bonds (Table 3) involving the perchlorate anions and the water and methanol molecules (Fig. 5). The two CH_3OH molecules, linked to the same coordinated water molecule of the first layer [O(1)···O(7): 2.65(2) Å], are also bonded to ClO_4^- groups [O(7)···O(3d): 2.76(2) Å, d: $-x$, y, $-0.5 + z$], which in turn are H-bonded to water molecules of the third layer [O(2)···O(6): 3.08(3) Å]. In a similar way, the cobalt atoms of the second layer are joined to the cobalt atoms of the fourth one.

Compound **3** is composed of regular chains of cobalt(II) ions bridged by two bpe groups with one nitrogen bound to one cobalt and the other one interacting through a hydrogen bond with the coordinated methanol molecule on the other cobalt atom [O(1)···N(2c) 2.71(1) Å; c: x, $1 + y$, $1 + z$]. These chains are further interlinked (Fig. 6) through hydrogen bonds by means of non-coordinated bpe molecules in such a way that a layered compound containing rectangular rings is formed [O(2)···N(3): 2.71(1) Å]. The cobalt–cobalt separation between two adjacent chains through the non-coordinated bpe is 16.8(1) Å. This distance constitutes the major edge of the rectangular ring, whereas the minor one (the intrachain Co···Co distance) is 14.6(1) Å. Compound **3** can arise from a 1 : 2 Co : bpe species (a hypothetical chain compound) when an excess of ligand is added to the methanolic solution of Co(II)–bpe. This hypothetical chain compound could be regarded as a precursor of **2** (the substantial difference with **2** is the occurrence of coordinated methanol molecules). The pyridine rings of the bpe ligand are planar but they form dihedral angles of 5.9(6), 3.9(8) (coordinated bpe) and 8(1)° (uncoordinated bpe) with the ethylene group. Each cobalt atom shows a slightly elongated octahedral geometry (Fig. 7), being *trans* bonded to two N atoms from bpe, two O atoms from methanol and two others from water (Table 4). The axial positions are filled by N atoms [2.18(1) Å for Co–N] whereas the equatorial plane is built from oxygen atoms [average Co–O bond length of 2.18(1) Å]. The metal atom lies in the equatorial plane. Two adjacent layers are parallel and the interlayer separation is 11.1(1) Å. Perchlorate ions and water of crystallisation molecules occupy the holes of the rings and contribute to the packing by forming hydrogen bonds.

Interesting conclusions can be extracted when examining the structures of bpe complexes with Co^{2+}, Mn^{2+} and Fe^{2+} cations. It is noteworthy that only Co^{2+} and Fe^{2+} ions are

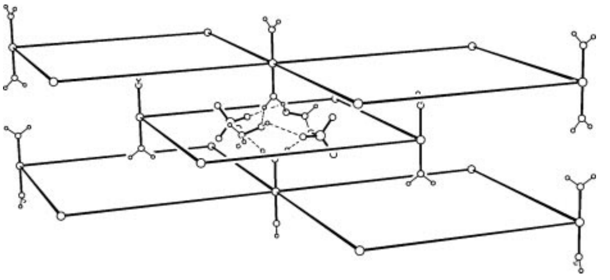

Fig. 5 A view of the shifted adjacent parallel layers of **2** made up of square motifs of cobalt(II) ions. Intra- and interlayer hydrogen bonds are illustrated by broken lines.

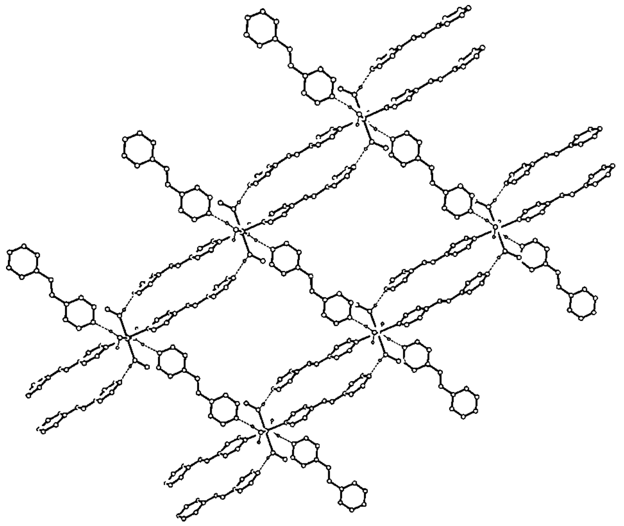

Fig. 6 A view of the layered structure of **3** made up of rectangular metal motifs.

Table 3 Selected interatomic distances (Å) and angles (°) for compound **2** with esds in parentheses[a]

Co(1)–O(1)	2.12(3)	Co(1)–O(2)	2.11(3)
Co(1)–N(1)	2.20(1)	Co(1)–N(2b)	2.17(1)
O(1)–Co(1)–O(2)	180.0(1)	O(1)–Co(1)–N(1)	95.6(4)
O(2)–Co(1)–N(1)	84.4(4)	N(1)–Co(1)–N(1a)	168.9(8)
O(1)–Co(1)–N(2b)	90.6(5)	O(2)–Co(1)–N(2b)	89.4(5)
N(1)–Co(1)–N(2b)	89.2(5)	N(1)–Co(1)–N(2c)	90.7(5)
N(2b)–Co(1)–N(2c)	178.7(10)		

Hydrogen bonds[b]

A	D	H	A···D	A···H	A···H–D
O(1)	O(7)	H(1w)	2.65(2)	1.71(4)	169(9)
O(2)	O(6)	H(2w)	3.08(3)	2.23(7)	147(5)
O(7)	O(3d)	H(7A)	2.76(2)	2.32(2)	112(2)

[a] Symmetry codes: (a) $-x$, $-y$, z; (b) $0.5 + x$, $0.5 - y$, z; (c) $-0.5 - x$, $-0.5 + y$, z; (d) $-x$, y, $-0.5 + z$. [b] A = acceptor, D = donor.

Table 4 Selected interatomic distances (Å) and angles (°) for compound **3** with esds in parentheses[a]

Co(1)–N(1)	2.183(6)	Co(1)–O(1)	2.107(5)
Co(1)–O(2)	2.100(6)	Co(1)–N(1a)	2.183(6)
Co(1)–O(1a)	2.107(5)	Co(1)–O(2a)	2.100(6)
N(1)–Co(1)–O(1)	92.9(2)	N(1)–Co(1)–O(2)	91.1(2)
O(1)–Co(1)–O(2)	89.3(2)	N(1)–Co(1)–N(1a)	180.0(1)
O(1)–Co(1)–N(1a)	87.1(2)	O(2)–Co(1)–N(1a)	88.9(2)
N(1)–Co(1)–O(1a)	87.1(2)	O(1)–Co(1)–O(1a)	180.0(1)
O(2)–Co(1)–O(1a)	80.7(2)	N(1a)–Co(1)–O(1a)	92.9(2)
N(1)–Co(1)–O(2a)	88.9(2)	O(1)–Co(1)–O(2a)	90.7(2)
O(2)–Co(1)–O(2a)	180.0(1)	N(1a)–Co(1)–O(2a)	91.1(2)
O(1a)–Co(1)–O(2a)	89.3(2)		

Hydrogen bonds[b]

A	D	H	A···D	A···H	A···H–D
O(1)	N(2c)	H(1A)	2.71(1)	2.32(1)	108.3(6)
O(2)	N(3)	H(2w)	2.71(1)	1.87(1)	170.7(7)

[a] Symmetry codes: (a) $-x, -y, -z$; (b) $-x, -1-y, -1-z$; (c) $x, 1+y, 1+z$; (d) $2-x, 1-y, -z$. [b] A = acceptor, D = donor.

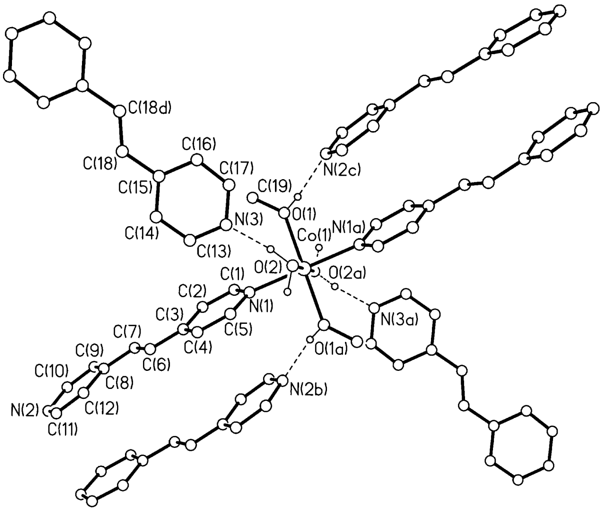

Fig. 7 A perspective view of the cobalt(II) environment in complex **3** along with the atom numbering. The hydrogen bonding involving coordinated water, methanol molecules and bpe groups is illustrated by broken lines.

able to form polycatenane compounds with this ligand and only when the counterion is a pseudohalide such as NCS^-. We can then conclude that both the nature of the metal and the counterion are fundamental in determining the final structure. In fact, when using Mn^{2+} instead of Co^{2+} or Fe^{2+}, no polycatenane formation was observed. In the case of Mn^{2+}, the low reactivity of this ion towards pyridine bases leads to a supramolecular network composed of $[Mn(bpe)_2(NCS)_2(CH_3OH)_2]$ chains linked *via* hydrogen bonds, in which coordinated methanol molecules are involved. Corrugated layers, made up of parallel chains spaced by hydrogen-bonded bpe molecules, are formed. These layers contain rectangular non-concatenated rings without direct links between bpe and Mn^{2+}. On the other hand, an analysis of compound **2** reveals that the counterion is also important for the polycatenane set up. The substitution of NCS^- by ClO_4^- leads to the formation of parallel sheets containing $Co_2(bpe)_2$ square rings, but the use of a non-coordinating counter ion precludes concatenation between the sheets, due to the formation of H-bonds between the coordinated water molecules, the uncoordinated methanol molecules and the perchlorate groups. Concerning the Co(II)–bpe system, recent work[17] revealed the formation of either a ladder compound or a mononuclear species, depending on the solvent used. It is interesting to note the occurrence of nearly square motifs (13.4 × 13.6 Å) within the ladder compound.

It would be reasonable to assume that the counterion also determines the nuclearity of the compounds. A compound with a 1 : 1 M : bpe molar ratio has been obtained only when the counterion is a thiocyanate. It is probably due to the great solubility of the hypothetical perchlorate compound, composed of chains of formula $[Co(bpe)(H_2O)_2(CH_3OH)_2](ClO_4)_2$, in which water and methanol molecules are coordinated to the cobalt(II) ions. In the same way, a compound with a 2 : 3 M : bpe molar ratio was obtained only from the $Co(ClO_4)_2$ solutions, because of the ability of water and methanol to form hydrogen bonds with bpe molecules. We can conclude that a large variety of bpe-containing metal complexes of different nuclearity and dimensionality will be prepared in the very near future by using as variables classical parameters in coordination chemistry such as the nature of the metal, counterion and solvent, as well as the metal-to-ligand molar ratio.

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