Chiral packing of chiral quintuple layers polycatenated to give a three-dimensional network in the coordination polymer

\[ \text{[Co}_5\text{(bpe)}_9\text{(H}_2\text{O})_8\text{(SO}_4\text{)}_4\text{]}\text{(SO}_4\text{)}\cdot14\text{H}_2\text{O [bpe = 1,2-bis(4-pyridyl)ethane]} \]

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The reaction of cobalt(II) sulfate with 1,2-bis(4-pyridyl)ethane gives a crystalline polymeric species comprised of chiral quintuple layers with five decks of linear chains rotated by 120° from level to level, that are perpendicularly joined via five-metal helical motifs; furthermore, each of these two-dimensional frames is catenated by the neighbouring layers to give an overall three-dimensional chiral nanoporous architecture.

There is much current interest for the crystal engineering of coordination frameworks, not only because of their potential applications as zeolite-like materials, for molecular selection, ion exchange and catalysis, but also for their intriguing architectures, new topologies and intertwining phenomena. Some recent examples have shown that topological types unprecedented in inorganic chemistry and in minerals can be achieved within the area of networked coordination polymers. Moreover, new types of supramolecular intertwinings of infinite motifs have been discovered, that open interesting perspectives in the study of these materials. Particularly attractive are polymeric systems sustained by supramolecular entanglements reminiscent of the mechanical bonds in molecular rotaxanes and catenanes, exhibiting constituent motifs of dimensionality lower than that of the resulting overall architecture. Known examples include polyrotaxanes and polycatenated one-dimensional and two-dimensional motifs. Species like these are expected to be of comparable robustness but more flexible than the usual networks entirely based on coordinative bonds with similar ligands. We report here on a new member of this class of polycatenated motifs, \([\text{Co}_5\text{(bpe)}_9\text{(H}_2\text{O})_8\text{(SO}_4\text{)}_4\text{]}\text{(SO}_4\text{)}\cdot14\text{H}_2\text{O [bpe = 1,2-bis(4-pyridyl)ethane]} \), that presents a new remarkable chiral three-dimensional architecture sustained by the catenation of chiral five-fold decked layers.

Compound 1 forms as beautiful flat hexagonal pink crystals by slow evaporation of solutions obtained on mixing bpe in ethanol and Co(II) sulfate in water, with metal-to-ligand molar ratios from 1:1.7 to 1:2. The crystals are stable in the air at room temperature for an extended time but start to lose solvated water molecules when heated above ca. 40 °C. The powdered material obtained in good yields by fast evaporation of more concentrated solutions of the reagents corresponds to almost pure 1, as confirmed by X-ray powder diffraction methods.

The crystal structure of 1 shows the presence of multiple layers containing five levels of one-dimensional linear polymers, all lying perpendicular to the crystallographic c axis, that are formed by Co(II) ions joined by bpe ligands in a trans conformation (Co⋯Co distances of 13.69 Å). These polymers run on the five decks in different directions rotated by 120° about the c axis on passing from one level to the successive one, thus resulting in a ABCAB sequence. The decks are connected along the normal direction via five-metal helical motifs, illustrated in Fig. 1, all exhibiting chirality (left handed chirality for the crystal examined). The resulting chiral multilayer thus formed is schematically shown in Fig. 2.

Fig. 1 A lateral (left) and a top (right) view of a single helical motif joining perpendicularly the quintuple layer (different colours are used to evidence the five decks). A two-fold axis passes through the central metal.

Fig. 2 A schematic view of a single five-decked layer with the same colours as in Fig. 1.

The cobalt ions of the two external levels are three-connected to bpe ligands (T-shaped geometry) while those of the three internal levels are four-connected to such ligands (square-planar geometry). The coordination spheres of the cobalt ions are completed by oxygen atoms of the sulfates and by water molecules (three \(\text{mer} \text{H}_2\text{O} \) for the two external Co, two sulfates for the central cobalt, one \(\text{H}_2\text{O} \) and one sulfate for the other two metal ions), resulting in all cases in distorted octahedral geometries. The five-metal helical chains are terminated at both ends by axial \(\text{H}_2\text{O} \) ligands, i.e. the external ‘surfaces’ of the multilayers are covered by coordinated water molecules. Though other examples of multiple layers are known within coordination polymers, the two-dimensional motif of 1 is...
unique in terms of topology, number of decks and thickness (see Fig. 2). To our knowledge, it is the largest two-dimensional coordination polymer ever reported.

We can rationalize this two-dimensional polymeric motif as a five-layer section of the chiral three-dimensional four-connected framework described by O’Keeffe as the ‘dense’ net. This shows an ABCABC infinite sequence of levels and exhibits the unusual (7 5 9) topology. The first real example of this framework (three-fold interpenetrated) has been recently observed in a copper(II) polymeric species. 2

The stacking distance between two adjacent levels of each quintuple layer lies in the range 12.26–13.10 Å, so that the resulting overall height is as large as 50.5 Å. Identical layers are superimposed along the $c$ crystallographic axis, with an interlayer gap of 13.4 Å (see Fig. 3). Two other sets of quintuple layers are generated by the $3_1$ symmetry axis, exhibiting sequences of their five levels of the BCABC and CABCA type, respectively, resulting in an overall chiral packing. The three sets are entangled in such a way that each layer is catenated not only by the two nearest neighbouring (upper and lower) layers but also by the two second nearest neighbouring ones, as illustrated in Fig. 3. Thus each layer is intertwined in a ‘parallel fashion’ with the other four, to give a fascinating polycatenated array. Infinite catenation of polymeric motifs represents a type of supramolecular entanglement that is still quite uncommon. Known examples include polycatenated one-dimensional ladders that give two-dimensional or three-dimensional arrays, as well as two-dimensional simple, double and quadruple layers, resulting in three-dimensional architectures. We have very recently reported also on a catenated three-dimensional system based on different polymeric motifs, i.e. one-dimensional ribbons of rings and two-dimensional (4,4)-layers, that exhibits a peculiar sponge-like nanoporous behaviour. 6, 6

heating. Thermogravimetric analyses of I, under a nitrogen flux, show that both the solvated and the coordinated water molecules are completely lost in a continuous fashion in the range 40–120 °C. Above this point the product loses crystallinity and becomes unstable; but if the samples are heated only up to ca. 80 °C the solvent loss (ca. 8% of the total weight, corresponding approximately to the solvated water molecules) can be regained by exposure to water vapour overnight, as confirmed by TGA and XRPD.

Since catenation of polymeric frameworks can allow a certain flexibility of the whole architecture, it can potentially favour solvent exchange processes, as observed in previous examples. 6 Compound I can be, therefore, considered as a model species for nanoporous arrays that present the additional features of non-rigidity and chirality.

Notes and references

1 Crystal data for compound I: [Co(bpe)5(H2O)8(SO4)4][SO4]·14H2O, M = 2829.43, trigonal, $P_3\text{1}$21 (no. 152), $a = b = 13.692(9)$ Å, $c = 63.880(9)$ Å, $\beta = 10358(3)$, $Z = 3$, $D_0 = 1.359$ Mg m$^{-3}$, Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu$(Mo-Kα) = 0.745 mm$^{-1}$, 61444 reflections measured, 9999 unique ($R_{int} = 0.043$), final $R1 = 0.088$ for 9343 independent reflections [$I > 2\sigma(I)$]. The data collection was performed at 293 K on a SMART-CCD Bruker diffractometer, by the $\omega$-scan method, within the limits 2 $\theta$ = 0 to 24°. The structure was solved by direct methods (SIR97) and refined by full-matrix least squares (SHELX97). The non coordinated sulfate anion is statistically distributed over two positions and was refined with half weight model. The handedness of the crystal was determined by testing the two enantiomeric models.

CCDC 182/1664. See http://www.rsc.org/suppdata/cc/b0/b002021o/ for crystallographic files in .cif format.

2 Two other weight losses are observed. The first in the range 120–250 °C (ca. 19%) corresponds approximately to three ligand molecules. The corresponding XRPD spectrum shows a completely different pattern arising from a new violet anhydrous phase. The second weight loss (ca. 36–37%), occurs in the range 280–430 °C and leads to a final residue of CoSO$_4$, as evidenced by XRPD.


