

A new type of entanglement involving one-dimensional ribbons of rings catenated to a three-dimensional network in the nanoporous structure of $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4)\cdot 7\text{H}_2\text{O}$ [bix = 1,4-bis(imidazol-1-ylmethyl)benzene]†

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Co^{II} sulfate reacts with the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) to yield the coordination network $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4)\cdot 7\text{H}_2\text{O}$, containing polymeric ribbons of rings which penetrate and catenate a 3D single frame of the CdSO_4 topology, to produce an open-channel entangled architecture with nanoporous behaviour.

Crystal engineering principles have been employed in recent years to produce a variety of coordination networks,¹ which are of great current interest not only for their potential properties as functional solid materials,² in host–guest chemistry, ion exchange, catalysis, and for the development of optical, magnetic and electronic devices, but also for their intriguing, often complicated, architectures and topologies. Among these, particular attention has been recently devoted to systems containing entanglements of individual motifs. Besides the common types of interpenetrating networks,^{1a} new more sophisticated families are now recognized, including polycatenated arrays, Borromean architectures, polyrotaxane-like species, interlocked motifs of different dimensionality, whose topological classification is in progress.³

Conformationally non-rigid ligands, showing varied geometries that often lead to supramolecular isomers,^{1c,4} can more easily produce these new classes of compounds. We are currently investigating the use of the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix), together with different MSO_4 salts, since this spacer has already proven a certain ability to give uncommon entanglements, including two remarkable polyrotaxane-like polymers,⁵ thanks to its different conformations. We report here on the 3D network of $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4)\cdot 7\text{H}_2\text{O}$ (**1**), containing ribbons of rings catenated to a 3D single frame. This species is remarkable in that: i) it is the first example of an inextricable (1D + 3D) array, ii) it contains two supramolecular isomers in the same crystal, and iii) it shows an interesting nanoporous behaviour, for the presence of open channels full of guest solvent molecules, that can be completely removed and regained in a reversible process.

Compound **1** is obtained in high yield as beautiful pink crystals by slow diffusion of solutions of bix in acetone into water solutions of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, with a metal-to-ligand molar ratio of 1 : 2. The crystals are stable in air for long periods. The bulk material obtained by mixing the reagents in the same conditions corresponds to almost pure **1**, as confirmed by X-ray powder diffraction.

The crystal structure of **1**† is comprised of two distinct and crystallographically independent polymeric motifs packed together, that have the same stoichiometry and contain almost identical four-connected ‘square-planar’ $\text{Co}(\text{II})$ nodes. One of these motifs consists of ribbons of 26-membered cycles, each ring involving two cobalt atoms and two bix ligands (see Fig. 1a). The ligands assume a C_s conformation, with the shortest N...N distance between the two donor atoms (9.63 Å). The metal coordination is octahedral, with four equatorially bonded imidazole groups [Co–N 2.120(3), 2.151(4) Å] and two axial water molecules [Co–O 2.172(3) Å]. All these ribbons run parallel to the [010] direction, with a period equal to the *b* axis, corresponding to the Co...Co

distance (12.62 Å). Adjacent ribbons show a relative displacement of $\frac{1}{2}b$.

The second motif of **1** is a single three-dimensional network of four-connected nodes with the ($6^5.8$) CdSO_4 topology⁶ (Fig. 1b). The network appears strongly distorted with respect to the ‘ideal’ reference tetragonal net (Fig. 1c). The bix ligands exhibit two different conformations: those bridging the Co...Co ‘horizontal’ edges, perpendicular to the ‘tetragonal’ axis, have C_i symmetry and work as the longer spacers (N...N and Co...Co 11.42, 15.42 Å), while those along the ‘vertical’ edges show C_2 symmetry (N...N and Co...Co 10.47, 13.30 Å). The coordination geometry of the cobalt atoms is very similar to that observed for the metals in the 1D polymers [Co–N 2.131(3), 2.149(3) Å and Co–O 2.178(3) Å]. Within a crystallographic unit cell there are four metals for each of the two motifs, which can be described as two supramolecular isomers embedded in the same crystal. This is possible because of the flexibility of the bix ligands, that is well evidenced on comparing the N...baricentre...N angles in the three observed conformations: 180° (C_i), 141.5° (C_2) and 116.8° (C_s). The intriguing topological feature of this species is that the penetrating ribbons are inextricably entangled with the 3D frame *via* catenation. All the rings of the ribbons are threaded by one ‘vertical’ edge of the net, as shown in Fig. 2 (top). The whole array is schematized in Fig. 2 (bottom).

The entanglement found here, of the (1D + 3D) type, is unprecedented. The known examples of interlocked polymeric motifs of different dimensionality are rare: these include a 3D array formed by ribbons of rings polycatenated with 2D stacked layers⁷ and three species involving 3D frames interlaced by square grid

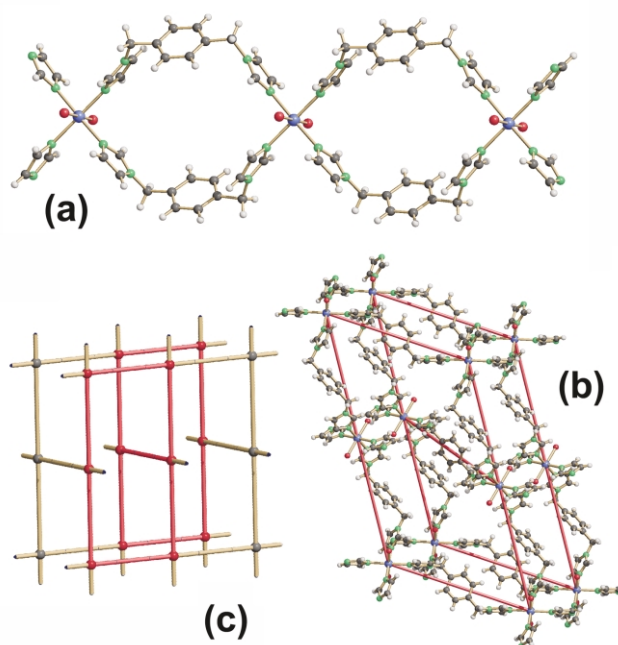


Fig. 1 The different motifs in **1**: a ribbon of rings (a) and a portion of the 3D net (b) with the CdSO_4 topology. The ideal tetragonal CdSO_4 net is also shown (c).

† Electronic supplementary information (ESI) available: details of the synthesis, structure of **2**, thermal analyses of **1**, XRPD monitoring for **1**: a) desolvation–rehydration, b) solvent substitution, c) thermal transformations. See <http://www.rsc.org/suppdata/cc/b3/b314322h/>

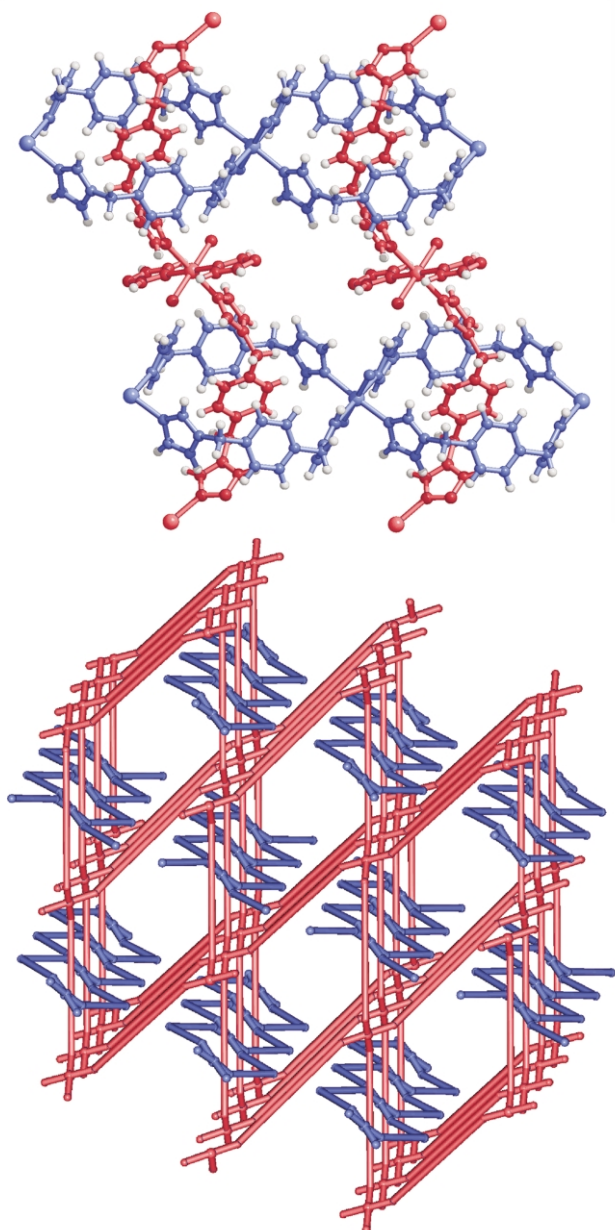


Fig. 2 A view of two adjacent ribbons threaded by 'vertical' edges of the 3D net (top) and a schematic view of the entangled array (bottom).

layers.⁸ It is noteworthy that in all these (3D + 2D) species the 3D frame has the same CdSO_4 topology, as in **1**. This is a special type of net in that it is self-dual and this can explain its propensity to give interpenetration in crystalline frameworks.⁹ It exhibits very large channels that can be filled by other nets of the same topology (up to four-fold interpenetration¹⁰) or by different motifs of lower dimensionality.⁸ Note that the CdSO_4 net in **1** is 'fully catenated'⁹ meaning that all the shortest rings of the 3D net are catenated by the ribbons.

The solvent system plays a fundamental role in the synthesis of **1**. When methanol, instead of water, is employed to dissolve the metal salt, and solvents such as acetone or CHCl_3 are used for the ligand, with a metal-to-ligand ratio 1 : 2, a different product is obtained, namely $[\text{Co}(\text{bix})(\text{H}_2\text{O})_2(\text{SO}_4)] \cdot x\text{Solv}$ (**2**), characterized by single crystal X-ray analysis[‡] as consisting of highly undulated simple polymeric chains (with C_s conformation of the *bix* ligands) joined by bridging sulfates into 2D (4,4) layers. The formation of **2** is probably due to the fact that, in contrast to water, these solvents are not efficient in preventing the coordination of the sulfates to the metal ions.

The ribbons do not completely fill the large voids in the 3D framework of **1**; open channels running along the [010] direction

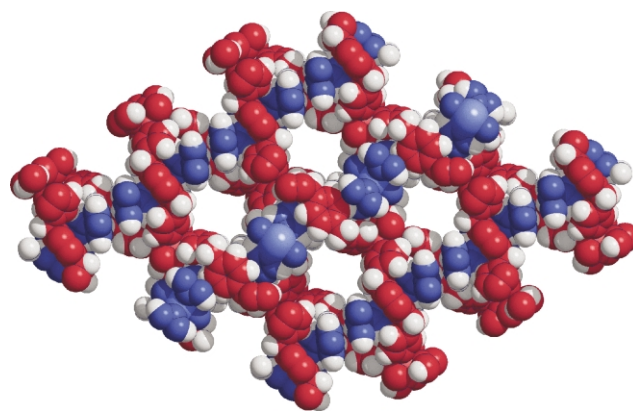


Fig. 3 The packing down [010] in **1**, showing the channels occupied by the anions and the solvated water molecules (omitted for clarity).

are present (see Fig. 3), containing the anions and the solvated water molecules. The free voids (estimated after removing all the uncoordinated H_2O molecules) represent *ca.* 27% of the cell volume. TGA and DSC show that **1** loses all the solvated H_2O molecules on heating the samples up to *ca.* 110 °C. XRPD analyses after desolvation reveal an almost amorphous pattern. However, upon exposure to water vapour for few hours the samples regain crystallinity, displaying the original diffraction pattern, thus indicating that the process is reversible. On the other hand, if the amorphous dehydrated samples of **1** are exposed to the vapour of methanol, ethanol, acetonitrile or acetone, solvent resorption and recovering of crystallinity takes place to some extent (especially with methanol) but with crystal modifications, as evidenced by the XRPD patterns (see ESI[†]). These transformations, as well as the complex thermal behaviour of **1** after dehydration, are under investigation.

Notes and references

[‡] Crystal data for compound **1**: $\text{C}_{28}\text{H}_{46}\text{CoN}_8\text{O}_{15}\text{S}$, monoclinic, $a = 28.132(5)$, $b = 12.615(2)$, $c = 24.746(4)$ Å, $\beta = 120.026(3)^\circ$, $U = 7604(2)$ Å³, space group $C2/c$ (no. 15), $Z = 8$. Least-square refinement based on 5620 reflections with $I > 2\sigma(I)$ and 480 parameters led to convergence, with final $R1 = 0.0683$, $wR2 = 0.1893$. **2** $\text{C}_{16}\text{H}_{26}\text{CoN}_4\text{O}_8\text{S}$, orthorhombic, $a = 9.270(3)$, $b = 11.819(4)$, $c = 20.539(8)$ Å, $U = 2261.3(14)$ Å³, space group $Pbcm$ (no. 57), $Z = 4$. Least-square refinement based on 1320 reflections with $I > 2\sigma(I)$ and 126 parameters led to convergence using SQUEEZE (see ESI), with final $R1 = 0.0518$, $wR2 = 0.1384$. CCDC 224542 & 224543. See <http://www.rsc.org/suppdata/cc/b3/b314322h/> for crystallographic data in .cif format.

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