

Supramolecular isomers in the same crystal: a new case involving two different types of layers polycatenated in the 3D architecture of [Cu(bix)₂(SO₄)]·7.5H₂O [bix = 1,4-bis(imidazol-1-ylmethyl)benzene]

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Paper

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The reactions of copper(II) sulfate with the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) in H₂O/acetone solution have afforded two novel coordination polymers, *i.e.* the 1D species [Cu(bix)(H₂O)₃(SO₄)]·H₂O and the 3D networked array [Cu(bix)₂(SO₄)]·7.5H₂O. The former polymer contains highly undulated chains that are joined into 2D layers *via* hydrogen bond bridges. The second species shows an unusual 3D architecture comprised of two interlocked sets of different 2D layers, giving inclined polycatenation. Both sets of layers display the same (4,4) topology but exhibit quite different tiling patterns (with 'ideal' plane symmetry *c2mm* and *p4gm*, respectively) because of the varied conformations of the bix ligands on passing from the first set to the second one. These two 2D motifs represent a new case of supramolecular isomerism in the same crystal. The sulfate anions form μ_2 -bridges between copper ions, that cross-link the two sets of layers, giving a single 3D self-penetrating 6-connected network. This shows channels (total free void *ca.* 27% of the cell volume) containing many solvated water molecules, that are lost upon thermal activation and regained with crystal modification. A brief analysis of the known examples of supramolecular isomers contained in the same crystal is also reported.

Introduction

The large number of coordination networks reported in the literature¹ offers a rich variety of structural types. A lot of attention has been given throughout the years to the rationalization and classification of the different topological types of single polymeric motifs² and to the categorization of the interpenetration³ and entanglement⁴ phenomena. Indeed, this topological approach, the 'network approach',⁵ is an important achievement in this area, as a useful tool for the analysis of network structures that may allow for the rational design of functional materials.

More recently, increasing interest has been devoted to another structural aspect concerning coordination polymers. Many cases are now known of polymers based on identical building blocks in the same ratio that exhibit different structures, thus suggesting the possibility to apply the well established concept of molecular isomerism also to these extended arrays. Zaworotko and coworkers have introduced for the first time the term 'supramolecular isomers' referred to such cases.⁶ This is a useful concept for classification purposes,⁷ considering the increasing number of isomers that are continuously reported and the occurrence of new cases, like the frequently found examples of isomeric motifs embedded in the same crystal.

We are currently investigating the reactivity of the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) with different metal salts. The bix ligand has already proven a certain ability to give uncommon species, including two remarkable polyrotaxane-like polymers.⁸ We have recently reported on a fascinating polymeric network, [Co(bix)₂(H₂O)₂](SO₄)·7H₂O, containing two different interlaced isomeric motifs (1D + 3D) in the same crystal,⁹ and we have now investigated the reactions of bix with copper(II) sulfate in H₂O/acetone, that give two novel products, [Cu(bix)(H₂O)₃(SO₄)]·H₂O (**1**) and [Cu(bix)₂(SO₄)]·7.5H₂O (**2**). Particularly interesting is the structure of compound **2** containing two different types of interlocked layers that have the

same topology but show different tilings and are supramolecular isomers. In this paper, we report on the synthesis and characterization of the polymeric species **1** and **2**, together with a survey of the known examples of supramolecular isomers contained in the same crystal.

Experimental

Materials

The 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligand was prepared according to the literature.¹⁰ All the other reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University. Thermal analyses were performed with a TGA7 Perkin-Elmer instrument using an heating rate of 10 °C min⁻¹ under a nitrogen flux.

Synthesis of the polymeric compounds

Compound 1. The bix ligand (39.8 mg, 0.167 mmol) was dissolved in acetone (5 mL) and then added, under stirring, to an aqueous solution (8 mL) of CuSO₄·5H₂O (41.8 mg, 0.167 mmol). On mixing the two solutions, a blue precipitate formed almost immediately. The reaction mixture was left to stir at room temperature for some hours. The pale blue polycrystalline material was recovered by filtration, washed with small amounts of acetone and dried in air. Yield (55 mg; 70%). Elemental analysis: calc. for C₁₄H₂₂CuN₄O₈S: C, 35.78; H, 4.72; N, 11.92%. Found: C, 36.12; H, 4.39; N, 12.14%.

Compound 2. An aqueous solution (6 mL) of CuSO₄·5H₂O (31.9 mg, 0.128 mmol) was added under stirring to the bix ligand (93.6 mg, 0.384 mmol) dissolved in 8 mL of acetone. A pale blue precipitate formed almost immediately. The mixture was left to stir for a night and then it was left to stay without

stirring in a closed vessel for two more weeks. During this time, fine crystals were grown that assumed a very dark blue colour. The material was recovered by filtration on a buchner funnel, washed with acetone to remove the excess of ligand and dried in air. Yield (81 mg, 83%). The purity of this material was confirmed by XRPD analysis. Elemental analysis: calc. for $C_{28}H_{43}CuN_8O_{11.5}S$: C, 43.60; H, 5.62; N, 14.53. Found: C, 44.33; H, 5.37; N, 14.81%.

Crystallography

Crystal data for the compounds examined are reported in Table 1. The data collections were performed by the ω -scan method using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), at room temperature on a SMART-CCD Bruker diffractometer. Empirical absorption corrections (SADABS) were applied for the data collections. The structures were solved by direct methods (SIR97)¹¹ and refined by full-matrix least-squares on F^2 (SHELX-97)¹² with WINGX and PLATON interface.¹³ Anisotropic thermal parameters were commonly assigned to all non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The clathrate water molecules in **2** were modelled with the oxygen atoms only and refined with isotropic thermal parameters. Due to the poor diffraction of the crystals of **2** significant data were collected only up to $\theta = 23^\circ$. All diagrams were performed using the SCHAKAL99 program.¹⁴

CCDC reference number 232405–232406, see <http://www.rsc.org/suppdata/ce/b4/b402935f> for crystallographic files in cif format.

Results and discussion

We are investigating the use of the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) with different $M^{II}SO_4$ salts. The interest for this ligand is due to the fact that conformationally non-rigid ligands, showing varied molecular geometries, often give interesting types of entangled polymers.

The reactions of $CuSO_4 \cdot 5H_2O$ with bix were carried out in water/acetone. Upon layering on a water solution of the metal salt a solution of bix in acetone, in the metal-to-ligand molar ratio 1 : 2 at room temperature, the formation of mixtures of block blue crystals on the walls of the reaction vessel is observed after few days. The samples contain light blue crystals of **1** and dark blue crystals of **2**, both stable in the air, that were submitted to single crystal X-ray analysis (see below). The bulk

Table 1 Crystallographic data for **1** and **2**

Compound	1	2
Formula	$C_{14}H_{22}CuN_4O_8S$	$C_{28}H_{43}CuN_8O_{11.5}S$
<i>M</i>	469.96	771.30
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1 (2)	<i>C</i> 2/ <i>c</i> (15)
<i>a</i> /Å	7.960(5)	23.548(11)
<i>b</i> /Å	10.122(5)	18.524(8)
<i>c</i> /Å	12.782(5)	16.469(8)
α /°	67.23(1)	90
β /°	84.41(1)	102.01(2)
γ /°	80.78(1)	90
<i>V</i> /Å ³	936.7(8)	7027(6)
<i>Z</i>	2	8
Density/g cm ⁻³	1.666	1.458
μ (Mo $K\alpha$)/mm ⁻¹	1.329	0.750
θ range/°	2–28	2–23
Reflections collected	9880	24638
Indep. refls, <i>R</i> (int)	4511, 0.0215	5061, 0.1433
Parameters/restrain	253/14	440/21
Observed [$F > 4\sigma(F)$]	3930	2481
<i>R</i> 1 [$F > 4\sigma(F)$]	0.0314	0.0884
<i>wR</i> 2 (all data)	0.0915	0.2967

product obtained on mixing the solutions of the reagents in the same molar ratio under stirring for a few hours consists again of a mixture of **1** and **2**, of poor crystallinity, as shown by the XRPD pattern. XRPD analyses of samples left in the reaction vessel for two weeks reveals a **1** : **2** relative % ratio of 13 : 87. On the other hand, when the bulk product is prepared on mixing the reagent solutions with a metal-to-ligand ratio 1 : 1, almost pure **1** is formed in good yields. Moreover, almost pure **2** in good yields is obtained when the above reaction is carried out using a metal-to-ligand ratio 1 : 3, according to the XRPD spectra. Probably, a three-fold excess of the ligand is necessary to remove the water molecules from the copper coordination sphere.

When compound **1**, suspended in H_2O /acetone, is treated with one additional equivalent of bix an incomplete solvent mediated transformation to **2** is observed, while the use of two equivalents of bix leads the transformation to completion, as evidenced on monitoring the process by XRPD.

The solvated water molecules in compound **2** are completely removed when the crystals are heated up to *ca.* 120 °C (19.2% calculated for 7.5 water molecules). Thermal gravimetric analysis shows that the dehydrated species is stable up to *ca.* 200 °C before decomposition. The dehydrated sample shows loss of crystallinity by XRPD. Crystallinity can be slowly recovered upon exposure to water vapours for many days. The XRPD pattern, however, reveals that crystal modifications have occurred during the desorption–sorption cycles that can be tentatively attributed to some change in the ligand conformations (see Fig. 1).

Description of the structures

The structure of **1** consists of 1D highly undulated chains (Fig. 2, top) all extending in the [100] direction, with a period equal to the *a* axis (7.96 Å). Viewed along the direction of

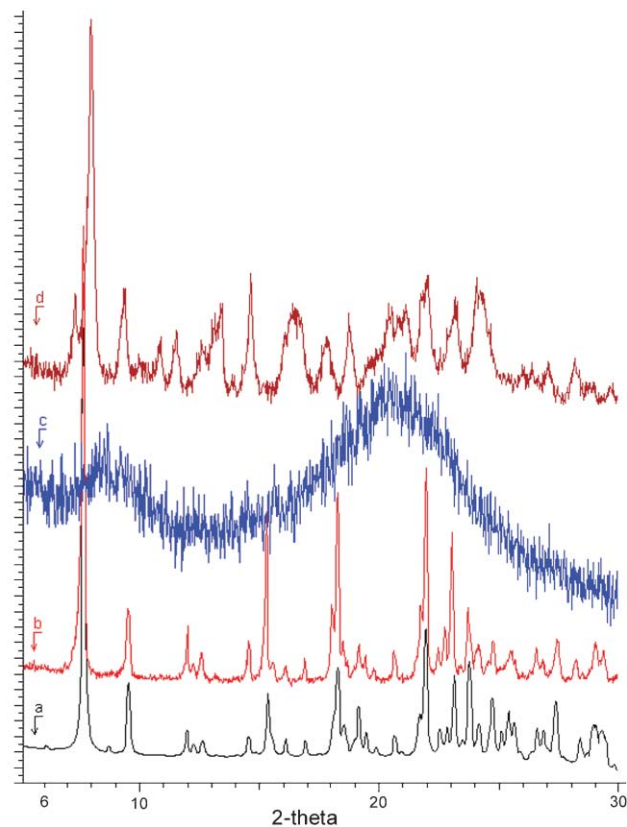


Fig. 1 XRPD patterns in monitoring the dehydration/hydration process for compound **2**. (a) Calculated from single crystal data; (b) experimental; (c) after dehydration; (d) after exposure of the dehydrated sample to water vapours for some days.

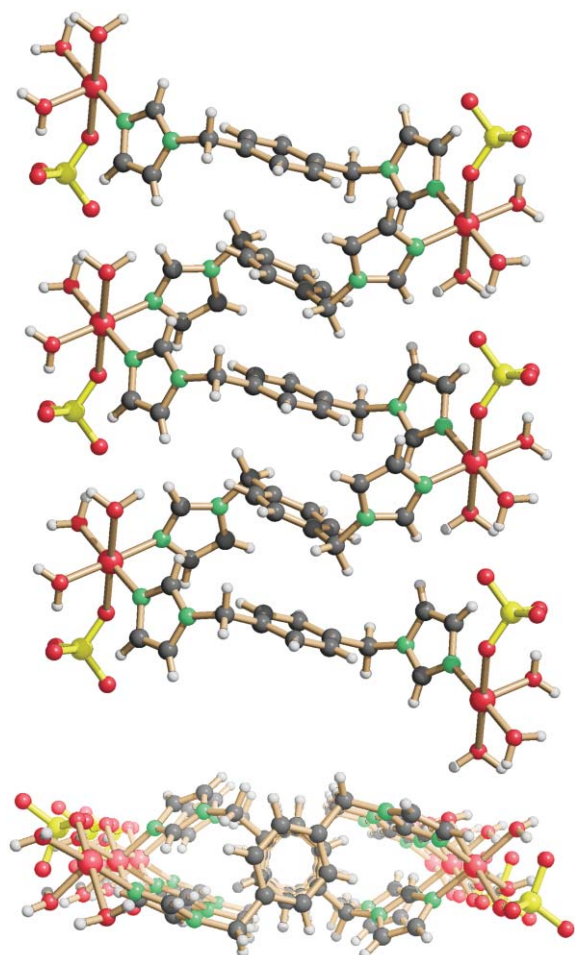


Fig. 2 The 1D chain in **1**: front view (top), that also illustrates the copper coordination geometry, and a view along the direction of propagation (bottom), showing the 'figure-of-eight' shape. [Click here to access a 3D view of Fig. 2.](#)

propagation, each chain traces a 'figure-of-eight', as illustrated in Fig. 2, bottom. This is a rather unusual shape for 1D polymers, when compared with the more common linear, zigzag and helical types that was, to our knowledge, rarely observed, *e.g.* in the $-\text{Au}-\text{S}-\text{Au}-\text{S}-$ chains of NaAuS .¹⁵ Another example¹⁶ will be discussed later. In compound **1**, this shape is due to the *cis*-coordination of the bix ligands at the metal centres and to the ligand conformation, leading to quite acute $\text{Cu}\cdots\text{Cu}\cdots\text{Cu}$ angles along the chains (34.2°). The $\text{Cu}(\text{II})$ ions display a Jahn–Teller distorted octahedral coordination geometry (see Fig. 2), with two *cis* imidazole groups [$\text{Cu}-\text{N}$ 1.9870(19), 2.0029(19) Å], three water molecules [$\text{Cu}-\text{O}$ *trans* to N 1.9750(16), 1.9821(17) Å, *trans* to the sulfate 2.594(3) Å] and a monodentate sulfate anion [$\text{Cu}-\text{O}$ 2.378(18) Å]. The bix ligands (two independent half ligands located on inversion centres) assume an *anti* conformation (C_i symmetry).

The coordinated sulfate anions and the coordinated water molecules form many lateral hydrogen bond bridges (range $\text{O}\cdots\text{O}$ 2.66–2.86 Å) involving also the free water molecules that originate columnar frames connecting the independent chain polymers into 2D layers. These layers, illustrated in Fig. 3, stack along the [01-1] direction.

The crystal structure of **2** is comprised of two distinct and crystallographically independent sets of polymeric 2D layers packed together, that have the same stoichiometry and contain almost identical four-connected 'square-planar' $\text{Cu}(\text{II})$ nodes.

Both types of layers display the same (4,4) topology but the tiling patterns are quite different. One set contains layers of 'idealized' 2D space group symmetry $c2mm$ (No. 9, type A layers, with rhombic meshes, see Fig. 4, top), while the second set shows layers of 'idealized' 2D space group symmetry $p4gm$ (No. 12, type B layers, with dumb-bell like meshes, see Fig. 4, bottom). The difference is related to the varied conformations of the bix ligands. All the ligands assume an *anti* conformation in type A layers ($\text{N}\cdots\text{N}$ distance 11.24 Å) and a *gauche* conformation in type B layers ($\text{N}\cdots\text{N}$ distance 9.71 Å). This produces larger grids in the former ($\text{Cu1}\cdots\text{Cu1}$ 14.98 Å) than in the latter layers ($\text{Cu2}\cdots\text{Cu2}$ 12.39 Å). The coordination

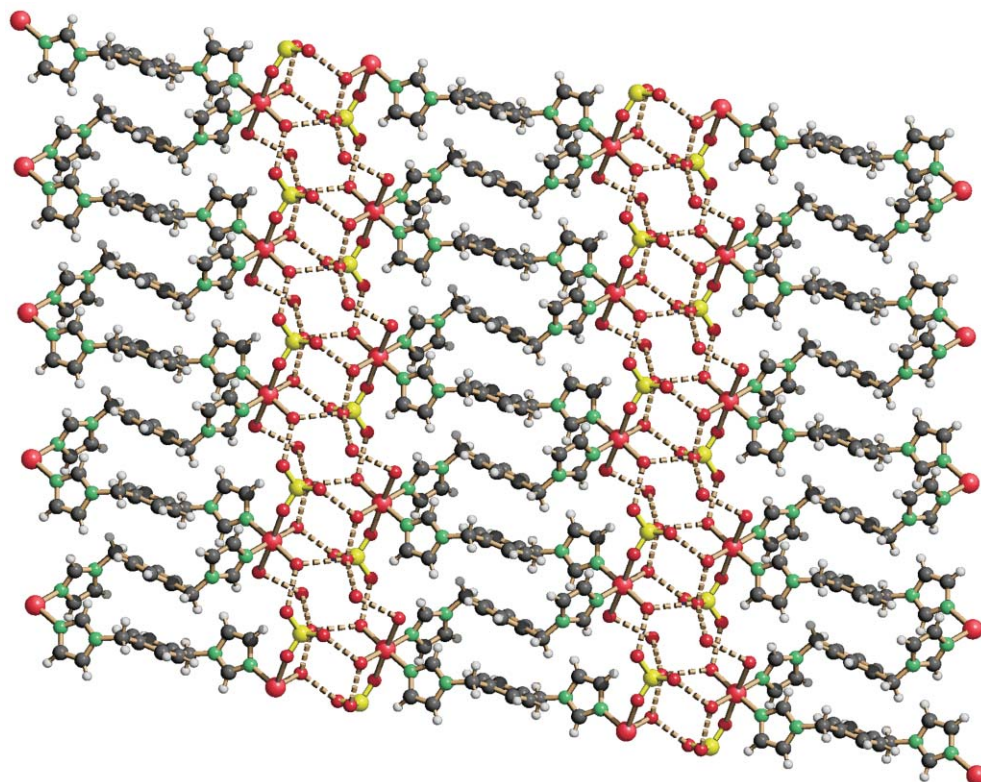


Fig. 3 A 2D layer in **1**, formed by the hydrogen bond bridges that connect the 1D polymeric chains.

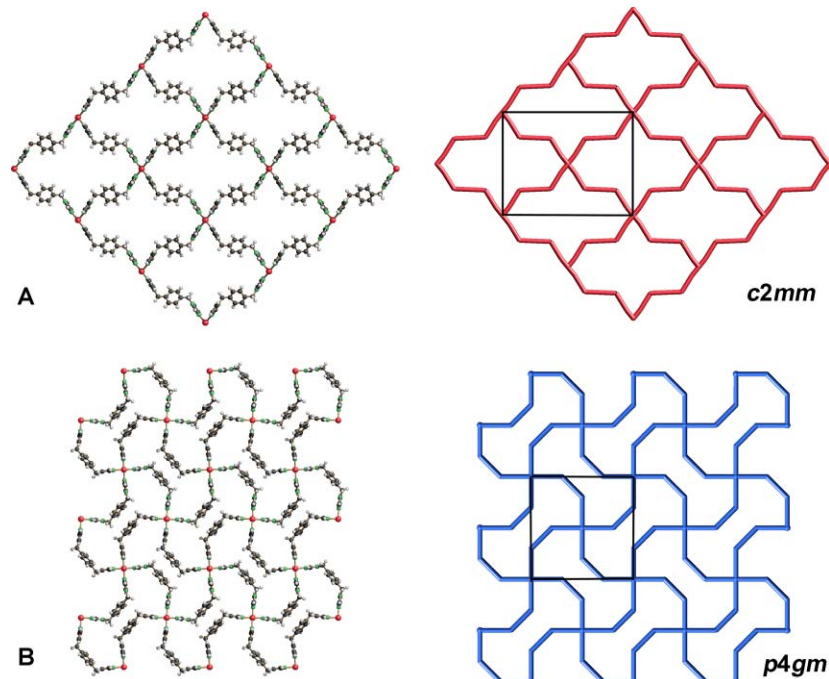


Fig. 4 The two types of layers in **2**, illustrated by their molecular diagrams (left) and by the idealized schemes with the highest possible symmetry (right).

geometries of the copper ions are quite similar in the two layers (Cu1 ions in layers A, lying on two-fold axes, and Cu2 ions in layers B, located on inversion centres). Both show octahedral Jahn–Teller distorted coordinations, with four equatorial imidazole moieties and two axial oxygen atoms of the sulfate anions [Cu1–N, 1.987(8), 2.011(8) Å, Cu1–O 2.592(7) Å; Cu2–N 1.976(7), 2.012(8) Å, Cu2–O 2.513(7) Å].

Layers A stack along the [001] direction with an *ABAB* sequence and an interlayer distance of 8.23 Å ($1/2c$), while layers B stack along the [100] direction with an *ABAB* sequence and an interlayer distance of 11.77 Å ($1/2a$).

The two independent sets give inclined polycatenation (see the schematic diagram in Fig. 5), with a dihedral angle of 78° ($180^\circ - \beta$). Each rhombic mesh of layers A is catenated by two layers B and each dumb-bell mesh of layers B is catenated by two layers A. According to our suggested notation^{4b} the ‘density of catenation’ is $\text{Doc} = (2/2)$.

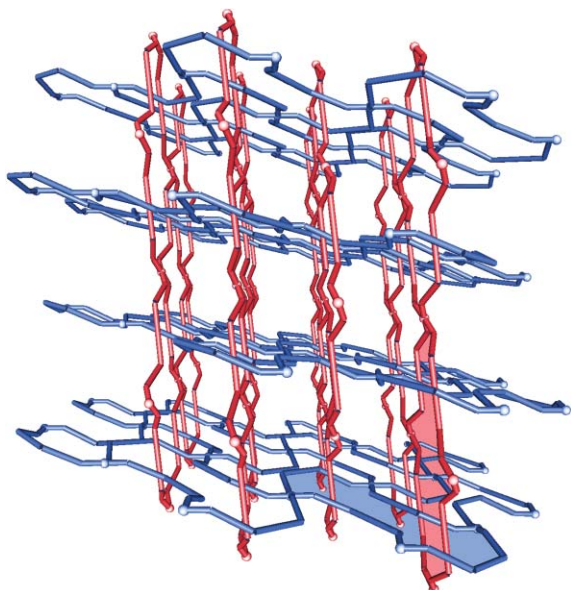


Fig. 5 Schematic view of the inclined polycatenation of the two types of layers in **2**.

The sulfate anions work as μ_2 - η^2 -bridging groups connecting the copper ions of the different sets (see Fig. 6). Each Cu^{2+} ion is thus joined to two metal ions lying on adjacent layers of different type by opposite sides. Each mesh of a layer of type A is connected to a catenated mesh of a layer of type B *via* three μ_2 -sulfate bridges and *vice versa*, as illustrated in Fig. 7.

Taking into account these bridges, a unique 3D network results, with 6-connected nodes. This is an uninodal net with $4^8 \cdot 6^7$ topological symbol, showing the structural peculiarity of self-catenation or polyknotting, a feature previously discussed in detail for other systems involving sets of interlocked layers cross-linked by the anions.^{4b}

Channels are present in the 3D net running in the [010] direction (see Fig. 6), that contain the sulfate anions and the uncoordinated water molecules. The free voids (calculated after removing the solvated water molecules)^{13b} correspond to *ca.* 27% of the cell volume.

The supramolecular isomerism observed for layers of types

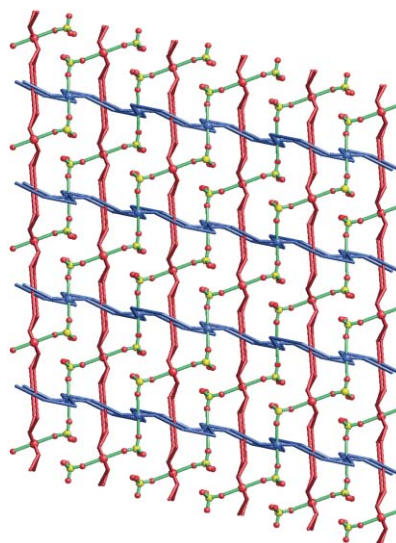


Fig. 6 View along [010] of the cross-linking of the two sets of layers by the sulfate anions in **2**, originating a single 3D self-catenated net.

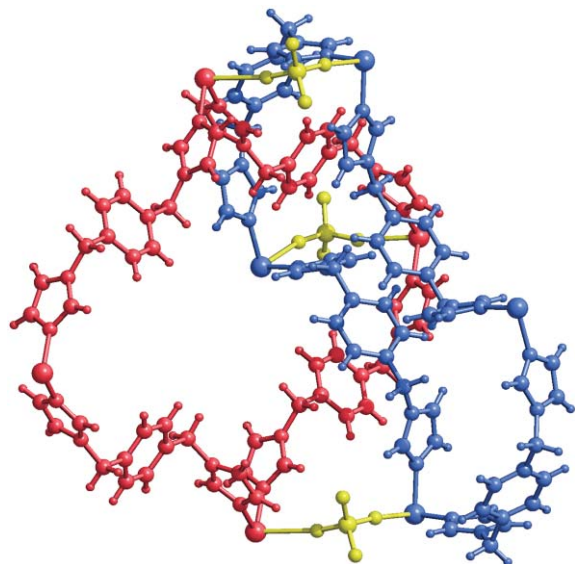


Fig. 7 Interlocking of two rings that belong to the different layers in **2**; the three sulfate anions connecting the rings are illustrated. Click here to access a 3D view of Fig. 7.

A and B in compound **2** is due to the presence of conformationally non-rigid ligands. The use of such ligands with different templating guest molecules has been successfully applied to synthesize distinct isomeric motifs, as in the case of $[\text{Cd}(\text{bpmfb})_2(\text{NO}_3)_2]$ [bpmfb = 1,4-bis(4-pyridyl)methyl-2,3,5,6-tetrafluorobenzene],¹⁷ that gives three different motifs, *i.e.* 1D ribbons of rings, 2D (4,4) layers and a 3D diamondoid 3-fold interpenetrated net, all containing similar nodes. Many other examples of supramolecular isomerism of this type have been reported, and Moulton and Zaworotko have suggested for such species the term ‘conformational isomers’.⁷ Among these is worth mentioning the recently reported case of $[\text{Cd}(\text{Me4bpz})_2(\text{NO}_3)_2]$ (Me4bpz = 3,3',5,5'-tetramethyl-4,4'-bipyrazole), that gives two distinct 2D polymeric isomers, with two types of layers of (4,4) and 3²-6² topology, depending on the conformation of the ligand.¹⁸

Layers A and B described above, however, are more unusual (see below) in that they are contained in the same crystal.

Supramolecular isomers in the same crystal

The finding of different polymeric species in the same crystal is quite uncommon, especially if these species are supramolecular isomers. Nonetheless, some cases have recently been reported and their number is growing. Moreover, few other examples of this isomerism can be found in the older literature on coordination polymers.

Different classes of supramolecular isomers have been envisaged: terms like ‘structural isomers’,^{7,19} ‘conformational isomers’,⁷ ‘catenane isomers’,⁷ ‘topological isomers’,^{20,21} ‘ring-opening isomers’²² and others, have been adopted to describe specific situations. Almost all of these classes have been observed also for motifs contained in the same crystal.

We can ascribe to the class of ‘topological isomers’ the cases observed in a series of compounds containing in the same crystal two topologically different motifs (2D + 3D) with the same composition, *i.e.* a 3D network (of the CdSO_4 6⁵-8 topology) interpenetrated by 2D layers of (4,4) topology (see Fig. 8A). In $[\text{Ni}(4,4'\text{-bipy})_2(\text{H}_2\text{PO}_4)_2]$ (4,4'-bipy = 4,4'-bipyridyl) a single 3D net is interpenetrated by 2D layers with identical composition and quite similar metal centres.²³ A similar (2D + 3D) entanglement is observed also in the species $[\text{Co}(\text{L})_2(\text{NCS})_2]$ [L = 1-methyl-1'-(4-pyridyl)-2-(4-pyrimidyl)ethene²⁴ or L = 1-methyl-1',2-bis(4-pyridyl)ethene²⁵], exhibiting the additional interesting feature that the crystals contain

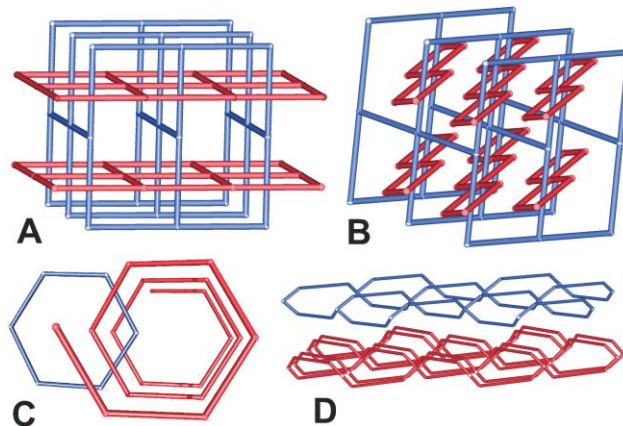


Fig. 8 Examples of supramolecular isomers in the same crystal: (a) 3D net (CdSO_4 like) plus square grid layers; (b) 3D net (CdSO_4 like) plus 1D ribbons; (c) hexagons and helical chains; (d) single and 2-fold parallelly interpenetrated (4,4) layers.

two interpenetrated 3D CdSO_4 -like nets. Another member of this family has also been reported, namely, $[\text{Cu}_2(\text{in})_4(\text{H}_2\text{O})_3][\text{Cu}_2(\text{in})_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (in = isonicotinate),²⁶ in which, however, the two motifs (the 2D layers and the 3D net) have different constitution of the nodes, showing different numbers of coordinated water molecules (we could speak of *pseudo*-isomers in this case).

To the same class we can also assign the recently reported $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot 7\text{H}_2\text{O}$ [bix = 1,4-bis(imidazol-1-ylmethyl)benzene],⁹ containing polymeric ribbons of rings which penetrate and catenate a 3D single frame of the CdSO_4 topology (see Fig. 8B). The two isomeric motifs show very similar coordination geometries of the metal centres.

Another class of supramolecular isomers of different topology is represented by species with the same composition affording both finite ring structures and polymeric chains that have also been called ‘ring-opening isomers’.²² We are aware of, at least, two examples of isomers of this class in the same crystal. The species $[\text{Ag}(\text{pydz})(\text{NO}_3)]$ (pydz = pyridazine) gives crystals containing both cyclic dimers and 2₁ helical chains.²⁷ A more intriguing material is $[\text{Cu}(\text{pymo})]$ (Hpymo = 2-hydroxypyrimidine)²⁸ whose crystals show the contemporary presence of hexagonal rings and helical 6₁ polymers (Fig. 8C).

Supramolecular isomerism can arise from the different conformations of flexible ligands (the term ‘conformational isomerism’ was suggested⁷), that can produce species of equal or different topology. In this class of isomers contained in the same crystal we can cite only the 2D (4,4) layers of compound **2** here reported (see Fig. 4).

Two distinct 1D chains, with ‘figure-of-eight’ arrangement and ‘S-shaped’ arrangement, have been found in the crystals of $[\text{Ag}_2(\text{L})](\text{NO}_3)_2$ [L = 2,5-bis(2-pyridylmethylsulfanyl)methylpyrazine],¹⁶ the two polymers differing in the donor atoms about the Ag^+ ions and in the arrangement of adjacent ligands along the chains.

Catenane isomerism,⁷ related to the occurrence of interpenetration and non-interpenetration for a certain polymeric motif, or to the different modes and degrees in which networks interpenetrate or interweave, has also been observed in a single crystal. In the two isomorphous compounds $[\text{Ag}(\text{bpp})_2](\text{PF}_6)$ and $[\text{Ag}(\text{bpp})_2](\text{AsF}_6)$ [bpp = 1,3-bis(4-pyridyl)propane]²⁹ two types of layers are observed: single (4,4) layers and 2-fold parallelly interpenetrated layers of the same topology, alternately stacked in the same direction (see Fig. 8D). The same isomerism, involving two single layers for each 2-fold interpenetrated layer, has been found in $[\text{Zn}_4\text{L}_8](\text{HL}) \cdot \text{H}_2\text{O}$ (HL = 3-[2-(4-pyridyl)ethenyl]benzoic acid).³⁰

Conclusions

Two new polymeric species obtained from Cu(II) sulfate and the bix ligand have been reported here. As expected, the flexibility of the bix ligand has produced novel structural features as, in particular, the presence in compound **2** of two different types of layers with the same topology but with different tilings, embedded in one crystal. Moreover, taking into account the links due to the bridging sulfate anions, an unique 3D self-catenated net (of 4⁸·6⁷ topology) results. The two different layers can be considered supramolecular conformational isomers. This observation has stimulated an analysis of the cases of isomerism in the same crystal, that has revealed the limited number of examples in this family but also the fact that they cover almost all of the classes previously envisaged within the broad area of supramolecular isomers.

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