

A new type of entanglement involving one-dimensional ribbons of rings catenated to a three-dimensional network in the nanoporous structure of [Co(bix)₂(H₂O)₂](SO₄)·7H₂O [bix = 1,4-bis(imidazol-1-ylmethyl)benzene].

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Supplementary Material

Synthesis of compound [Co(bix)₂(H₂O)₂](SO₄)·7H₂O (**1**): To a water solution (5 mL) of CoSO₄·7H₂O (21 mg, 0.0747 mmol) was added under stirring the ligand bix (35.5 mg, 0.149 mmol) dissolved in 5 mL of acetone. The reaction mixture was left to stir for about 2 hours and then it was left to concentrate in the air. After few days a pink microcrystalline precipitate was recovered by filtration on a buckner. It was washed with small amounts of acetone and dried in the air (Yield: 43 mg; 71%). Elemental analysis: calcd. For C₂₈H₄₆CoN₈O₁₃S: C 42.37 %, H 5.84 %, N 14.12%. Found: C 42.14 %, H 5.84 %, N 13.28%. IR (nujol mull, cm⁻¹): 3370vb, 3123m, 2724m, 1523m, 1243m, 1111s, 1092s, 1080s, 1055s, 1031s, 971w, 942m, 845m, 810w, 722s, 662m, 617w.

Synthesis of compound [Co(bix)(H₂O)₂(SO₄)]·xSolv (**2**): CoSO₄·7H₂O (20.0 mg, 0.0711 mmol) was dissolved in 6 mL of methanol and to this solution was added the ligand bix (0.0713 mmol, 17.0 mg) dissolved in 5 mL of chloroform. A precipitate formed on stirring the reaction mixture for some hours which was recovered by filtration on a buckner, washed with small amount of chloroform and dried in the air. (Yield: 20.2 mg, 66.7%). Single crystals were obtained as violet needle by the method of slow diffusion on layering a solution of the metal salt dissolved in methanol on a solution of the ligand dissolved in chloroform. Elemental analysis: calcd. For C₁₄H₁₈CoN₄O₆S·CH₃OH: C 39.05 %, H 4.81 %, N 12.14 %. Found: C 38.15 %, H 4.83 %, N 12.27 %. IR (nujol mull, cm⁻¹): 3596m, 3350vb, 3110m, 2726m, 1516m, 1296w, 1245m, 1138s, 1119s, 1092vs, 1070s, 1033s, 982w, 944m, 864w, 799w, 751m, 722m, 664m.

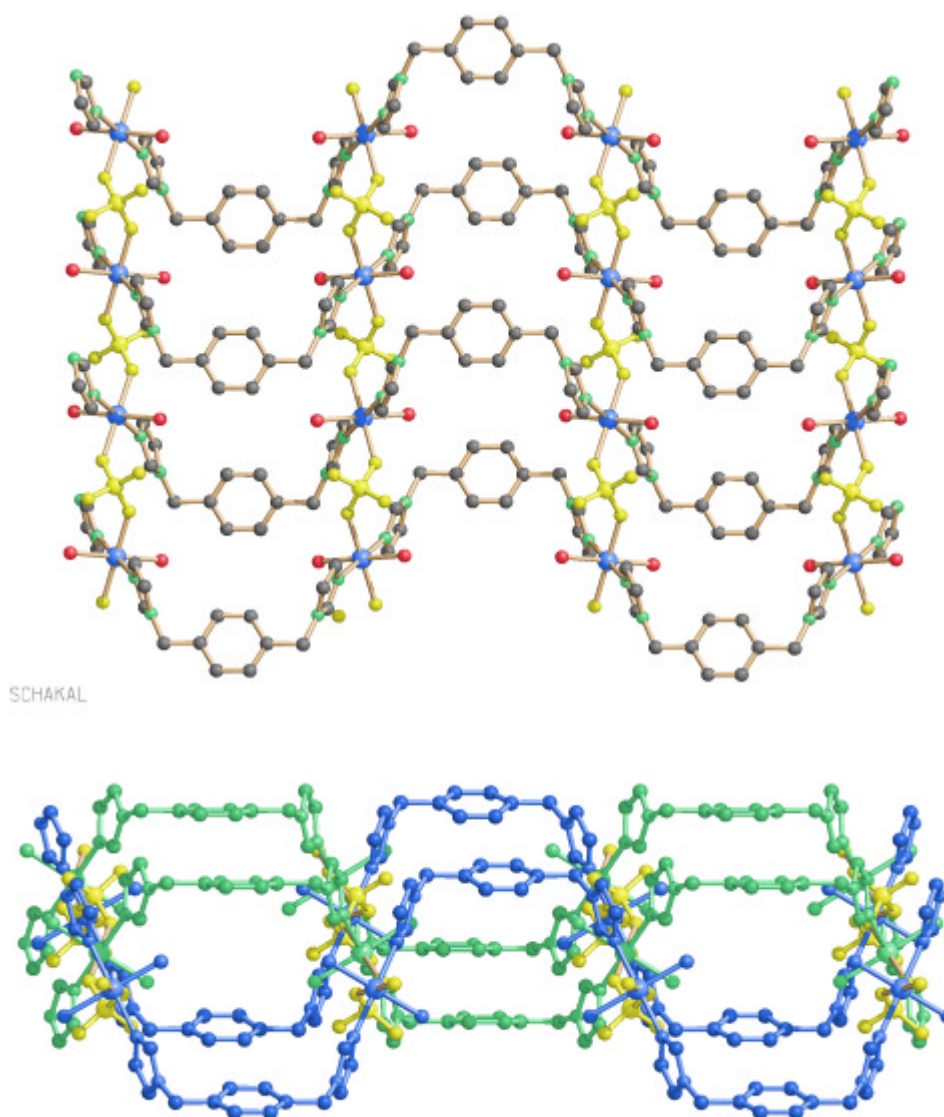


Figure 1S Top and side views of a 2D layer in compound **2**.

The solvent-accessible volume (32.1%) in the product obtained from methanol/chloroform was assessed using the PLATON software (A. L. Spek, *Acta Cryst.*, **1990**, *A46*, C34). The contribution of the disordered solvent (located in the voids of the channels of the lattice) to the diffraction pattern was subtracted from the observed data by the "SQUEEZE" method as implemented in PLATON (P. Van der Sluis, A. L. Spek, *Acta Cryst.*, **1990**, *A46*, 194: The SQUEEZE-Bypass method referred therein is widely used in crystallographic analysis of compounds containing substantial amounts of disordered solvent that can not be located precisely from diffraction data.) The residual agreement factor for all data before SQUEEZE are $R1 = 0.1663$, $wR2 = 0.3543$, and after $R1 = 0.0863$, $wR2 = 0.1532$. The final formulation of the compound, in agreement with the residual volume is $2 \cdot 2\text{CH}_3\text{OH}$.

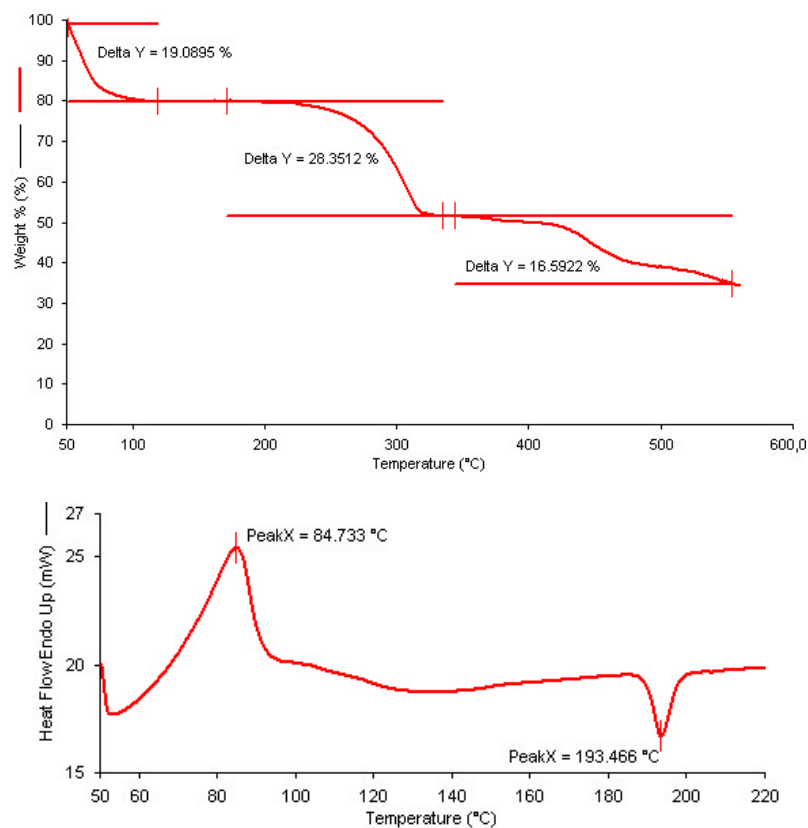


Figure 2S TG (top) and DSC (bottom) analyses of **1**. The TGA has been carried out on a Perkin-Elmer TGA7 instrument at a scan rate of 10°C/min under nitrogen flux. The first weight loss of *ca.*19.1% is due to desolvation (the seven solvated water molecules *per* formula unit give 15.9% and a probable partial loss of the coordinated water molecules takes also place); the second weight loss of *ca.* 28.4% could be tentatively attributed to elimination of one bix ligand. The DSC has been carried out on a Perkin-Elmer DSC7 instrument at a scan rate of 10°C/min under nitrogen flux.

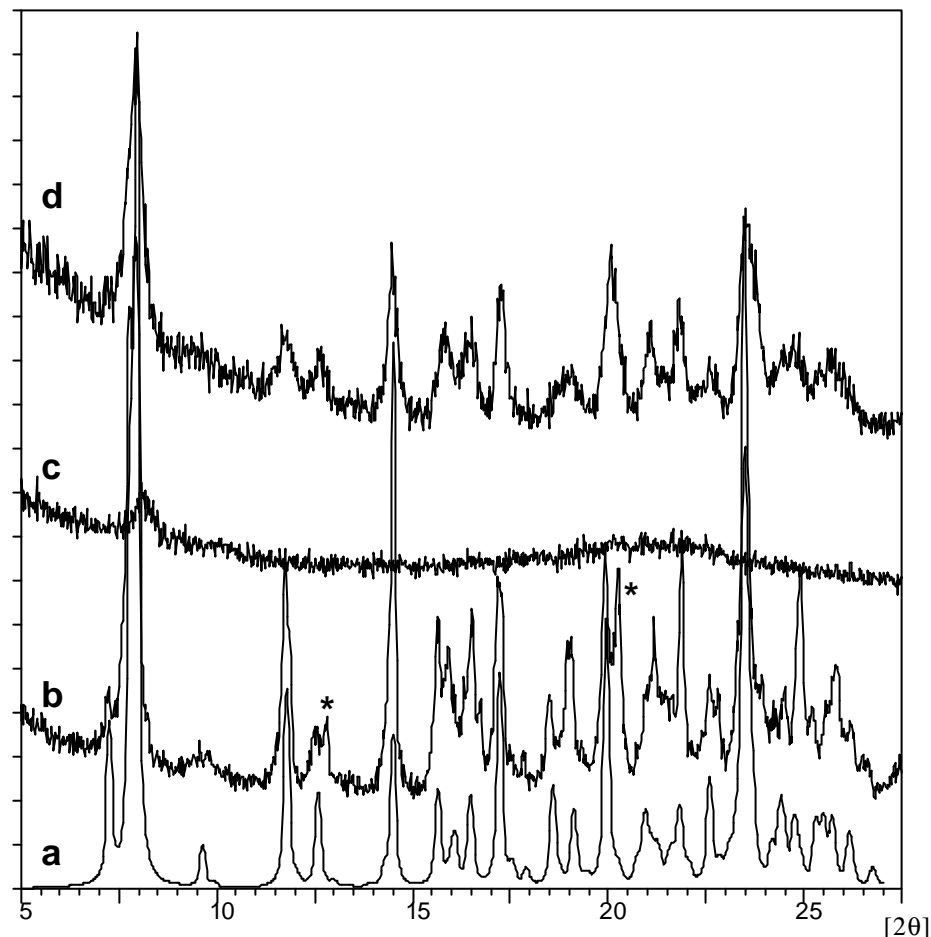


Figure 3S XRPD monitoring of the thermal dehydration and re-hydration processes in **1**: a) the calculated pattern, b) the pattern of the bulk material at room temperature (few impurities are present, see asterisks), c) the pattern after dehydration at 110 °C and d) the pattern obtained after exposure of the dehydrated sample for few hours to water vapours.

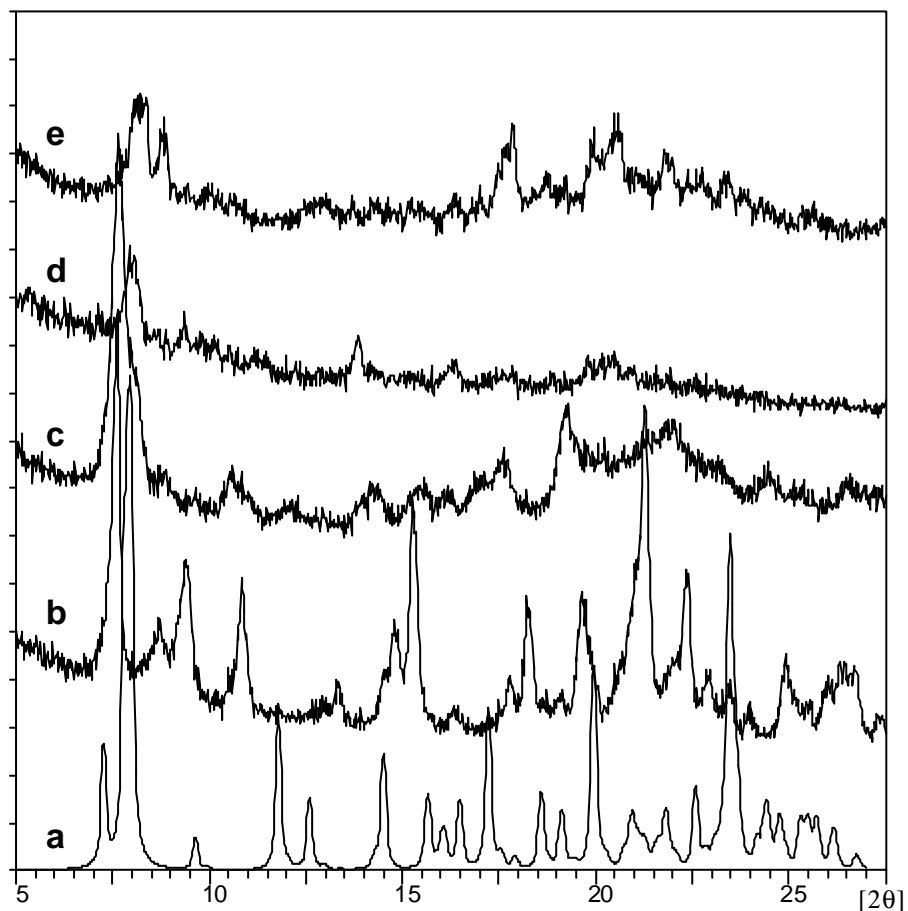


Figure 4S XRPD spectra obtained after exposure of the amorphous dehydrated samples of **1** to different vapours: b) methanol, c) ethanol, d) CH₃CN, e) acetone. For comparison, the calculated pattern of **1** is shown (a).

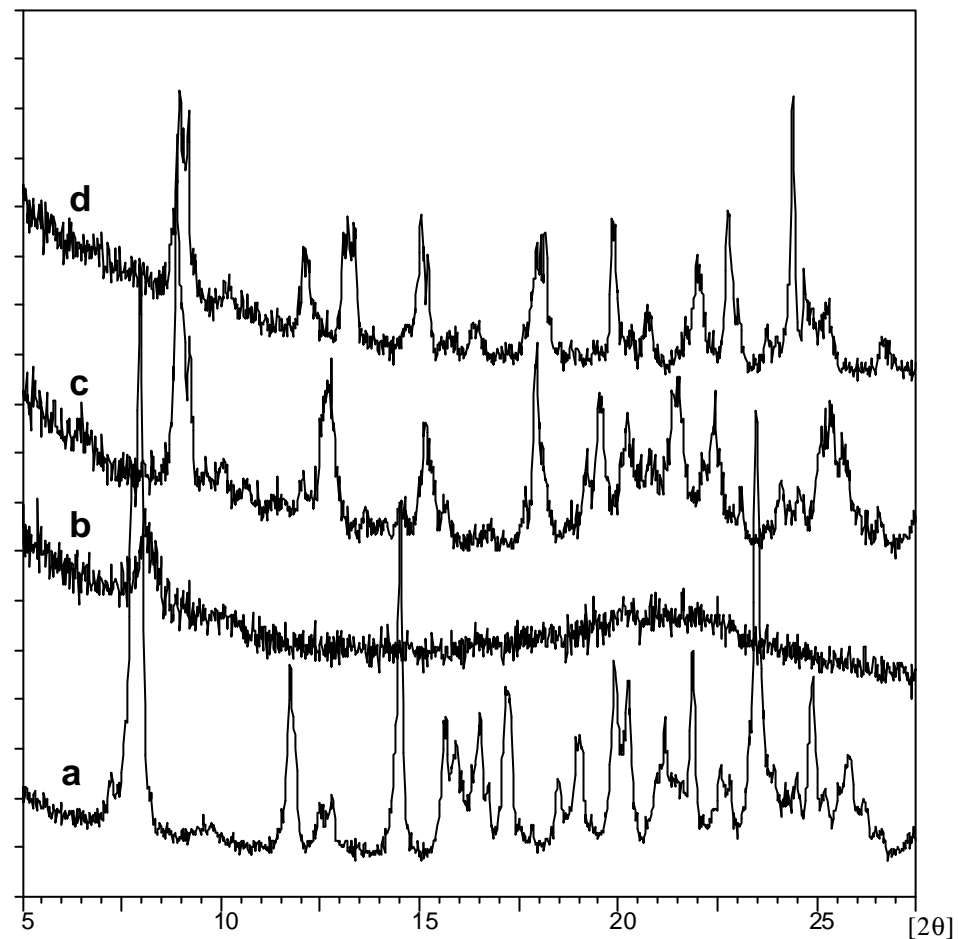


Figure 5S XRPD monitoring of the thermal behaviour of **1**: a) sample at room temperature, b) sample heated up to 150 °C (after dehydration), c) sample heated up to 200 °C (after a phase change observed in DSC), d) sample heated to 330 °C (after loss of about one ligand *per* metal atom). The diffraction patterns in c) e d) clearly show that two crystal transformations have occurred after dehydration.