

Three-dimensional architectures of intertwined planar coordination polymers: the first case of interpenetration involving two different bidimensional polymeric motifs

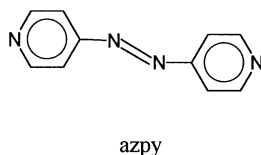
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Letter

The novel bidimensional coordination polymers $[\text{Zn}(\text{azpy})_2(\text{H}_2\text{O})_2]\text{SiF}_6 \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{azpy})_2(\text{NO}_3)_2]_2[\text{Ni}_2(\text{azpy})_3(\text{NO}_3)_4] \cdot 4\text{CH}_2\text{Cl}_2$, assembled with *trans*-4,4'-azobis(pyridine) (azpy), show *inclined* interpenetration of their layers, i.e. (4,4) planes in the former species, and (4,4) and (6,3) planes, in the second one, which represents the first example of intertwining of different two-dimensional coordination motifs.

The recent studies on the self-assembly of coordination polymers,¹ of interest for their potential properties as novel materials, have afforded many noteworthy frameworks, topologically related to common models, like diamond² and α -polonium,³ or to less common ones,⁴ exhibiting different degrees of interpenetration. However, the use of new suitably designed ligands offers the chance of isolating frames unprecedented in inorganic chemistry, as well as novel intertwining phenomena, that have been recently reviewed.⁵ Within simple two-dimensional nets there are two common topological types, i.e. three-connected planes of hexagons or bricks, with (6,3) topology, and four-connected planes of squares or rhombuses, with (4,4) topology. Intertwining of these two-dimensional motifs can occur in different ways: the known examples include *parallel* and *perpendicular* or *inclined*⁵ interpenetration. In the former case undulating layers are required, which interpenetrate to give an overall two-dimensional array, the maximum known numbers of interweaving motifs being two for (4,4) layers⁶ and six for (6,3) ones.⁷ On the other hand, in the *inclined* interpenetration infinite motifs intertwine to produce three-dimensional architectures, the reported examples involving both (4,4)⁸ and (6,3) topologies.⁹ The variety of possible situations is confirmed by a remarkable species, recently reported, containing pairs of parallelly intertwined (4,4) layers which also present *inclined* interpenetration.¹⁰ We are studying the self-assembly of some bis(4-pyridyl) ligands with metal dications and here we report on two novel examples of *inclined* interpenetration of two-dimensional layers based on the *trans*-4,4'-azobis(pyridine) ligand (azpy), namely $[\text{Zn}(\text{azpy})_2(\text{H}_2\text{O})_2]\text{SiF}_6 \cdot \text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{azpy})_2(\text{NO}_3)_2]_2[\text{Ni}_2(\text{azpy})_3(\text{NO}_3)_4] \cdot 4\text{CH}_2\text{Cl}_2$ **2**, the second one showing, for the first time, the interpenetration of two different types of coordination layers.



azpy

Compound **1** was obtained as large red crystals by reacting $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ dissolved in ethanol with azpy in CH_2Cl_2 solution in a 1 : 2 molar ratio. One of the aims of this reaction was to compare the behaviour of azpy with that of the shorter 4,4'-bipyridyl (4,4'-bpy) ligand, which gives with ZnSiF_6 both interpenetrated^{8a} and not interpenetrated¹¹ (4,4) layered polymers. The structure of **1**¹² contains two-dimensional layers of

rhombic meshes (see Fig. 1, top). The Zn^{2+} cations are octahedrally coordinated, with four equatorial azpy ligands and two axial water molecules. Two sets of parallel layers, stacked with a separation of 7.61 Å, give *perpendicular* interpenetration, as shown in Fig. 1 (bottom). The situation is similar to that found in $[\text{Zn}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]\text{SiF}_6$,^{8a} the main differences being that **1** shows much more marked rhombic distortion of the meshes, stretched in the direction of the tetragonal *c* axis (ratio long/short diagonal of rhombuses of

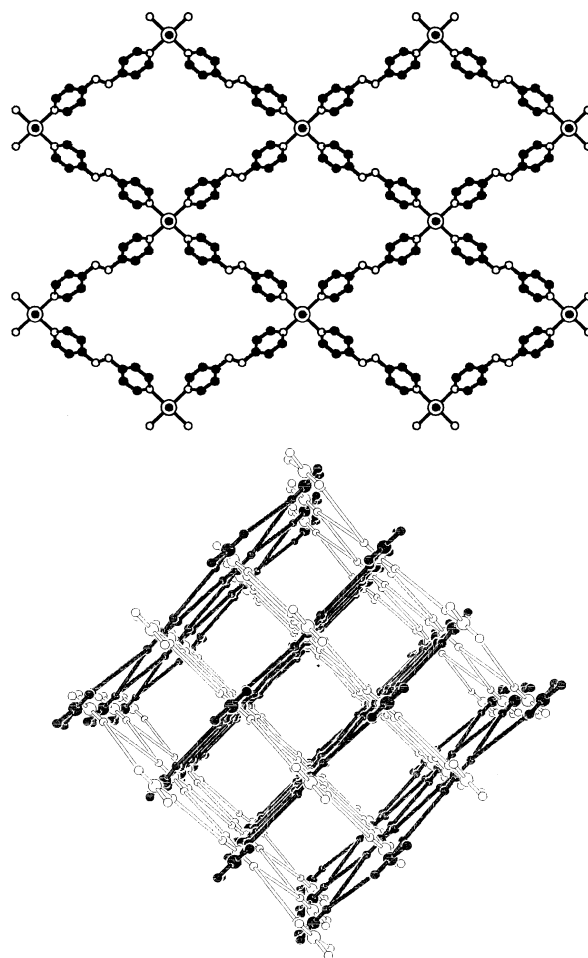


Fig. 1 A view of a single layer (top) and a schematic representation, down the tetragonal *c* axis, of the *perpendicular* interpenetration of the layers (bottom) in compound **1**

1.43 vs. 1.11) and longer Zn...Zn contacts (13.26 vs. 11.44 Å). The enlargement of the meshes of *ca.* 27% creates new voids that are only in part filled by the additional solvated water molecules. The reactions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with azpy, performed in the same way as for **1**, give mixtures containing species which were unstable when removed from the mother-liquor. Upon concentration dark-red air stable crystals of compound **2** separated, whose nature has been established by single crystal X-ray analysis.¹² The structure of **2** contains two completely different and crystallographically independent two-dimensional polymeric species packed together, *i.e.* layers of almost regular squares [planes I, (4,4) topology, see Fig. 2, top] and brick-wall layers [planes II, (6,3) topology, see Fig. 2, bottom] in the ratio 2 : 1. In both types of layers the Ni^{2+} ions display more or less distorted octahedral coordinations: each metal is bound in the squares to four equatorial azpy and to two axial oxygen atoms of two terminal NO_3^- anions, while in the bricks to three *mer* azpy and to three oxygen atoms of two nitrate groups (one terminal and one chelating). The Ni...Ni contacts in the two types of layers are in the range 13.13–13.24 Å.

Both types of sheets form parallel sets, but while type II layers [parallel to the (1 1 – 2) planes] are all stacked at the same distance (6.60 Å), type I layers [parallel to the (0 0 1) planes] show the alternance of shorter and longer stacking separations (of 5.94 and 8.14 Å, respectively). The two sets intercross at an angle of *ca.* 45°, thus interpenetrating to give a three-dimensional array, illustrated in Fig. 3, which displays large rhombic channels along the [1 –1 0] direction that contain the guest CH_2Cl_2 molecules and the nitrate anions. It is noteworthy that while each square of a layer I is interpenetrated by a single layer of type II, each brick-like mesh is entangled with two planes of type I.

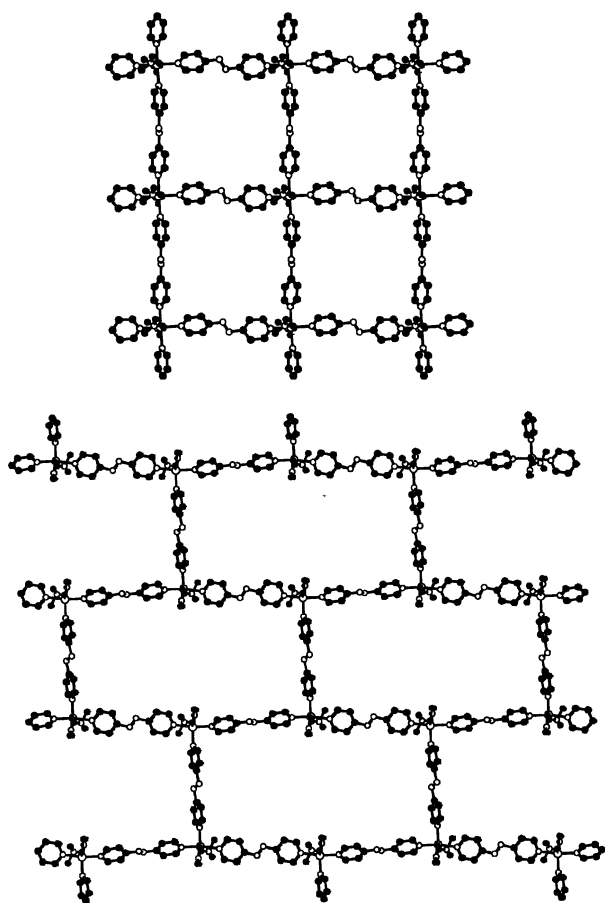


Fig. 2 The two types of layers present in compound **2**: layers I top, and II bottom

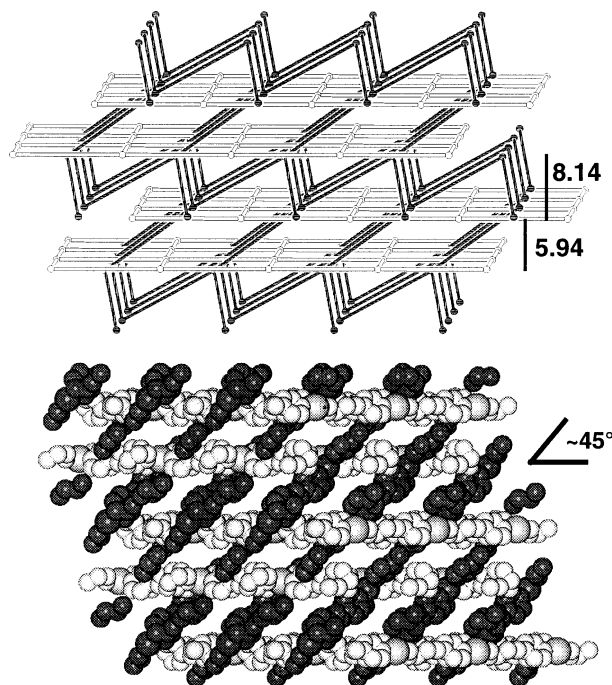


Fig. 3 A schematic view of the interpenetration of the layers approximately down the *a* axis (top) and a sphere packing diagram, without the anions and the solvent molecules, showing the *inclined* interpenetration of the layers and the channels down [1, –1 0] (bottom) in compound **2**

Intertwining of different motifs is quite rare both in inorganic and in coordination polymer chemistry,⁵ and compound **2** is the first example of interpenetration of two types of bidimensional coordination polymers having different topology. This species and other recent examples of unusual intertwining,^{10,13} beside their aesthetic appeal, represent useful basic contributions to the foundation of a new 'topology of interpenetration phenomena' in infinite entanglements, which is not at hand today, but is a necessary tool for the development of the area of supramolecular chemistry.

Notes and References

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- 12 *Crystal data*: compound **1**: [Zn(azpy)₂(H₂O)₂] SiF₆·H₂O, tetragonal, space group *P4/ncc* (no. 130), *a* = *b* = 10.756(1), *c* = 21.725(2) Å, *V* = 2513.4(4) Å³, *Z* = 4, *D*_c = 1.665 Mg m⁻³, *μ* = 1.110 mm⁻¹, final *R* value 0.0756 for 931 independent absorption corrected (SADABS) reflections [*I* > 2σ(*I*)]. Compound **2**: [Ni(azpy)₂(NO₃)₂][Ni₂(azpy)₃(NO₃)₄]·4CH₂Cl₂, triclinic, space group *P1* (no. 2), *a* = 13.230(1) *b* = 13.241(1), *c* = 14.907(1) Å, *α* = 107.15(1), *β* = 98.13(1), *γ* = 90.73(1)°, *V* = 2466.1(3) Å³, *Z* = 1, *D*_c = 1.589 Mg m⁻³, *μ* = 1.058 mm⁻¹, final *R* value 0.0754 for 6273 independent absorption corrected (SADABS) reflections [*I* > 2σ(*I*)]. The data collections were performed by the ω-scan method, Mo-Kα radiation (*λ* = 0.71073 Å), at 293 K on a SMART-CCD area-detector diffractometer, within the limits 2 < *θ* < 30° (**1**) and 1 < *θ* < 36° (**2**). The structures were solved by direct methods (SIR97) and refined by full-matrix least squares (SHELX97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms. All the diagrams were obtained using the SCHAKAL97 program. CCDC reference number 440/069.
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