Two different one-dimensional structural motifs in the same coordination polymer: a novel interpenetration of infinite ladders by bundles of infinite chains

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Two different one-dimensional structural motifs in the same coordination polymer: a novel interpenetration of infinite ladders by bundles of infinite chains

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A coordination polymer with a novel structural motif consisting of stacks of infinite ladders interpenetrated by bundles of infinite chains is described; geometrical arguments are made for the requirements that can lead to such interpenetration as a function of ligand dimensions.

To date, a large number of one-, two- and three-dimensional infinite frameworks, such as helical, brick wall, ladder, honeycomb, square grid, parquet, diamondoid and more complex 3D connectivities have been generated from tetrahedral, trigonal, and octahedral metal templates in combination with linear and nonlinear bidentate spacers.1–3 Product topology can often be influenced by selecting the coordination geometry of the metals and the chemical nature of the organic ligands. In particular, the T-joint building block, defined by the coordination of a metal center by three N,N'-bidentate ligands, has given rise to several isomeric framework types via different orientation of the T-joints relative to one another.4–6

While different structural isomers can form from T-shaped building blocks, and while it is not unusual to find multiple structural isomers within the same batch of crystals,4,7 it is quite rare to find two structural motifs within the same crystal structure.8–11 The use of the long ligand 1,4-bis[(4'-pyridylethynyl)benzene] (1)12 has led to the formation of a highly unusual interpenetrated network in [Cu(1)(solv)(NO3)2] [Cu(1)(solv)2][NO3]2 (solv = solvent; EtOH for 2 and MeOH for 3) where two dissimilar motifs co-exist in the same crystal structure: stacks of infinite ladders of composition [Cu(1)(solv)(NO3)2] are interpenetrated by infinite chains of composition [Cu(1)(solv)(NO3)2].

A blue solution of Cu(NO3)2·3H2O (12.2 mg, 0.05 mmol) in ethanol and/or methanol (3 mL) was carefully layered onto an ethanol and/or methanol (3 mL) solution of 1,4-bis[(4'-pyridylethynyl)benzene] (14.4 mg, 0.05 mmol). Light green precipitates formed immediately. After two weeks, green crystals of 2 and 3 grew at the interface of the two layers and also at the top of the mixture. Single crystals suitable for X-ray analysis were isolated and their structures determined.‡

The one-dimensional ladders are composed of T-shaped building blocks with the copper center in a five-coordinate trigonal bipyramidal environment (Fig. 1a) consisting of three pyridyl nitrogen donors (two axial and one equatorial), one from each of the three ligands, 1, and two equatorial oxygen donors from two monodentate nitrate ions. The ladders stack in a terraced fashion with an offset of 1/2 the ladder width along the crystallographic a-axis and with a close intralayer separation of 6.1 Å.12 The one-dimensional chains (Fig. 1b) also feature five-coordinate copper, but now in a square pyramidal coordination environment, with the basal plane consisting of two pyridyl nitrogen donors, from two trans ligands of 1, and two oxygen donors from two monodentate nitrate ions. The apical site is occupied by an oxygen donor from a coordinated ethanol (2) or methanol (3) solvent molecule.

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Fig. 1 Perspective view (top) and schematic representation (bottom) of a single (a) ladder motif and (b) chain motif in compounds 2 and 3.
The structural motif described in this communication fulfills that suggestion, however, not by using a self-inter-penetrated structure, but rather by using two different structures, i.e. ladders and chains, that interpenetrate.

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Notes and references

12 The N-to-N distance in 1,4-bis[(4'-pyridyl)ethyl]benzene (1) is 16.5 Å, which is about 9.0 Å longer than 4,4'-bipyridine. The convenient route for the synthesis of 1 is described in J. T. Lin, S.-S. Sun, J. J. Wu, L. Lee, K.-J. Lin and Y. F. Huang, Inorg. Chem., 1995, 34, 2323.