

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**)_{1.5}(NO₃)₂]·2solv (solv = solvent; EtOH for **2** and MeOH for **3**) where two dissimilar motifs co-exist in the same structure: stacks of infinite ladders of composition [Cu(**1**)_{1.5}(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.¹³ 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.

We can consider the ladder to be a 'double-chain', formed *via* the crosslinking of two chains by the ligand, **1**. The square opening is divided into two infinite rectangular channels by the ladders located above and below. These channels in turn are occupied by the single-chains, as shown schematically in Fig. 2, such that the chains fill the square openings in bundles of four. Further supramolecular interactions exist between the two structural motifs in the form of weak O–H...O hydrogen bonds between the coordinated solvent in the chains and the nitrate ions in the ladders (O–O distance = 2.72 Å for **2** and 2.75 Å for **3**). The interpenetration of stacks of ladders by bundles of chains together with the hydrogen bonding between the two distinct one-dimensional structural motifs combine to form the virtual three-dimensional frameworks of **2** and **3**.

It is interesting to note that this structural motif has not previously been observed, a fact that can be accounted for by the geometrical requirement of this double motif. The square openings between the rungs must be large enough to accommodate a bundle of four chains arranged in a 2 × 2 pattern. With the proviso that both the ladder and the chains that fill the ladder are constructed from the same ligand/metal pair, then the ligand (plus metal bonds) length-to-diameter ratio must fall within a fairly narrow size regime. A simple geometrical argument using space-filling models indicates that a length-to-diameter ratio of 3:1 would allow 4 chains to exactly occupy the opening in the ladder. Since in the structures of **2** and **3**, the chains pass through two ladders offset by 1/2, a ratio of 4:1 (a loose fit in the ladder

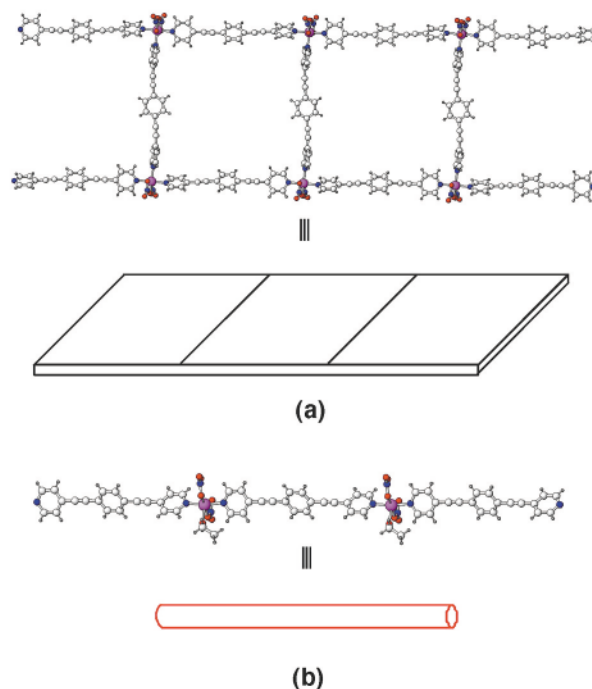


Fig. 1 Perspective view (top) and schematic representation (bottom) of a single (a) ladder motif and (b) chain motif in compounds **2** and **3**.

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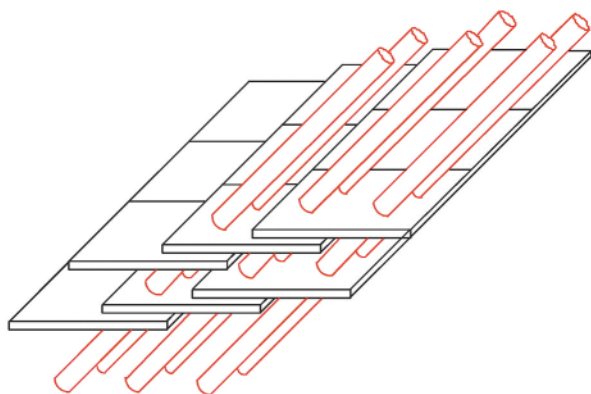


Fig. 2 Schematic view of the terraced stacks of ladders offset by 1/2 relative to each other along the crystallographic *a*-axis. The interpenetration by bundles of chains through the square openings is shown. For clarity only six chains in a square opening of a ladder are presented.

direction and an exact fit in the direction incident to the ladder) is required to allow for the space blocked by the second ladder. The experimentally determined ratio for both **2** and **3** is approximately 4.2:1. (The Cu–Cu distance is 20.4 Å while the approximate van der Waals diameter of the ligand (**1**) ranges from 3.40 Å at the most narrow to 6.43 Å at the widest point—yielding a crude ‘average’ vdW radius of 4.9 Å.)

Interestingly, one might have expected that shorter ligands such as 4,4'-bipyridine, which have been used extensively in the past, would have resulted in the discovery of a 1×1 pattern.⁸ This would necessarily consist of parallel stacks of ladders without an offset. The fact that this has not been observed suggests that such a structural motif may require some hydrogen bonding between ladders for added stability. Offset systems, as described in this paper, allow for a virtual three-dimensional structure with, apparently, enhanced stability. By extension, longer ligands might form ladders and/or square grids that are interpenetrated by bundles of 9 or 16 chains in 3×3 or 4×4 patterns, respectively, with ladder offsets of 1/3 and 1/2 (or possibly 1/4). Such structures would require length-to-diameter ratios of at least 6:1 and 8:1 for 3×3 and 4×4 patterns, respectively (Fig. 3). Assuming that the ‘average’ vdW diameter of a typical unencumbered N,N'-bidentate ligand is ~5 Å, the lengths of the requisite ligands (assuming a 2 Å nitrogen–metal distance) would have to be ~26 and ~36 Å, respectively. (The fact that the rings in the ligand result in a ‘plank-like’ rather than a true ‘spherical’ shape should be an advantage for this type of offset structure.)

It is likely that the driving force for the formation of this type of interpenetration is the need to fill empty space in the structure. Typically, as suggested by Batten and Robson,¹⁴ longer ligands will lead to more highly interpenetrated struc-

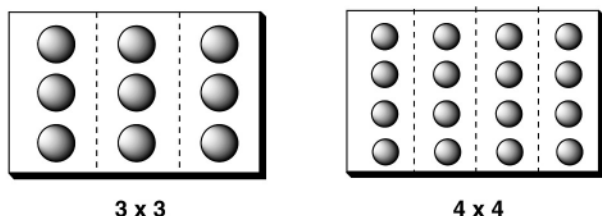


Fig. 3 Schematic representation of 3×3 and 4×4 bundles interpenetrating a stacked ladder structure. Chains (shaded circles) are running through the stacked ladders where dashed lines indicate the lateral offset of the ladders, 1/3 and 1/4, respectively.

tures. The structural motif described in this communication fulfils that suggestion, however, not by using a self-interpenetrated structure, but rather by using two different structures, *i.e.* ladders and chains, that interpenetrate.

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Notes and references

‡ *Crystal data for 2*: $C_{56}H_{48}Cu_2N_9O_{15}$, $M = 1214.11$, triclinic, space group $P\bar{1}$, $a = 12.248(2)$, $b = 13.771(3)$, $c = 18.257(4)$ Å, $\alpha = 108.078(4)^\circ$, $\beta = 97.890(4)^\circ$, $\gamma = 103.139(5)^\circ$, $V = 2778.1(9)$ Å³, $Z = 2$, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.842 \text{ mm}^{-1}$, $R_1 = 0.052$ and $wR_2 = 0.094$ for 9758 data with $I > 2\sigma(I)$. *Crystal data for 3*: $C_{53}H_{42}Cu_2N_9O_{15}$, $M = 1172.04$, triclinic, space group $P\bar{1}$, $a = 12.136(1)$, $b = 13.738(2)$, $c = 17.563(3)$ Å, $\alpha = 107.663(3)^\circ$, $\beta = 94.805(4)^\circ$, $\gamma = 104.021(4)^\circ$, $V = 2667.6(7)$ Å³, $Z = 2$, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.874 \text{ mm}^{-1}$, $R_1 = 0.050$ and $wR_2 = 0.086$ for 7669 data with $I > 2\sigma(I)$. X-Ray intensity data were measured on Bruker SMART APEX CCD-based diffractometer system. Both structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2 , using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and refined using a riding model with the exception of the coordinated solvent hydrogens, which were located and refined subject to an O–H distance restraint of 0.9(1) Å and given a U_{eq} value 1.5 times the parent atom. CCDC reference numbers 167941 and 167942. See <http://www.rsc.org/suppdata/cc/b1/b106190a/> for crystallographic data in CIF or other electronic format.

Yield for **2**: 18% (crystals only) based on $Cu(NO_3)_2 \cdot 3H_2O$. Elemental analysis (%): calc. C 55.54, H 3.96, N 10.38; found C 53.79, H 3.90, N 10.74. Yield for **3**: 24% (crystals only) based on $Cu(NO_3)_2 \cdot 3H_2O$. Elemental analysis (%): calc. C 54.36, H 3.59, N 10.77; found C 54.14, H 3.61, N 10.52.

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