# New Crystalline Frameworks Formed from 1,2-Bis(4-pyridyl)ethyne and $Co(NO_3)_2$: Interpenetrating Molecular Ladders and an Unexpected Molecular Parquet Pattern from T-Shaped Building Blocks

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The directed supramolecular assembly of organic, inorganic, or organometallic modules into functional solids with, for example, pores of defined size, shape, and chemical environment, or a specified three-dimensional structure is currently an active topic in solid-state and supramolecular chemistry.[1,2] Developments in this field could potentially lead to true crystal engineering, i.e., a situation where it is possible to predict the topology and/or the periodicity of the crystalline lattice from the molecular structure of the participating small building block(s).[3] Dramatic progress has been made in recent years with regard to the discovery of discrete packing motifs. The formation of specific substructures from geometric constraints can now be expected in accord with the chemistry of metal cations and basic ligands. However, while an *accurate prediction* of the overall crystal structure currently is almost impossible,[3] it may be achieved in the future. In the meantime, however, new structural motifs must be identified and the reaction chemistry leading to them investigated to generate a sufficiently large database from which crystal-packing rules for specific classes of materials can be deduced.

An attractive group of novel materials is formed by the combination of organic bi- or multidentate ligands with transition-metal cations.[4] Particularly, linked pyridines such as 4,4′-bipyridine, dipyridylethane, and structurally similar ligands are popular for the construction of mesoporous organic−inorganic hybrid solids with potential applications as catalytic or molecular sieve materials. A combination of a metal, anion, and ligand makes the formation of different architectures feasible, and recently Ciani[5] reported the self-assembly of copper(II) nitrate and 1,2-bis(4-pyridyl)ethyne. We have an interest in exploiting alkyne-bridged ligands for the construction of novel organic−inorganic hybrid networks and were prompted by Ciani's work to report here the solid-state structures which form by crystallization of 1,2-bis(4-pyridyl)ethyne with cobalt(II) nitrate.

So far, a number of one-, two-, and three-dimensional infinite frameworks, such as diamondoid,[6] helices,[7] brick wall,[8] ladder,[8,9] honeycomb,[10] square grid,[11] tire-tread (parquet),[12] and 3D frameworks[13] from tetrahedral, trigonal, and octahedral metal templates (e.g., $Zn^{II}$, $Cd^{II}$, $Ag^{I}$, $Cu^{I}$, and $Co^{II}$) have been generated with linear and nonlinear bidentate spacers. The topology of the material can be controlled by selecting the coordination geometry of the metals and the chemical nature of the organic ligands.

We have initiated a synthetic program for the preparation of interpenetrating and noninterpenetrating open frameworks with variable cavities or channels, in which the rodlike rigid and flexible ligands such as 1,2-bis(4-pyridyl)ethyne and related species are chosen as the building blocks. In the present work, we report the preparation and crystal structures of an unexpected molecular parquet motif **1** (Figure 1a), and a molecular ladder **2** (Figure 1b), both having the formula $Co(NO_3)_2(C_{12}N_2H_8)_{1.5}\cdot MeOH$. Both compounds were constructed simultaneously by the reaction of 1,2-bis(4-pyridyl)ethyne with cobalt(II) nitrate hexahydrate. The parquet pattern in **1** is quite unexpected and distinctly different from the brick wall motif (Figure 1c), although both patterns are made up of pseudorectangular units.

In principle, the architecture of the polymers is limited by the metal−ligand ratio. For example, if the ratio of metal to ligand is 1:1.5 or 1:2, molecular square grids[9b,11a] or molecular ladders[8,9a] will be obtained, respectively. However, the reaction of cobalt(II) nitrate hexahydrate with 1,2-bis(4-pyridyl)ethyne in the ratio 1:1.5, 1:2, or even 1:3 in a solution of MeOH/MeCN always afforded both isomers, **1** and **2**.

Single crystals of complexes **1** and **2** were obtained by adding a solution of $[Co(NO_3)_2]\cdot 6H_2O$ (73 mg, 0.25

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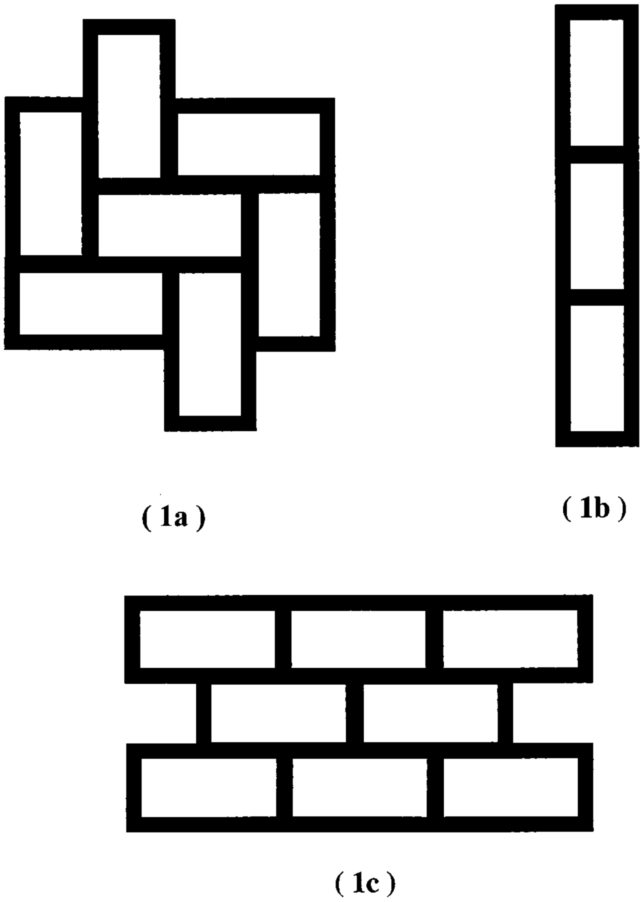
(1a)

(1b)

(1c)

**Figure 1.** Schematic diagrams of three inorganic–organic hybrid framework structural motifs. (a) Unusual parquet motif reported for isomer **1**. (b) Infinite molecular ladder motif found in isomer **2**. (c) Previously reported brick wall motif.

mmol) in MeOH (5 mL) to a solution of 1,2-bis(4-pyridyl)ethyne (67 mg, 0.38 mmol) in MeCN (5 mL). Transparent red crystals of **1** and **2** were isolated after the red-brown mixture was left at room temperature for 2 h. The combined crystal yield was 52 mg (43%). Crystals of both complexes **1** and **2** lose solvent molecules rapidly and turn opaque within minutes under ambient atmosphere, consistent with their thermal behavior, as observed by simultaneous TGA–DTA[14] of a mixed sample of **1** and **2**. The TGA showed a gradual weight loss over the temperature range of 25–182 °C, while at the same time the DTA trace was featureless. Such a result is consisitent with solvent evaporation,[15] and the large 157 °C range suggests the loss of both surface and interior solvent molecules.[16] No decomposition of the parquet or ladder skeletons was observed below 230 °C in a helium atmosphere; however, all three 1,2-bis(4-pyridyl)ethyne ligands were lost over the temperature range of 240–300 °C (observed 59.5%; calculated 59.6%). Both isomers were investigated by single-crystal X-ray analysis,[17] which revealed that the Co(II) centers of both **1** and **2** lie in a heptacoordinate environment (Figure 2). The three 1,2-bis(4-pyridyl)ethyne ligands form a "T-joint" at the Co(II) atoms, which is slightly distorted (for **1**, N(3)–Co–N(4) = 97.1(1)°, N(4)–Co–N(5) = 91.2(1)°, and N(3)–Co–N(5) = 170.4(1)°; for **2**, N(3)–Co–N(4) = 96.5(1)°, N(4)–Co–N(5) = 89.0(1)°, and N(3)–Co–N(5) = 173.9(1)°); the remaining coordination sites are occupied by two bidentate nitrate anions. Selected bond distance ranges are as follows (in Å): for **1**, Co–N, 2.159(3)–2.163(3) and Co–O, 2.187(3)–2.246(4); for **2**, Co–N, 2.148(3)–2.159(3) and Co–O, 2.180(3)–2.233(3). One of the nitrate ligands is bound in a regular bidentate fashion while the other nitrate ligand approaches a unidentate coordination having one long Co–O distance, for **1**, Co–O(5) = 2.351(3) Å and, for **2**, Co–O(5) = 2.444(4) Å.

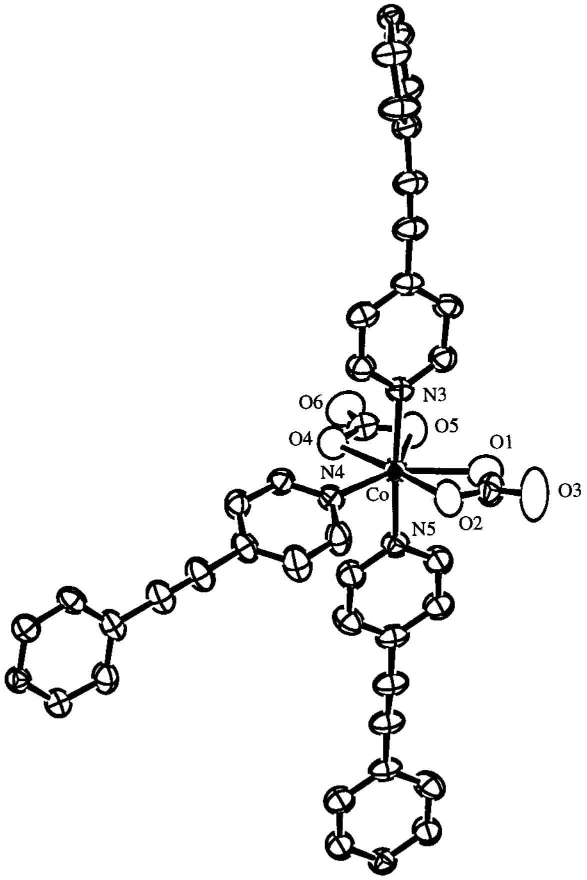

**Figure 2.** Coordination environment around the cobalt atom in **1** and **2**.

Isomer **1** adopts an infinite interpenetrating molecular parquet motif, in which each parquet tile in the

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[14] Thermogravimetric analyses and differential thermal analyses (TGA–DTA) were carried out using a TA Instruments SDT 2960 simultaneous DTA–TGA. The sample was heated at 10 °C/min in a helium atmosphere from 25 to 500 °C at a He flow rate of 60 mL/min.

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[17] Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The unit cell was determined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Silicon Graphics INDIGO$^2$ computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, The Woodlands, TX. An absorption correction (DIFABS) was applied to the data. All non-hydrogen atoms were refined with anisotropic thermal parameters while all hydrogen atoms were calculated and not refined. Crystal data for **1**: monoclinic, space group $C2/c$ (#15), $a = 20.655(5)$ Å, $b = 11.348(2)$ Å, $c = 22.183(6)$ Å, $\beta = 122.76(2)°$, $V = 4373(2)$ Å$^3$, $Z = 8$, $D_{calc} = 1.462$ g/cm$^3$, $R$(based on $F$) = 0.047, $R_w = 0.066$, and GOF = 2.71, for 2457 independent reflections having $2\theta \leq 45.0°$ and $I > 3\sigma$ with 284 variables. Crystal data for **2**: monoclinic, space group $C2/c$ (#15), $a = 20.621(6)$ Å, $b = 17.286(5)$ Å, $c = 14.275(5)$ Å, $\beta = 130.25(1)°$, $V = 3884(2)$ Å$^3$, $Z = 8$, $D_{calc} = 1.619$ g/cm$^3$, $R$(based on $F$) = 0.035, $R_w = 0.039$, and GOF = 1.74, for 1936 independent reflections having $2\theta \leq 43.0°$ and $I > 3\sigma$ with 278 variables.

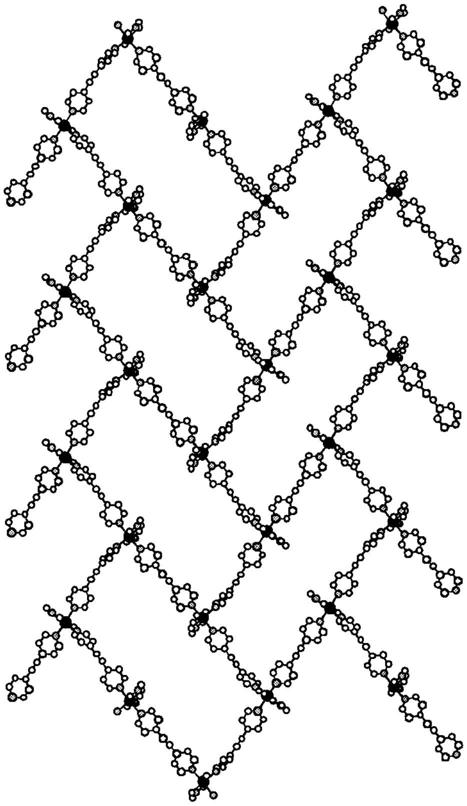

**Figure 3.** A view of a single layer in the infinite two-dimensional structure of **1**.

pattern consists of six 1,2-bis(4-pyridyl)ethyne ligands and six cobalt atoms. In fact, it is a 66-membered ring structure. The two-dimensional parquet layers are not perfectly flat, but undulate due to the distorted T-joint ligand coordination geometry around the cobalt atoms. This parquet pattern is distinctly different from the brick wall pattern reported previously for Cd[1,4-methylenepyridyl)-2,3,5,6-tetrafluorobenzene)$_{1.5}$]$_n$-(NO$_3$)$_2$,[8] in which the rectangular units are joined together parallel to each other (Figure 1c). In **1**, two sets of tiles are joined together nearly perpendicular to each other. Each tile is offset by half a “step” along each axis (Figure 3). During the X-ray analysis, significant electron density was found within the cavities of the parquet framework. This is consistent with a disordered methanol solvent molecule, a common phenomenon in coordination polymer chemistry. It was refined with the methanolic carbon position fully occupied and two oxygen sites each half-occupied. This disorder model reasonably accounted for all significant residual electron density found in the Fourier analysis.

Isomer **2** has an infinite one-dimensional structure with interpenetrating molecular ladders (Figure 4), which involves a 44-membered square structure. The square structure consists of four 1,2-bis(4-pyridyl)ethyne ligands and four cobalt atoms. The ladder pattern is generated via the 1,2-bis(4-pyridyl)ethyne ligands with each bridging two Co(II) centers. A disordered solvent molecule is present, which was modeled as a methanol in a fashion similar to that in compound **1**. Isomer **2** may be termed a flat ladder with all linking ligands coplanar, of which there are few known examples, [Co(NO$_3$)$_2$(1,2-bis(4-pyridyl)ethane)$_{1.5}$]$_n$,[9a] Co(NO$_3$)$_2$(4,4′-bpy)$_{1.5}$]$_n$,[9b] and [Cd(NO$_3$)$_2$(1,4-bis(4-methylenepyridyl)benzene)$_{1.5}$]$_n$.[8] It is, however, quite different from the ladder generated from the reaction of [Cu(MeCN)$_4$]PF$_6$ with 1,4-bis(4-pyridyl)butadiyne, the structure of which contains an undulating ladder that results from the tetrahedral Cu(I) centers.[9c]

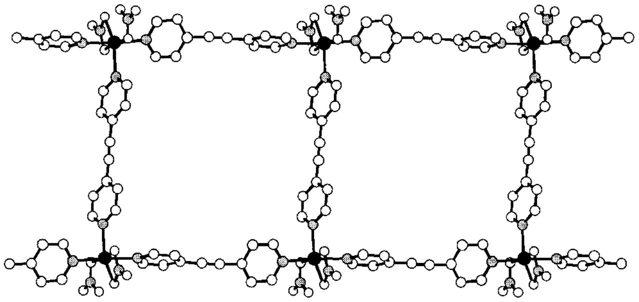

**Figure 4.** A view of a single ladder in the infinite one-dimensional structure of **2**.

The T-joint defined by the coordination of the metal centers by the 1,2-bis(4-pyridyl)ethyne ligands can be considered the basic “building block” of the two structures reported here. Interestingly, in both **1** and **2**, two of the three ligands of this T-joint have the terminal pyridine groups rotated by about 90° with respect to one another, while the pyridine groups in the third coordinating ligand are strictly coplanar. Thus far, this T-joint building block with linear spacer ligands has given rise to five isomers via different orientations of the T-joints relative to one another: molecular ladder, molecular brick wall, three-dimensional framework, molecular bilayer (all of which were summarized by Zaworotko very recently[18]), and now the parquet motif of isomer **1**.

In conclusion, we have been able to show that a one-pot reaction of the ligand 1,2-bis(4-pyridyl)ethyne with cobalt(II) nitrate in methanol leads to the simultaneous formation of two isomeric coordination polymers with different structural motifs: a known “molecular ladder” type and an unusual parquet motif. In light of this structural versatility observed in the MeOH/CH$_3$CN solvent system, we are currently expanding our work on the Co(NO$_3$)$_2$/1,2-bis(4-pyridyl)ethyne system by experimenting with different solvent systems to better elucidate the structure-directing effects of various solvents and to gain a better understanding of the possibilities of crystal engineering.

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**Supporting Information Available:** Tables of crystal data, structure solution and refinement, atomic coordinates, bond length and angles, anisotropic thermal parameters, and structure factor tables for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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