Letter

Crystal structure of kinetic and thermodynamic coordination networks formed between 3,3′-dipyridylethyne and copper bromide

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Reaction of copper(I) bromide with 3,3′-dipyridylethyne yielded rhomboid yellow crystals that are stable when removed from the mother liquor. X-Ray crystallographic analysis identified the one-dimensional coordination polymer formed with pairs of dipyridyl ligands bridging rhombic $CuBr_2Cu$ units. The crystals left in the mother liquor re-dissolved and formed orange hexagonal prisms that were shown to be a stable three-dimensional network comprising interwoven ligand–copper ribbons linked together by infinite copper–bromide chains.

The engineering of supramolecules based on the self-assembly of coordination networks has attracted intense interest recently as a result of the wide range of potential applications.[1] Prominent amongst these are molecular electronics,[2] magnetic and optical devices,[3] nanoporous zeolite mimics,[4] chemical sensors[5] and novel catalysts.[6] The successful engineering of one-, two- and three-dimensional coordination networks is predicated on a sound understanding of the preferred coordination geometry of both the ligand and the metal. The preparation of coordination networks using copper halides as the inorganic component has recently been the focus of attention and a variety of structural forms have been identified.[7] In this paper we report the unusual kinetic crystallization of a one-dimensional bridging coordination polymer followed by the thermodynamic crystallization of a three-dimensional network on dissolution of the kinetic crystals.

In this study the self-assembly of the bidentate ligand 3,3′-dipyridylethyne with copper(I) bromide led to the isolation and characterization of two distinct products with the same stoichiometry. The structure of the first-formed yellow product **2** was determined by single-crystal X-ray crystallography and found to be a one-dimensional coordination polymer. The polymer comprises pairs of the bidentate ligand **1** bridging rhomboid $CuBr_2Cu$ connecting units as shown in the partial structure in Fig. 1. The ligand is twisted out of planarity with an interplanar angle between the pyridyl rings of approximately 50°. In addition, the alkyne is bent by approximately 5°. The twisted nature of the ligand presumably precludes any π-stacking interactions as were noted in several recent copper halide coordination polymers.[9] Indeed, the packing of adjacent ribbons of the one-dimensional polymer is dominated by C–H···arene nonbonding interactions shown as A and B in Fig. 2. Interaction A, C(10)–H(10)···PyrN(1), occurs between adjacent ribbons of the

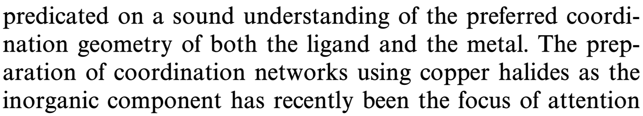

Fig. 1 Ortep[8] representation of three repeating units of the one-dimensional coordination polymer **2**, the kinetic product, formed between **1** and copper(I) bromide. Thermal ellipsoids drawn at 50% level.

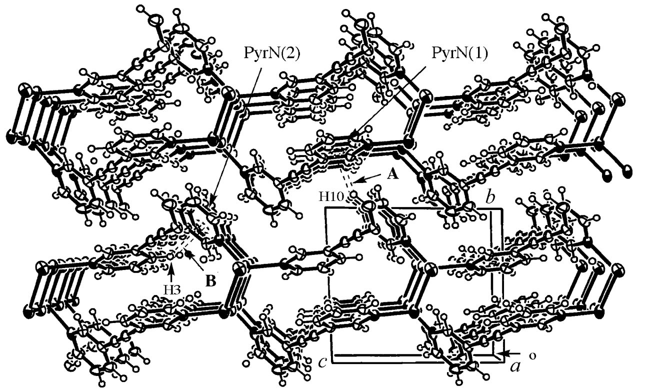

Fig. 2 Plot showing the packing of the one-dimensional network **2** along the *a* axis with the C–H···arene interactions, A and B, highlighted.

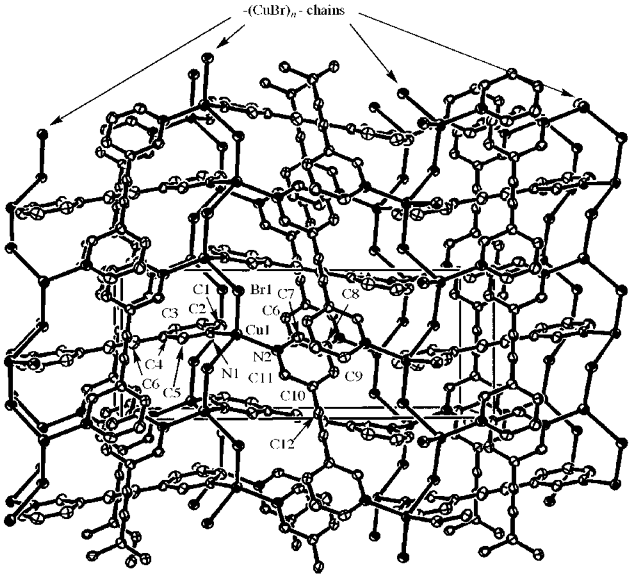

Fig. 3 View parallel to the *a* axis of the three-dimensional, thermodynamic, network **3** formed between ligand **1** and copper(I) bromide showing the linking $(CuBr)_n$ chains. Hydrogen atoms omitted for clarity.

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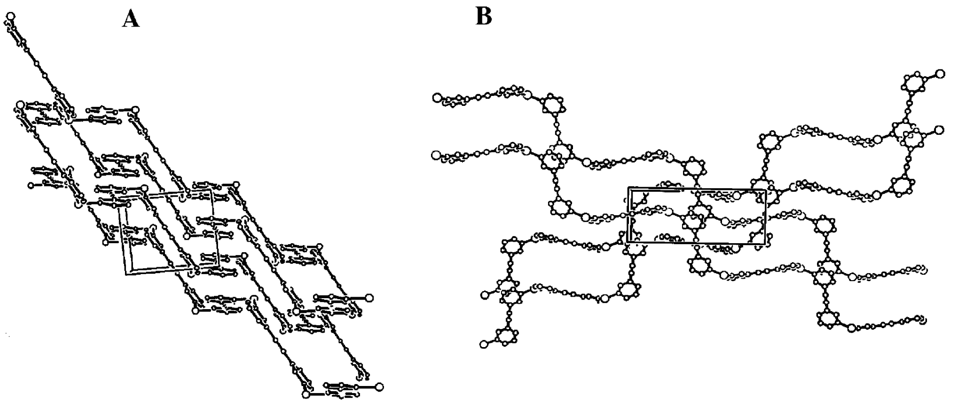

Fig. 4 Two orthogonal views of four interwoven –(Cu–**1**)$_n$– ribbons in the three-dimensional network **3** with the bromine and hydrogen atoms deleted for clarity. (A) Parallel to the *b* axis. (B) Parallel to the *a* axis.

polymer along the *b* axis. The distance from H(10) to the six atoms in the pyridine ring of the adjacent polymer strand lie in the range 2.835–3.128 Å and the interaction is clearly of the H···ring centroid type. The distance from H(10) to the centroid of the pyridyl ring, PyrN(1), is 2.627 Å with the angle C–H–centroid being 146.2°.[10] Interaction B, C(3)–H(3)···PyrN(2), occurs between ribbons of the polymer along the *a* axis. The distance from H(3) to the centroid of the pyridyl ring, PyrN(2), is 2.657 Å and the angle C–H–centroid is 129.2°.[11] These values are well within the accepted range for C–H···arene nonbonded interactions.[12]

These crystals did not persist in solution and were transformed into a stable orange form, **3**, over the period of one week in the mother liquor. The crystal structure of the orange form revealed a three-dimensional network shown in Fig. 3. This network consists of ribbons of copper coordinated ligands, –(Cu–**1**)$_n$–, that are interwoven through three-dimensional space as shown in Fig. 4. These ribbons are then interlinked by the copper–bromide chains as shown in Fig. 3.

The copper atoms have similar pseudo-tetrahedral geometry in both the one-dimensional and the three-dimensional networks, being bonded to two bromine atoms and two pyridyl groups. Indeed, the bond distances and bond angles about the copper atom are similar in each network. The Cu–N bond distances are 2.020(3) and 2.028(3) Å and the Cu–Br distances are 2.5048(7) and 2.5193(8) Å in the one-dimensional network with a resultant Cu–Cu distance of 2.8098(12) Å, typical for the rhombic CuBr$_2$Cu moiety.[7] By comparison the Cu–N bond distances are 2.029(3) and 2.028(3) Å and the Cu–Br bond distances are 2.4538(6) and 2.5363(5) Å in the two-dimensional network. The N–Cu–Br bond angles are 108.13(9), 104.16(9), 106.73(10) and 106.03(10)° and the N–Cu–N bond angle is 119.78(9)° in the one-dimensional network **1** while the N–Cu–Br bond angles are 109.69(9), 107.03(8), 114.63(9) and 101.05(8)° and the N–Cu–N bond angle is 119.04(12)° in the three-dimensional network. In contrast to the similar coordination about the copper atoms in these two structures, the geometry adopted by the ligand **1** is very different in the two structures. The ligand is non-planar and bent in the linear polymer **2** but essentially planar in the three-dimensional network **3** as shown in Fig. 5. We believe that this extra strain in the conformation of the ligand in the linear polymer **2** is the major reason that this network is not stable in the mother liquor. It is significant that the yellow linear polymer is formed under conditions of higher concentration whereas the orange three-dimensional network is formed at significantly lower concentrations. It is possible that the transformation of the yellow crystals to the orange crystals occurs by partial dissolution of the yellow form, followed by recrystallization at very low concentrations.

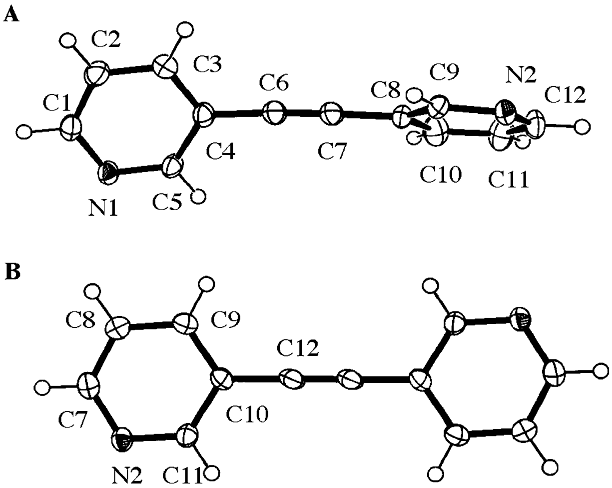

Fig. 5 Comparison of the geometry of the ligand **1** in the structures **2** and **3**. (A) The one-dimensional form **2**. (B) The three-dimensional form **3**.

In summary we have described the unusual isolation of two distinct coordination networks with the same molecular composition by self-assembly of copper(I) bromide with 3,3′-dipyridylethyne. This serves to highlight the difficulty in predictably preparing coordination networks. In the near future we will describe the similar formation of silver(I) based one-dimensional and three-dimensional networks with the ligand 3,3′-dipyridylethyne.

Experimental

Synthesis

The ligand 3,3′-dipyridylethyne, **1**, was prepared in 84% yield by the palladium catalyzed coupling[13] of 3-ethynylpyridine[14] and 3-bromopyridine. ^{1}H NMR: δ 8.79 (dd, $J = 1.0$, 1.8 Hz, 2H), 8.58 (dd, $J = 1.8$, 5.0 Hz, 2H), 7.83 (td, $J = 1.8$, 8.0 Hz, 2H), 7.31 (ddd, $J = 1.0$, 5.0, 8.0 Hz, 2H). Anal. calc. for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.52; found C, 79.86; H, 4.45; N, 15.52%.

The coordination networks, **2** and **3**, reported here were formed on mixing equimolar solutions of the two components, **1** and copper(I) bromide. A golden-yellow precipitate formed immediately on mixing a colorless 0.1 M acetonitrile solution of **1** with a pale green solution of copper(I) bromide. Slow diffusion of more dilute, 0.003 M, solutions resulted in the direct formation of orange microcrystalline material.

Crystallography

Yellow rhomboid shaped crystals, **2**, suitable for X-ray analysis, were formed on slow diffusion between layered 0.03

M acetonitrile solutions of **1** and CuBr.[16] These yellow crystals were stable provided that they were removed from the mother liquor. A crystal of dimensions 0.35 × 0.25 × 0.15 mm was selected for analysis. Those crystals that remained in the mother liquor were transformed into orange hexagonal prisms, **3**, over the course of one week in the dark. Anal calc. for $C_{12}H_8BrCuN_2$ (**3**): C, 44.53; H, 2.49; N, 8.65; found C, 44.43; H, 2.49; N, 8.60%. A crystal of dimensions 0.35 × 0.25 × 0.20 mm was selected for analysis. For both determinations, the crystals were mounted on the diffractometer and cooled in a flow of cold nitrogen gas (173 K) during data collection. Data were collected using Mo-Kα radiation and a Bruker SMART CCD area detector. Corrections for decay and absorption were made using the program SADABS.[15] For **2**, 2504 unique reflections were collected with $2.19° < \theta < 27.13°$, and for **3**, 2437 unique reflections were collected with $2.31° < \theta < 27.13°$. The structures were solved using SHELXS-97[16] and refined using SHELXL-97.[17] Hydrogen atoms were included in the calculated positions. Crystal data for **2**: $C_{12}H_8BrCuN_2$, $M = 323.65$, triclinic, $P\bar{1}$, $a = 7.2312(12)$, $b = 8.9917(15)$, $c = 9.4175(16)$ Å, $\alpha = 84.667(3)$, $\beta = 81.705(3)$, $\gamma = 73.315(3)°$, $U = 579.57(17)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\mu = 5.301$ mm^{-1}; 4124 reflections collected, 2504 unique ($R_{\text{int}} = 0.0244$), final $R_1 = 0.0462$, $wR_2 = 0.1178$ (based on F^2) for 2504 $[I > 2\sigma(I)]$ observed reflections. Crystal data for **3**. $C_{12}H_8BrCuN_2$, $M = 323.65$, monoclinic, $P2_1/c$, $a = 8.5820(7)$, $b = 17.6497(13)$, $c = 7.3216(6)$ Å, $\beta = 91.720(2)°$, $U = 1108.50(15)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\mu = 5.543$ mm^{-1}; 6794 reflections collected, 2437 unique ($R_{\text{int}} = 0.0315$), final $R_1 = 0.0342$, $wR_2 = 0.0785$ (based on F^2) for 2437 $[I > 2\sigma(I)]$ observed reflections.

CCDC reference numbers 170399 and 170400. See http://www.rsc.org/suppdata/nj/b1/b106221m/ for crystallographic data in CIF or other electronic format.

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