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Molecular tectonics: tuning dimensionality and topology of extended cyanocuprate networks by bisamidinium cation

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Upon combining $\text{KCu}(\text{CN})_2$ with six different symmetrical dicationic bisamidinium moieties possessing different shapes and geometries, seven new coordination networks of the cyanocuprate type displaying 1-, 2- and 3-D dimensionality have been obtained. The formation of networks results from the interconnection of $\text{Cu}(\text{I})$ centres by cyanide anions through different bridging modes. The organic dicationic tectons interact with the anionic networks by charge-assisted H-bonds and, depending on their geometric features, they play different structuring roles. In the case of the 1D cyanocuprate networks, the organic cation interconnects consecutive anionic chains increasing thus the overall dimensionality of the arrangement to 2D. For the 2D networks, either riveting or intercalation has been observed. For the riveting case, either the process takes place only between two consecutive sheets leading to a double layer type arrangement and thus without increase of dimensionality, or between consecutive 2D networks in an alternate fashion. In the latter case, the dimensionality of the overall architecture is increased to 3 as for the intercalated case. For the 3D architectures, the dicationic moieties are located within the generated channels.

Introduction

The design and formation of extended coordination networks is a matter of current investigations. The interest in this type of solid-state materials arises from their possible applications in sensing, gas storage and/or separation, catalysis, drug delivery etc. Since two decades, many examples of coordination networks,¹ in particular of the MOFs² type have been described over the last two decades.

Cyanometallates³ form a large and attractive class of compounds displaying a variety of properties.⁴ Among many reported examples, 3D Prussian blue type coordination networks have been extensively studied.⁵ Within this variety of compounds, cyanocuprates based on d^{10} $\text{Cu}(\text{I})$ cation are interesting entities.

Whereas, owing to their kinetic inertness, dicyanoaurate and dicyanoargentate form mainly discrete species, cyanocuprate generates a variety of extended architectures through self-bridging processes. It is interesting to note that, whereas in dicyanometallates ($\text{M}(\text{I}) = \text{Ag}, \text{Au}$) the metal adopts a linear coordination geometry, for cyanocuprate, several geometries such as linear $[\text{Cu}^{\text{I}}(\text{CN})_2]^-$, trigonal $[\text{Cu}^{\text{I}}(\text{CN})_3]^{2-}$ and tetrahedral $[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$ are encountered (Scheme 1 top).⁶ Furthermore, owing to the ambivalent nature of the cyanide ligand, the latter adopts different coordination modes such as end-to-end (bridging) or end-on (μ_2 or μ_3 -bridging) as illustrated in scheme 1 (bottom). Finally, due to cuprophilic interactions⁷ between d^{10} $\text{Cu}(\text{I})$ centres, the formation of dimers displaying luminescence⁸ has been reported.

Scheme 1: Schematic representations of the three most encountered coordination geometry around $\text{Cu}(\text{I})$ cation (top); bridging modes of CN^- anion (bottom) in cyanocuprates. Grey spheres represent a $\text{Cu}(\text{I})$ centre, blue and red cylinders represent bridging and terminal cyanide respectively.

Applying the concepts developed in molecular tectonics,⁹ an approach dealing with the formation of infinite networks between complementary tectons¹⁰ or building blocks capable of mutual interconnection, we have explored combinations of discrete cyanometallate with organic cationic tectons.¹¹ These combinations, based on strong charge assisted hydrogen bonds,¹² led to the formation of a variety H-bonded networks displaying various dimensionalities.¹³ For example, combinations of some of bisamidinium dications ($[\text{X}-2\text{H}^+]$, $\text{X} = 1-6$, see scheme 2) with linear $(\text{M}^{\text{I}}(\text{CN})_2)^-$ ($\text{M} = \text{Ag}$ or Au) leads to luminescent crystals.¹⁴ Examples of other luminescent $\text{Ag}(\text{CN})_2^-$ or $\text{Au}(\text{CN})_2^-$ based architectures stabilized by H bonds and metallophilic interactions have been also reported.¹⁵ On the other hand, some of their associations with octahedral $\text{M}^{\text{III}}(\text{CN})_6^{3-}$ ($\text{M} = \text{Fe}, \text{Co}$ or Cr) cyanometallates leads to porous crystals.¹⁶

Scheme 2: Dicationic bisamidinium compounds **1-6**.

Based on our previous studies mentioned above, we have investigated the formation of extended architectures using dicyanocuprate. In particular, we were interested in exploring the possibility of stabilizing discrete $\text{Cu}(\text{CN})_2$ unit through the formation of H-bonded networks using dicationic tectons of the bis-cyclic amidinium type.¹⁷ Here we report on combinations of $\text{KCu}(\text{CN})_2$ ¹⁸ with organic compounds X-2H^+ ($\text{X} = 1-6$) in solution and in the solid state using mechanochemistry,¹⁹ leading to seven crystalline materials characterized by both X-ray diffraction on single crystals (XRD) and X-ray diffraction on powders (PXRD).

Experimental section

FT-IR spectra were recorded on a Perkin Elmer ATR spectrometer.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Materials

$\text{KCu}(\text{CN})_2$ was synthesized following a reported procedure.¹⁸

Bisamidinium dicationic **1-6** have been used either as their HCl or TsOH (*p*-toluenesulfonic acid) salts. Compounds **1-2TsOH**,¹⁶ **3-2HCl**,^{13a,b,17} **4-2HCl**,¹⁶ **5-2TsOH**^{13d} and **6-2TsOH**²⁰ have been prepared as described. The synthesis of **2-2HCl** is described below.

Whereas crystalline materials **A-F** were colourless, **G** was found to be orange.

The synthesis by mechanochemistry employed for the preparation of polycrystalline materials **A-G** was based on the grinding, at room temperature, of mixtures of 0.1 mmol of bisamidinium salts (X-2H^+ , 2Y^- , $\text{X} = 1-6$; $\text{Y} = \text{Cl}^-$ or TsO^-) and 0.2 mmol of $\text{KCu}(\text{CN})_2$ using a Retsch MM400 shaker mill with a 5 ml agate vessel and two 5 mm agate balls. In all cases, the powder obtained was washed with water (50 ml), MeOH (10 ml) and dried in air, and only characterized using PXRD.

Synthesis of **2-2HCl**

A mixture of 1,4-dicyanobenzene (1 eq., 15.6 mmol, 2 g) and 1,2-diaminoethane (2 eq., 31.2 mmol, 1.88 g) and of P_2S_5 (15 mg) as catalyst²¹ was heated to 120 °C under a gentle flux of argon during 1.5 hours. The solid thus obtained was cooled and acidified with an aqueous HCl solution (1N) until pH 5 was reached. After 15 min of stirring, the mixture was filtered and the

filtrate evaporated. The pure compound **2-2HCl** was obtained in 80 % yield as a slightly yellowish solid upon crystallizations from distilled water. ¹H-NMR ($\text{D}_2\text{O} + t\text{BuOH}$, 300 MHz, 25 °C, δ ppm): 3.98 (m, 8H, $\text{CH}_2\text{-NH}$); 7.93 (s, 4H, CH arom.); ¹³C-NMR ($\text{D}_2\text{O} + t\text{BuOH}$, 75 MHz, 25 °C, δ ppm): 45.0 ($\text{CH}_2\text{-NH}$); 153.0 (CH arom.); mp = 300 °C decomp.; ES MS: m/z : found 108.16, calculated: 108.14. Elemental analysis (%): calc. for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_4 \cdot 3\text{H}_2\text{O}$: C = 42.23; H = 6.49; N = 16.42; found: C = 43.01; H = 6.40; N = 16.32.

Synthesis of network **A** ($[\text{3-2H}^+][\text{Cu}(\text{CN})_2]_2$)

The network **A** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of **3-2HCl** $\cdot 3\text{H}_2\text{O}$ (3.7 mg, 0.01 mmol) in distilled H_2O (3 ml) with a solution of $\text{KCu}(\text{CN})_2$ (3.1 mg, 0.02 mmol) in distilled H_2O (5 ml). After one day, crystals of formula $[\text{C}_{14}\text{H}_{20}\text{N}_4][\text{Cu}(\text{CN})_2]_2$ were formed (81 % yield).

Elemental analysis: calc. (%) for $\text{C}_{18}\text{H}_{20}\text{N}_8\text{Cu}_2$: C = 45.46; H = 4.24; N = 23.57. Found: C = 46.08; H = 4.54; N = 23.45. IR data (cm^{-1}): 3375, 3323, 3034, 3012, 2970, 2365, 2342, 2128, 2111, 1738, 1654, 1426, 1354, 1218, 1198, 857, 658.

Using the same stoichiometry, this compound was also obtained in 70 % yield as a microcrystalline powder by mechanochemistry upon grinding a mixture of the two powders during 10 minutes at 25 Hz (37 mg, 0.1 mmol for **3-2HCl** $\cdot 3\text{H}_2\text{O}$ and 31 mg, 0.2 mmol for $\text{KCu}(\text{CN})_2$).

Synthesis of network **B** ($[\text{5-2H}^+][\text{Cu}_2(\text{CN})_3]_2$)

The network **B** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of **5-2TsOH** $\cdot 2\text{H}_2\text{O}$ (7.6 mg, 0.01 mmol) in distilled CH_3OH (3 ml) with a solution of $\text{KCu}(\text{CN})_2$ (3.1 mg, 0.02 mmol) in distilled H_2O (3 ml). After two days, crystals of the following formula $[\text{C}_{26}\text{H}_{44}\text{N}_4][\text{Cu}_2(\text{CN})_3]_2 \cdot 2\text{CH}_3\text{OH}$ were formed (67 % yield).

Elemental analysis: calc. (%) for $\text{C}_{34}\text{H}_{52}\text{N}_{10}\text{O}_4\text{Cu}_4$: C = 46.04%; H = 5.91; N = 15.79. Found: C = 46.16; H = 6.02; N = 15.75%. IR data (cm^{-1}): 3375, 3325, 3034, 3014, 2970, 2365, 2342, 2131, 2116, 1738, 1654, 1466, 1426, 1366, 1218, 1203, 856, 647.

Using the same stoichiometry, this compound was also obtained in 56 % yield as a microcrystalline powder by mechanochemistry upon grinding a mixture of the two powders during 10 minutes at 25 Hz (76 mg, 0.1 mmol for **5-2TsOH** $\cdot 2\text{H}_2\text{O}$ and 31 mg, 0.2 mmol for $\text{KCu}(\text{CN})_2$).

Synthesis of network **C** ($[\text{4-2H}^+][\text{Cu}_3(\text{CN})_4]_2$)

The network **C** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of **4-2HCl** $\cdot 3\text{H}_2\text{O}$ (2.2 mg, 0.006 mmol) in distilled H_2O (3 ml) with a solution of $\text{KCu}(\text{CN})_2$ (1.9 mg, 0.012 mmol) in distilled H_2O (3 ml). After one day, crystals of the following formula $[\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_2][\text{Cu}_3(\text{CN})_4]_2$ corresponding to the solid state material **C** were formed (15 % yield). The isolated crystals were found to be stable outside the mother liquor. However, upon standing in solution for 2 days, the crystalline material was converted into a yellow powder which could not be structurally characterized.

Elemental analysis: calc. (%) for $\text{C}_{22}\text{H}_{20}\text{N}_{12}\text{O}_2\text{Cu}_6$: C = 30.52; H = 2.33; N = 19.41. Found: C = 31.82; H = 2.26; N = 19.52%. The discrepancy between the calculated and determined % for C was observed on several attempts. IR data (cm^{-1}): 3486, 3365, 3283, 3246, 3228, 3219, 3179, 3052, 2971, 2108, 2099, 2065, 1748, 1659, 1600, 1515, 1466, 1366, 1337, 1307, 1228, 1218, 1109, 1019, 900, 856, 732, 647 and 597.

Using the same stoichiometry, only the yellow powder was obtained by mechanochemistry in 50 % yield as a microcrystalline powder upon grinding during 10 minutes at 25 Hz the mixture of the two solids (37 mg, 0.1 mmol for 4-2HCl·3H₂O and 31 mg, 0.2 mmol for KCu(CN)₂).

Synthesis of network D ([6-2H⁺][Cu₂(CN)₄]²⁻)

The network **D** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of 6-2TsOH·2H₂O (2.1 mg, 0.004 mmol) in distilled H₂O (3 ml) with a solution of KCu(CN)₂ (1.2 mg, 0.008 mmol) in distilled H₂O (3 ml). After one week, crystals of the following formula [C₈H₁₂N₄][Cu₂(CN)₄] were formed (73 % yield).

Elemental analysis: calc. (%) for C₁₂H₁₂N₈Cu₂: C = 34.98; H = 3.52; N = 24.48. Found: C = 34.44; H = 3.25; N = 24.43. IR data (cm⁻¹): 3377, 2978, 2964, 2116, 2099, 2068, 1653, 1592, 1515, 1466, 1371, 1333, 1307, 1228, 1218, 1109, 1019, 900, 863, 813 732, 633, 514.

Using the same stoichiometry, this compound was also obtained in 66 % yield as a microcrystalline powder by mechanochemistry upon grinding a mixture of the two powders during 10 minutes at 25 Hz (53 mg, 0.1 mmol for 6-2TsOH·2H₂O and 31 mg, 0.2 mmol for KCu(CN)₂).

Synthesis of network E ([1-2H⁺][Cu(CN)₂]₂)

The network **E** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of 1-2TsOH·3H₂O (2.7 mg, 0.005 mmol) in distilled H₂O (4 ml) with a solution of KCu(CN)₂ (1.5 mg, 0.001 mmol) in a H₂O/MeOH 1/1 mixture (4 ml). Crystals of compound **E** ([C₁₀H₂₀N₄][Cu(CN)₂]₂) were obtained overnight (23 % yield). The isolated crystals were found to be stable outside the mother liquor. However, upon standing in H₂O/MeOH solution for a longer period of time (2 days), the compound **E** was found to be partially converted into the compound **F** without complete conversion. It is worth noting that we were unable to prepare the compound **E** by mechanochemistry.

Elemental analysis: calc. (%) for C₁₄H₂₀N₈Cu₂: C = 39.34; H = 4.72; N = 26.21. Found: C = 41.40; H = 4.63; N = 26.05. Again, the discrepancy between the calculated and determined % for C was observed on several attempts. IR data (cm⁻¹): 3266, 3228, 3189, 3045, 2108, 2096, 2078, 1639, 1609, 1484, 1461, 1317, 1257, 1126, 1094, 990, 837, 732, 687, 643 and 476.

Synthesis of network F ([1-2H⁺][Cu₂(CN)₃]₂)

The network **F** was obtained at 25 °C in a crystallization tube (8 mm diameter) upon layering a solution of 1-2TsOH·3H₂O (2.7 mg, 0.005 mmol) in distilled H₂O (3 ml) with a solution of KCu(CN)₂ (1.5 mg, 0.01 mmol) in distilled H₂O (3 ml). After four days, crystals of the following formula [C₁₀H₂₀N₄][Cu₂(CN)₃]₂·2H₂O were formed (38 % yield).

Elemental analysis: calc. (%) for C₁₆H₂₄N₁₀Cu₄O₂: C = 29.90; H = 3.76; N = 21.80. Found: C = 29.40; H = 3.45; N = 22.36. IR data (cm⁻¹): 3609, 3540, 3365, 3300, 3261, 3201, 3075, 2953, 2923, 2852, 2125, 2106, 2080, 1671, 1609, 1483, 1448, 1381, 1319, 1285, 1213, 1185, 1128, 1111, 1092, 1014, 992, 841, 781, 774, 700, 647, 625, 518 and 476.

Using the same stoichiometry, this compound was also obtained in 30 % yield as a microcrystalline powder by mechanochemistry upon grinding a mixture of the two powders during 10 minutes at 25 Hz (54 mg, 0.1 mmol for 1-2TsOH·3H₂O and 31 mg, 0.2 mmol for KCu(CN)₂).

Synthesis of network G ([2-2H⁺][Cu₃(CN)₅]²⁻)

The network **G** was obtained in a crystallization tube (8 mm diameter) at 25 °C upon layering a solution of 2-2HCl (2.6 mg, 0.01 mmol) in distilled H₂O (3 ml) with a solution of KCu(CN)₂ (3.1 mg, 0.02 mmol) in distilled H₂O (3 ml). Orange crystals of formula [C₁₂H₁₆N₄][Cu₃(CN)₅] appeared after one day (78 % yield).

Elemental analysis: calc. (%) for C₁₇H₁₆N₉Cu₃: C = 38.02; H = 3.00; N = 23.47. Found: C = 37.51; H = 3.17; N = 22.60. IR data (cm⁻¹): 3315, 2973, 2107, 2094, 2083, 2059, 1607, 1592, 1555, 1505, 1363, 1283, 1281, 1193, 1037, 987, 950, 912, 843, 685, 614, 461 and 423.

Using the same stoichiometry, this compound was also obtained in 80 % yield as a microcrystalline powder by mechanochemistry upon grinding a mixture of the two powders during 10 minutes at 25 Hz (26 mg, 0.1 mmol for 2-2HCl and 31 mg, 0.2 mmol for KCu(CN)₂).

Structural studies

Single-Crystal Studies.

Data were collected at 173(2) K on a Bruker SMART CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and refined using a riding model.²²

In most, but not all, cases, carbon and nitrogen atoms of the cyano groups were found to be disordered. When required by crystallographic symmetry, occupancies of 50% carbon and 50% nitrogen were used; otherwise relative carbon and nitrogen occupancies were refined. The former and latter cases are indicated in the text as symmetrically and non-symmetrically disordered atoms, respectively. For structural parameters see table 1.

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-Kα radiation with a scanning range between 3.8 and 30° using a scan step size of 2°/mn. For powder patterns, see figures 1-7.

Results and discussion

All six tectons **1-6** were combined with the potassium salt of dicyanocuprate KCu(CN)₂,¹⁸ under the same crystallization conditions (25 °C, in either H₂O or H₂O/MeOH mixture in the case of **B** and **E**). All crystalline materials have been characterized by X-ray diffraction on single crystals (see table 1)²³ and their purity checked by X-ray diffraction on crystalline powders (see figures 1-7).

Since structural characteristics (distances and angles) for the organic tectons **1-6** were close to those previously reported for other combinations,¹⁴⁻¹⁷ they will not be discussed in detail here. As often observed for cyanocuprates, for the bridging cyanide, owing to close electron density, the C and N atoms cannot be easily distinguished by X-ray diffraction. However, by considering that *d*(Cu-C) < *d*(Cu-N), in some cases the nature of the two atoms could be assigned. For fully disordered cases, as

observed for CuCN ,²⁴ they can not be assigned and were labelled X in the crystallographic files.

Table 2: Representation of the observed building block for the formation of networks A-G.

Dication Network	Anionic unit	Coordination node	Metal geometry
<p>A</p>	$[\text{Cu}(\text{CN})_2]^-$		1 Trigonal
<p>B</p>	$[\text{Cu}_2(\text{CN})_3]^-$		2 Trigonal
<p>C</p>	$[\text{Cu}_3(\text{CN})_4]^-$		1 linear + 2 Trigonal
<p>D</p>	$[\text{Cu}_2(\mu_2\text{-CN})_2(\text{CN})_2]^{2-}$		2 Tetrahedral
<p>E</p>	$[\text{Cu}(\text{CN})_2]^-$		1 Tetrahedral
<p>F</p>	$[\text{Cu}_4(\mu_3\text{-CN})_2(\text{CN})_4]^{2-}$		2 Trigonal + 2 Tetrahedral
<p>G</p>	$[\text{Cu}_4(\mu_3\text{-CN})(\text{CN})_3]^{2-}$		1 Trigonal + 2 Tetrahedral

The combination of $\text{KCu}(\text{CN})_2$ with $\mathbf{3}\cdot 2\text{HCl}\cdot 3\text{H}_2\text{O}$ leads to formation of crystals **A** ($[\text{C}_{14}\text{H}_{20}\text{N}_4][\text{Cu}(\text{CN})_2]_2$). Crystals were exclusively composed of Cu^+ cation, CN^- anion and the organic tecton $\mathbf{3}\cdot 2\text{H}^+$ (Table 1). No solvent molecules were found to be present in the crystalline material. The structural study revealed that Cu^+ and CN^- ions form a zig-zag type 1D anionic network along the b axis (Fig. 1 left) with $[\text{Cu}(\text{CN})_2]^-$ units as repeating structural node (Table 2). Within the network, two types of CN^- moieties (terminal and bridging) are encountered. The Cu(I) center adopts a deformed trigonal geometry with C-Cu-N angles varying between $110.82(7)^\circ$ and $133.53(8)^\circ$. The Cu-C distances are equal to $1.9056(19)$ Å and $1.9033(18)$ Å for the bridging and terminal cyanides respectively. The Cu-N distance is equal to $2.0143(17)$ Å. For the CN^- anion, two CN distances of $1.148(2)$ Å

and $1.152(3)$ Å are observed. Within the anionic network, the Cu-Cu distance between consecutive cations is 4.765 Å. It is worth noting that, the 1D network obtained is the same as the one observed for $\text{KCu}(\text{CN})_2$.¹⁸

The bisamidinium cation **3** behaves as a H-bond donor unit and interconnects consecutive anionic 1D networks along the a axis leading thus to the extension of the dimensionality of the architecture from 1D (coordination network) to 2D (Fig. 1 middle). The interconnection occurs through both electrostatic attractive interactions and by H-bonding between the dicationic tecton $\mathbf{3}\cdot 2\text{H}^+$ and two terminal cyanides ($d_{\text{N-N}} = 2.835(3)$ Å), and two bridging cyanides ($d_{\text{N-N}} = 3.105(4)$ Å). Within the 2D arrangement, the shortest Cu-Cu distance, between two consecutive 1D arrays is 8.656 Å. Consecutive planes are packed in staggered fashion along the c axis with the shortest Cu-Cu distance of $5.524(4)$ Å. It is worth noting that under the used conditions, the obtained crystalline phase was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 1 right). Interestingly, the same crystalline phase **A** was obtained by mechanochemistry by grinding a mixture of powders of $\text{KCu}(\text{CN})_2$ and $\mathbf{3}\cdot 2\text{HCl}\cdot 3\text{H}_2\text{O}$.

Figure 1: Portions of the structure of **A** showing the formation of the anionic 1D cyanocuprate network along the b axis (top left), the interconnection of consecutive 1D coordination networks into a 2D arrangement (aOb plane) by the dicationic tecton $\mathbf{3}\cdot 2\text{H}^+$ behaving as H-bond donor (top right) and the comparison between XRPD patterns of the simulated (a), observed using growth in solution (b) and observed using mechanochemistry (c) (bottom). Some of the H atoms are not shown for clarity and H-bonds are presented by dashed lines.

The reaction of $\text{KCu}(\text{CN})_2$ with $\mathbf{5}\cdot 2\text{TsOH}\cdot 2\text{H}_2\text{O}$ leads to the crystalline material **B** ($[\text{C}_{26}\text{H}_{44}\text{N}_4][\text{Cu}_2(\text{CN})_3]_2\cdot 2\text{CH}_3\text{OH}$). The crystal (Table 1) is composed of Cu^+ , CN^- ions, tecton $\mathbf{5}\cdot 2\text{H}^+$ and

MeOH solvent molecules. The same phase was obtained by mechanochemistry by grinding a mixture of powders of 5-2TsOH·2H₂O and KCu(CN)₂. The cyanocuprate network is an anionic 2D honeycomb (6,3) type architecture²⁵ resulting from the interconnection of Cu(I) centres adopting a trigonal coordination geometry by CN⁻ ligands (Fig 2 left). The repeating structural node is a [Cu₂(CN)₃]⁻ anionic unit (Table 2). The 2D honeycomb network is the most encountered architecture for cyanocuprates and has been already observed with a variety of positively charged species such as alkali, BEDT-TTF, diammonium, phosphonium and tetraalkylammonium cations.²⁶

The Cu-X and X-Cu-X (X = C or N) distance and angle are in the 1.899(3) - 1.933(3) Å and 113.19(12)° and 129.45(11)° range respectively. These values are similar to those usually observed for cyanocuprates. A short Cu-Cu distance of 4.959(6) Å is observed within the 2D architecture. Consecutive anionic sheets are packed in a parallel fashion along the *c* axis with a slight translation in the (001) plane. The organic tectons 5-2H⁺ are located within the channels and oriented almost perpendicularly to the 2D planes (Fig. 2 middle). They behave as H-bond donor units and form rather weak hydrogen bonds (shortest X-N distance of 3.170(4) Å) with the anionic networks. Interestingly, 5-2H⁺ dicationic species serve as rivets and interconnect two consecutive anionic layers. Thus, their presence does not alter the dimensionality of the architecture that remains 2D. Within the riveted sheets dimer, the shortest Cu-Cu distance between the two planes is 6.489(6) Å. The riveted sheets dimers are packed in a parallel fashion giving rise to interdigitation through van der Waals contacts (shortest C-C distances of *ca* 4.3 Å) between the pendant propyl chains belonging to the organic tecton 5-2H⁺. The distance between two consecutive parallel dimeric sheets is equal to 9.605 Å. The disordered methanol molecules, located between anionic planes, form H-bonded dimers with O-O distances of 2.205(5) and 2.862(5) Å and do not interact with the other components.

Under the conditions used, the obtained crystalline phase was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 2 right).

Figure 2: Portions of the crystal structure of **B**, showing the anionic (6,3) cyanocuprate honeycomb network (top left), the localization of the dicationic tecton 5-2H⁺ within the channels and their role as rivet connecting two consecutive anionic sheets and the packing of the sheets dimers along the *c* axis together with the disordered MeOH molecules (top right) and the comparison between XRPD patterns of the simulated (a), observed using growth in solution (b) and observed using mechanochemistry (c) (bottom). H atoms are omitted for clarity.

The reaction of KCu(CN)₂ with 4-2HCl·3H₂O leads to the crystalline material **C** ([C₁₄H₂₀N₄O₂][Cu₃(CN)₄]₂). Crystals were exclusively composed of Cu⁺ cation, CN⁻ anion and the organic tecton 4-2H⁺ (Table 1). No solvent molecules were found to be present in the crystalline material. As for **B**, again a 2D architecture is observed for the cyanocuprate part of the assembly. However, here because of the insertion of a Cu(I) centre adopting a linear coordination geometry between two Cu(I) displaying a trigonal environment, the architecture is not of the honeycomb type but an almost planar 2D network offering deformed octagonal channels (Fig. 3 left). The repeating motif is a [Cu₃(CN)₄]⁻ unit displaying three crystallographically independent copper centres (Table 2). The same type of architecture, although rare, has been also previously reported.²⁷ As stated above, among the three Cu centres of [Cu₃(CN)₄]⁻ unit, two adopt a trigonal geometry with X-Cu-X (X = C or N) angles varying between 131.3(7)° and 109.6(6)°. For the third one with a rather rare distorted linear geometry,²⁷ the X-Cu-X angle is 164.1(7)°. The Cu-X distances are 1.813(16) Å and 1.841(18) Å for the Cu atom adopting a linear geometry and between 1.894(18) Å and 1.949(15) Å for the two with trigonal environment. Within the 2D arrangement, the Cu-Cu distance varies between 4.926 Å and 4.988 Å. Consecutive anionic sheets are packed in a parallel fashion along the *a* axis with a slight translation in the (001) plane leading thus to channels (Fig. 3 middle). Whereas the shortest Cu-Cu distance between two consecutive sheets is 2.909(3) Å, the distance between consecutive parallel planes containing the layers is 3.22 Å.

The bisamidinium cations are included within the channels and oriented almost perpendicular to the 2D networks. They form weak H-bonds with the cyanide groups (shortest d_{NH-CN} = 3.173(4) Å). The OH groups do not form H bonds with anionic moieties (d_{O-X} (X = C or N) = 3.649(6) Å), but act as a hydrogen bond acceptor with the NH groups of neighbouring amidinium molecules (d_{O-N} = 2.907(5) Å). Interestingly, again the dicationic organic tecton behaves as a rivet and interconnect consecutive sheets. In contrast with **B** for which the riveting process connects two consecutive sheets, here the process takes place in an alternate fashion thus leading to interconnection of all consecutive 2D arrangements. Consequently, when taking into

account both types of connectivity patterns (coordination- and H-bonds), the overall architecture is a 3D network. As in the case of **A** and **B**, **C** forms a single pure crystalline phase as evidenced by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 3 right). It is worth noting that the same phase was obtained by mechanochemistry upon grinding a powder mixture of **4**-2HCl·3H₂O and KCu(CN)₂.

Figure 3: Portions of the crystal structure of **C**, showing the anionic cyanocuprate network (top left), the localization of the dicationic tecton **5**-2H⁺ within the channels and their role as rivet connecting consecutive anionic sheets along the *c* axis (top right) and the comparison between the simulated (a) and observed (b) powder diffraction patterns showing the purity of the crystalline material (bottom). H atoms are omitted for clarity.

The reaction of KCu(CN)₂ with **6**-2TsOH·2H₂O leads to the crystalline material **D** ([C₈H₁₂N₄][Cu₂(CN)₄]). The latter is exclusively composed of Cu⁺ cation, CN⁻ anion and tecton **6**-2H⁺ (Table 1). The cyanocuprate part of the structure is a 2D network (Fig. 4 left) with [Cu₂(μ₂-CN)₂(CN)₂]²⁻ as the translating building unit (Table 2). This type of 2D arrangement has, to the best of our knowledge, never been described. The latter is composed of a Cu dimer maintained by two CN⁻ anions in the C μ-bridging mode and two CN⁻ moieties insuring the connectivity between consecutive dimers within the 2D assembly. All Cu(I) atoms are of the same type adopting a tetrahedral coordination geometry. The X-Cu-X (X = C or N) angle varies between 95.54(6)° and 119.57(8)° and the Cu-X distance is in the 1.9609(18) - 2.3688(18) Å range. Within the dimeric unit, the short Cu-Cu distance of 2.6153(4) Å implies cuprophilic interactions.^{7,8} The sheet type architecture displays deformed hexagons with two long Cu-X≡X-Cu and two short Cu-Cu distances (Fig. 4 left). The latter distance results from the μ₂-(CN) bridging process. The 2D arrays are perfectly superimposable along the *c* axis leading thus to channels with *ca* 6.3 x 6.2 Å dimension based on Van der Waals radii. The organic dications, in marked contrast with compounds **B** and **C**, are not located within channels but rather lay between anionic layers with a tilt angle of *ca* 45° between the plane formed by its aromatic ring and the anionic sheet (figure 4

middle). The organic tecton is H-bonded to both bridging and terminal cyanide anions. Based on X-N distances, the H-bond with the terminal CN is strong (2.891(5) Å), whereas the one for the bridging anion is rather weak (3.305(6) Å). Under the conditions used, the crystalline phase **D** was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 4 right). The same phase was also obtained by mechanochemistry upon grinding a mixture of powders of **6**-2TsOH·2H₂O and KCu(CN)₂.

Figure 4: Portions of the crystal structure of **D**, showing the anionic cyanocuprate network (top left), the localization of the dicationic tecton **6**-2H⁺ between consecutive anionic sheets along the *c* axis (top right) and the comparison between XRPD patterns of the simulated (a), observed using growth in solution (b) and observed using mechanochemistry (c) (bottom). Some H atoms are omitted for clarity.

The combination of the tecton **1**-2TsOH·3H₂O with KCu(CN)₂ is rather interesting since it leads to two different architectures **E** and **F** depending on the experimental conditions used. Whereas the crystalline material **E** seems to be the kinetic product, the compound **F** is likely the thermodynamic species.

At 25 °C, in a H₂O/MeOH mixture, the reaction of Cu(CN)₂ with **1**-2H⁺ (see experimental part) leads overnight to the crystalline material **E** ([C₁₀H₂₀N₄][Cu(CN)₂]₂) (Table 1). The latter, when isolated, is a perfectly stable crystalline solid which could be characterized by both XRD and PXRD. However, when left in mother liquor, for 2 days compound **E** partially converts into the compound **F**. It is worth noting that in contrast with all other 6 crystalline materials, compound **E** could not be prepared by mechanochemistry.

The cyanocuprate network is a 3D diamond type anionic framework (Fig. 5 left) with the [Cu(CN)₂]⁻ unit as the unique structural node (Table 2). This type of architecture has been previously encountered with ammonium cation or copper(II) cationic complexes.^{24f,28}

Only one type of tetrahedral Cu(I) centre is present in the framework. The Cu-X (X = C or N) distance and X-Cu-X angle vary between 1.9581(17) Å and 2.0764(16) Å and 101.61(6)° and 114.60(7)° respectively. The organic dicationic tectons **1**-2H⁺ are hosted within the diamondoid cavities (*ca* 8.3 Å diameter) and lay on centre of symmetry centre (Fig. 5 middle). The anionic 3D

framework and the organic tectons interact through several weak hydrogen bonds with the shortest amidinium/cyanide N-X distance of 3.148(5) Å (Fig. 5 middle).

Under the used conditions, the isolated crystalline phase **E** was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 5 right).

Figure 5: Portions of the crystal structure of **E**, showing the anionic cyanocuprate 3D diamond type network (top left), the localization of the dicationic tecton **1-2H⁺** within the anionic cavities (top right) and the comparison between the simulated (a) and observed (b) powder diffraction patterns showing the purity of the crystalline material (bottom). Some of the H atoms are omitted for clarity.

In contrast to the aforementioned case, in pure water, the combination of $\text{KCu}(\text{CN})_2$ with **1-2TsOH**·3H₂O leads to the crystalline material **F** ($[\text{C}_{10}\text{H}_{20}\text{N}_4][\text{Cu}_2(\text{CN})_3]_2 \cdot 2\text{H}_2\text{O}$) (Table 1). This compound is stable as isolated solid and in aqueous solution. It was also obtained by mechanochemistry upon grinding a mixture of powders of **1-2TsOH**·3H₂O and $\text{KCu}(\text{CN})_2$.

Compound **F**, composed of Cu^+ , CN^- anion, **1-2H⁺** dication and H₂O solvent molecule, is a 3D deformed cubic network (Fig. 6 left) with the octahedral $[\text{Cu}_4(\mu_3\text{-CN})_2(\text{CN})_4]^{2-}$ moiety as the translating unit (Table 2). The type of cuboid arrangement has been previously described when using protonated dmpa (3-dimethyl-aminopropylamino).²⁹

Two types of geometry (tetrahedral and trigonal) for Cu(I) centres, are observed in the structure. For the one with Td geometry, two CN in end-to-end, and two in end-on bridging modes are present. The Cu-X (X = C or N) distance varies between 1.952(4) Å and 1.966(5) Å for the CN^- units in end-to-end bridging mode and between 2.075(5) Å and 2.128(5) Å for disordered CN^- anion in end-on bridging mode. The angle around the Cu(I) atom varies between 114.66(17)° and 105.34(18)°. The bridging mode leads to the formation of a dimeric Cu(I) unit $[\text{Cu}_2(\text{CN})_6]^{4-}$ with a rather short Cu-Cu distances of 2.4555(11) Å. The other Cu(I) center in trigonal coordination geometry bridges consecutive dimeric units. The Cu-X (X = C or N) distance is in the 1.900(4) - 1.939(4) Å range and the XCuX

angle of 126.3(2)° and 123.50(19)°. The dicationic tectons **1-2H⁺**, included in the channels (7.2 x 6.4 Å, based on Van der Waals radii), interact with the 3D anionic cyanocuprate framework through several weak H-bonds with N-X distance of 3.282(4) Å (Fig. 6 middle). The two water molecules present in the crystal are also located within the channels and form strong H-bonds with NH moieties of the bisamidinium cations ($d_{\text{O-N}} = 2.804(6)$ Å). Under the conditions used, the crystalline phase **F** was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 6 right).

Figure 6: Portions of the crystal structure of **F**, showing the anionic cyanocuprate 3D cuboid type network along the a axis (top left), the localization of the dicationic tecton **1-2H⁺** and water molecules within the anionic cavities (top right) and the comparison between XRPD patterns of the simulated (a), observed using growth in solution (b) and observed using mechanochemistry (c) (bottom). H atoms and H₂O solvent molecules are not presented for clarity.

The combination of $\text{KCu}(\text{CN})_2$ with **2-2HCl** leads to the crystalline material **G** ($[\text{C}_{12}\text{H}_{16}\text{N}_4][\text{Cu}_3(\text{CN})_5]$). The cyanocuprate framework is a 3D diamondoid type architecture (Fig. 7 left) with $[\text{Cu}_3(\mu_3\text{-CN})(\text{CN})_4]^{2-}$ as a severely deformed tetrahedral translating unit (Table 2). The type of diamondoid architecture has been previously described when using protonated me₂pip (2 N,N-dimethylpiperazine).²⁵ The crystal (Table 1) is exclusively composed of Cu(I), CN^- and **2-2H⁺** ions. The anionic portion of the crystal contains one Cu(I) centre in triangular and two in tetrahedral environments. Whereas one of the five CN^- anions present in the translating node behaves as a end-on bridging ligand, the other four adopt the end-to-end connecting mode. For the Cu(I) centre with triangular geometry, the Cu-X (X = C or N) distance ranges between 1.935(2) Å and 1.949(2) Å and the XCuX angle varies between 117.72(10)° and 121.63(10)°. For the tetrahedral Cu(I) atoms, the Cu-X (X = C or N) distance is in the 1.972(2) - 2.252(3) Å range and the X-Cu-X angle varies between 101.99(9)° and 115.39(9)°. In terms of connectivity, one of the two tetrahedral Cu(I) centres is connected by CN^- ligands to two Cu atoms in trigonal geometry and two in tetrahedral environment. The Cu(I) with trigonal geometry is connected

through three cyanide anions to three Cu(I) with Td environment. As the result of the end-on bridging mode of the two CN⁻ anions, coordinated by two C and one N atoms, a dimeric unit is generated with a rather short Cu-Cu distance of 2.5195(6) Å indicating again cuprophilic interactions. The anionic 3D deformed diamondoid architecture displays cavities, which are filled with 2-2H⁺ cations (Fig. 7 middle). The latter interact with the cyanocuprate framework through rather weak H-bonds between the amidinium H-bond donor and CN⁻ acceptor sites (with the shortest X-N distance of *ca* 3.154 Å). Under the used conditions, the crystalline phase **G** was pure as demonstrated by the fit between the observed and simulated powder pattern using the single crystal data (Fig. 7 right). It is worth noting that the same compound was obtained by mechanochemistry upon grinding a mixture of powders of 2-2HCl and KCu(CN)₂.

Figure 7: Portions of the crystal structure of **G**, showing the anionic cyanocuprate 3D diamondoid type network along the *c* axis (top left), the localization of the dicationic tecton 2-2H⁺ within the anionic cavities (top right) and the comparison between XRPD patterns of the simulated (a), observed using growth in solution (b) and observed using mechanochemistry (c) (bottom). Some H atoms are not presented for clarity.

It should be noted that, other related 3D networks based on the particular end-on bridging mode of the cyanide ligand forming [Cu₃(CN)₅]²⁻, [Cu₄(CN)₇]³⁻ or [Cu₂(CN)₃]⁻ units have been already described.³⁰

Conclusions

In conclusion, upon combining KCu(CN)₂ with symmetrical dicationic bisamidinium moieties **1-6** possessing different shapes and geometries, seven (**A-G**) new coordination networks of the cyanocuprate type displaying 1-, 2- and 3-D dimensionalities have been obtained (Fig. 8). These compounds contain Cu⁺ cations, CN⁻ anions, organic cationic tectons and, in some cases, solvent molecules. The formation of networks results from the interconnection of Cu(I) centres by cyanide anions by different bridging modes. For all cases, only two types of building subunit [Cu_x(CN)_{x+1}]⁻ or [Cu_x(CN)_{x+2}]²⁻ (*x* = 1-3) have been observed. Among the seven networks, when considering only Cu-CN type connectivity, one monodimensionnal (**A**), three bidimensionnal (**B**, **C** and **D**) and three tridimensionnal (**E**, **F** and **G**)

architectures have been obtained. For the formation of the above mentioned solid state compounds, the nature of the organic dication appears to play a decisive role (see Fig. 8). For the 1D arrangement **A**, consecutive networks are interconnected by the tecton 3-2H⁺ through charge-assisted H-bonds leading thus to a 2D architecture. In the case of 2D anionic networks **B**, **C** and **D**, whereas for tectons 4-2H⁺ (**B**) and 5-2H⁺ (**C**) the consecutive sheets are riveted through inclusion of the organic moieties within the honeycomb type channels and establishment of H bonds with the anionic cyanocuprate networks, for tecton 6-2H⁺ (**D**), the consecutive sheets are interconnected by H-bonds through intercalation of the organic cations between anionic layers. Whereas for **B**, the riveting process takes place only between two consecutive sheets and thus the overall architecture remains a 2D arrangement for which the consecutive double layers are separated through interdigitation of the propyl chains, for **C**, the riveting occurs in an alternating fashion. Consequently, the dimensionality of the architecture is increased to 3 by taking into account both H- and coordination-bonding processes. The same holds for the intercalated arrangement **D**. Finally, for the 3D cyanocuprate networks (**E**, **F** and **G**), the organic dications, forming H bonds with some of the cyanide moieties, are included within the channels.

Combinations of other bisamidinium type dicationic tectons with [CuCN₂]⁻ anion are currently under investigation.

Figure 8: Summary of all seven cyanocuprate type networks (**A-G**) formed upon combining the organic dicationic tectons X-2H⁺ (*X* = 1-6) with Cu(CN)₂⁻. The yellow cylinders and spheres represent schematically the organic dications and their localization within the structures.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystal data of **A-G** have been deposited at the Cambridge Crystallographic Data Centre (CCDC 924952 - 924958). See DOI: 10.1039/b000000x/

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Table 1 : Crystallographic Parameters for crystals A-G recorded at 173 K.

Formula	A	B	C	D	E	F	G
	C ₉ H ₁₀ CuN ₄	C ₁₇ H ₂₆ Cu ₂ N ₅ O	C ₁₁ H ₁₀ Cu ₃ N ₆ O	C ₁₂ H ₁₂ Cu ₂ N ₈	C ₇ H ₁₀ CuN ₄	C ₁₆ H ₂₄ Cu ₄ N ₁₀ O ₂	C ₁₇ H ₁₆ Cu ₃ N ₉
Molecular weight	237.75	443.51	432.87	395.38	213.73	642.61	537.01
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/c	P-1	P-1	P-1	P2(1)/n	Pbcn	P2(1)/n
a(Å)	12.3350(3)	8.3378(7)	8.5782(15)	6.6681(3)	8.4930(2)	12.1846(4)	10.7515(3)
b(Å)	7.7340(2)	8.4859(7)	9.0487(16)	6.7635(3)	8.3120(3)	14.9832(4)	12.6791(3)
c(Å)	11.4860(3)	16.0299(15)	9.1472(16)	8.9552(4)	11.7280(3)	13.1581(4)	13.7566(4)
α(deg)	90	93.171(3)	96.855(4)	96.837(2)	90	90	90
β(deg)	117.5791(13)	92.107(3)	97.5510(10)	108.930(2)	94.3450(19)	90	93.894(2)
γ(deg)	90	115.690(2)	105.014(4)	99.618(2)	90	90	90
V(Å ³)	971.24(4)	1018.17(15)	678.7(2)	370.11(3)	825.54(4)	2402.20(13)	1870.96(9)
Z	4	2	2	1	4	4	4
Colour	colourless	colourless	colourless	colourless	colourless	colourless	orange
Crystal dim (mm)	0.15 x 0.14 x 0.11	0.16 x 0.14 x 0.10	0.04 x 0.04 x 0.02	0.10 x 0.07 x 0.06	0.08 x 0.06 x 0.05	0.12 x 0.08 x 0.06	0.12 x 0.08 x 0.06
D _m (gcm ⁻³)	1.626	1.447	2.118	1.774	1.720	1.777	1.906
F(000)	484	458	426	198	436	1288	1072
μ (mm ⁻¹)	2.211	2.102	4.663	2.881	2.590	3.527	3.404
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Number of data meas.	3092	11641	4934	2561	4342	27778	19934
Number of data with I > 2σ _{int}	2508 [R(int) = 0.0201]	4633 [R(int) = 0.0296]	3413 [R(int) = 0.0388]	1573 [R(int) = 0.0152]	2621 [R(int) = 0.0190]	2769 [R(int) = 0.0418]	4513 [R(int) = 0.0356]
R	R1 = 0.0330, wR2 = 0.0843	R1 = 0.0400, wR2 = 0.0978	R1 = 0.1009, wR2 = 0.2637	R1 = 0.0210, wR2 = 0.0601	R1 = 0.0322, wR2 = 0.0771	R1 = 0.0423, wR2 = 0.1163	R1 = 0.0298, wR2 = 0.0721
R _w	R1 = 0.0454, wR2 = 0.0898	R1 = 0.0579, wR2 = 0.1045	R1 = 0.1613, wR2 = 0.2909	R1 = 0.0219, wR2 = 0.0605	R1 = 0.0452, wR2 = 0.0836	R1 = 0.0522, wR2 = 0.1257	R1 = 0.0430, wR2 = 0.0767
GOF	1.042	1.034	1.244	1.074	1.029	1.030	1.037
Largest peak in final difference (eÅ ⁻³)	0.347 and -0.454	0.779 and -0.585	1.386 and -1.937	0.455 and -0.324	0.432 and -0.993	1.252 and -0.936	0.907 and -0.857

Graphical Abstract

Upon combining $\text{KCu}(\text{CN})_2$ with symmetrical dicationic bisamidinium, seven new coordination networks of the cyanocuprate type displaying 1-, 2- and 3-D dimensionalities have been obtained. In these architectures, the cyanocuprate species and the bisamidinium organic tectons behave as H-bond acceptors and donors respectively. The connectivity between cyanide anions and Cu(I) cations leading to different anionic extended cyanocuprate coordination assemblies is strongly influenced by the nature of the organic tectons.