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Solid state coordination chemistry of the copper cyanide–organoamine system: hydrothermal synthesis and structural characterization of $[\{Cu_2(bpy)_2(CN)\}_2Cu_5(CN)_7]\cdot0.17H_2O$

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The hydrothermal reaction of CuCN, KCN, 2,2′-bipyridyl (bpy) and water yields $[\{Cu_2(bpy)_2(CN)\}_2Cu_5(CN)_7]\cdot0.17H_2O$ 1, a two-dimensional copper–cyano network intercalated by $[(bpy)_2(Cu)_2(CN)]^+$ cations and water of crystallization.

The diversity of properties associated with solid state inorganic materials, which gives rise to applications ranging from heavy construction to integrated optical systems,[1] provides a context for the significant contemporary interest in design and synthesis of new structural types. Such materials may exhibit significant architectural complexity and potentially functionality, as a consequence of the incorporation of the inorganic constituent into a hierarchical structure,[2,3] evolving from the synergistic interaction between the organic and inorganic substructures. Manipulation of the organic–inorganic interface in the hydrothermal domain provides a powerful synthetic approach for the manipulation of solid phase microstructures, a strategy which has proved fruitful in the preparation of four families of oxide based phases for which organic materials provide structurally important components: zeolites,[4] mesoporous oxides of the MCM-41 type,[5] microporous octahedral–tetrahedral framework transition metal phosphates[6] and organically templated molybdenum oxides.[7] Biomineralized materials represent the fifth class of organically templated oxide phases.[8]

We have recently extended this concept of templating anionic networks with organic constituents to the copper halide system, represented by $[\{Cu(en)_2\}_2Cu_7Cl_{11}]$,[9] and the copper–cyano system, exemplified by $[\{Cu_2(bpy)_2(CN)\}Cu_5(CN)_6]$ **2**, which was synthesized during preliminary investigations of the hydrothermal reactions of the copper–cyano–organoamine system.[10] Minor variations in synthetic conditions, such as the addition of KCN, resulted in the synthesis of a new phase, $[\{Cu_2(bpy)_2(CN)\}_2Cu_5(CN)_7]\cdot0.17H_2O$ **1**, as well as other copper–cyano–organoamine phases to be reported elsewhere.

Compound **1**† was prepared as clear dark red crystals in *ca.* 40% yield from the reaction of CuCN, KCN, bpy and water in the mole ratio 1 : 0.23 : 0.22 : 63 at 180 °C and autogenous pressure for 72 h. Orange and yellow solid phases were also observed as reaction products.

As shown in Fig. 1a, the structure of **1**‡ exhibits anionic two-dimensional nets of alternating fused rows of pseudo-hexagonal $\{Cu_6(CN)_6\}$ rings and six-sided $\{Cu_8(CN)_8\}$ rings. The 18-membered $\{Cu_6(CN)_6\}$ rings, which extend *ca.* 10.1 Å from vertex to opposing vertex, contain exclusively distorted trigonal planar copper atoms at the vertices linked by disordered cyano groups. The 24-membered $\{Cu_8(CN)_8\}$ rings contain disordered cyano groups, linking distorted trigonal planar copper atoms, as well as two linear two-coordinate copper atoms disposed on either elongated edge of the heterocycle. The $\{Cu_8(CN)_8\}$ rings have dimensions of *ca.* 8.8 × 15 Å. The individual rings of both types are puckered which results in the slight folding of an entire layer, illustrated in Fig. 1b. The distortion of the anionic network rings of compound **1** is not as pronounced as was previously observed for compound **2**, as shown in Fig. 2. The layers of compound **1** form two distinct interlamellar regions with spacings of 6.5 Å (region A) and 7.0 Å (region B), respectively. The interlamellar regions of compound **1** contain not only the intercalated cations in two different conformations per layer (Fig. 3) but region A contains the water of crystallization as well, giving rise to an ABBABB repeat pattern shown in Fig. 4a.

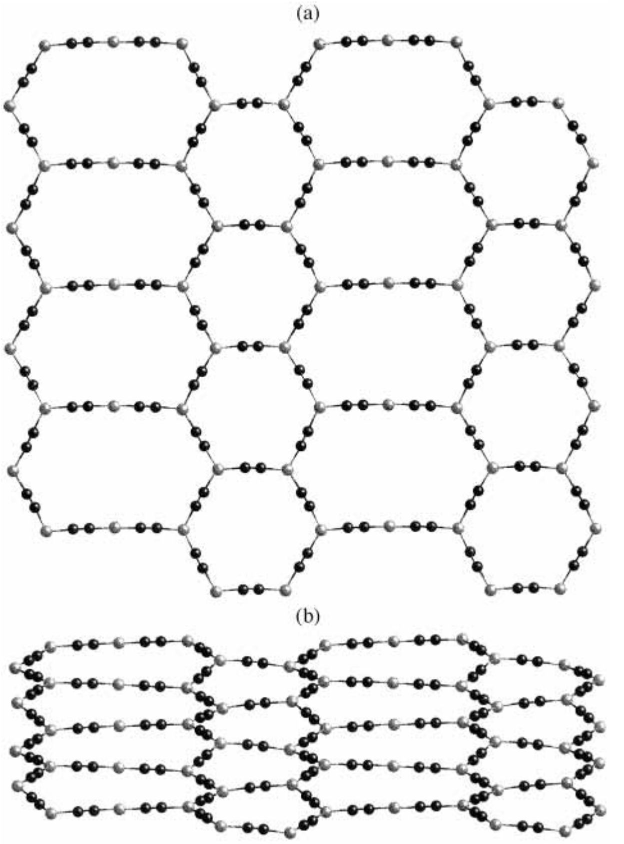

Fig. 1 (a) A view down the crystallographic *a*-axis of **1** perpendicular to a single anionic layer showing the 18- and 24-member rings; (b) an oblique view to the anionic layer showing the distortion of the rings and layer. Black spheres represent cyano groups and gray spheres represent Cu atoms.

Two sets of cations are disposed such that those of different regions but similar conformation form columnar arrays (Type I) within each region. Each bpy unit of a cation overlaps a bpy group of an adjacent cation in the same columnar array, as illustrated in Fig. 4b. The columns propagate parallel to the crystallographic *c*-axis. The cations of the second conformation form arrays (Type II) exhibiting overlap of single pyridyl rings of bpy groups of adjacent cations arranged in a zig-zag array propagating parallel to the cationic arrays of Type I within the interlamellar regions (Fig. 4b). At no point do the cations of either type interpenetrate the rings of the anionic layers.

The cations composing the Type I arrays are similar in conformation to the cations previously observed for compound **2**. Cations of this conformation in compound **1** are observed to

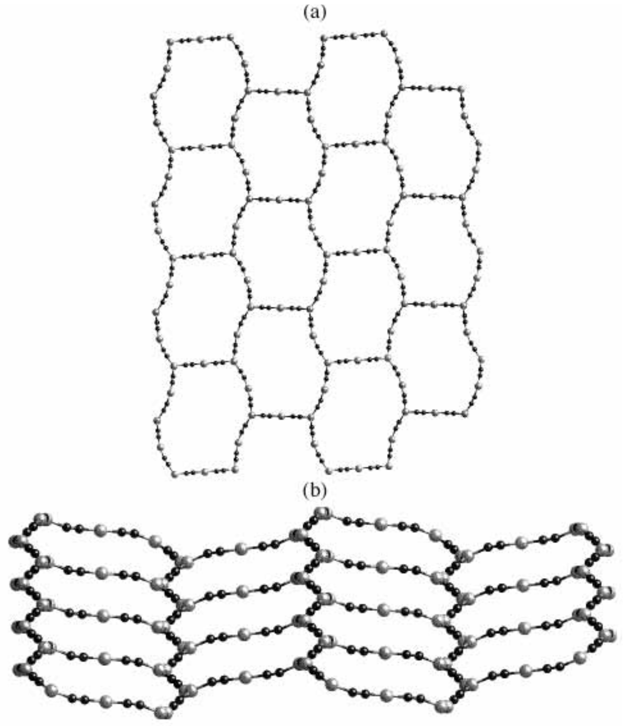

Fig. 2 (a) A view perpendicular to the anionic layer of **2**; (b) a view oblique to the anionic layer showing the extreme distortion from planarity of the rings and the resulting "ruffling" of the layer. Black spheres represent cyano groups and gray spheres represent Cu atoms.

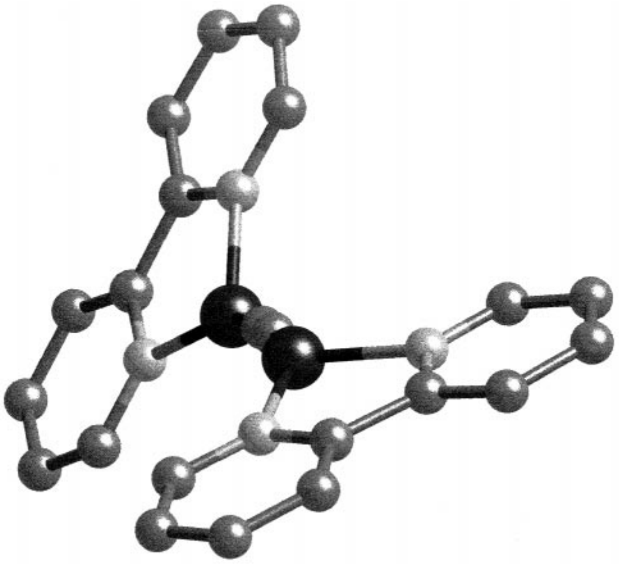

Fig. 3 A view of a cation of Type II approximately parallel to the {Cu–CN–Cu} axis. The deviation of the bpy units from the parallel conformation described for compound **2** by *ca.* 45° is apparent (Cu atoms and C atoms of the bpy and the CN groups are represented by black and dark gray spheres respectively; N atoms of the bpy units are represented by light gray spheres).

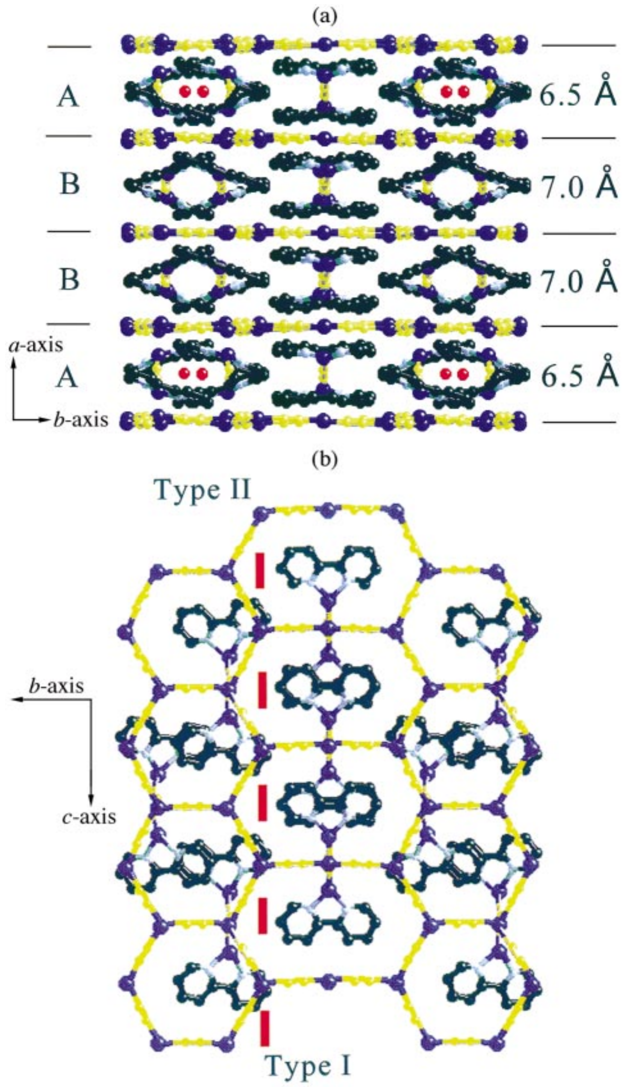

Fig. 4 (a) A view perpendicular to the crystallographic *ab*-plane showing the layers with (region A) and without water of crystallization (region B); (b) a view perpendicular to the crystallographic *bc*-plane showing the disposition of adjacent cations, their disposition relative to the rings of the anionic layer and the cationic arrays of Type I and Type II which are separated by red bars (Cu atoms, cyano groups, C atoms of the bpy, N atoms of the bpy and waters of crystallization are represented by purple, yellow, black, light blue and red spheres respectively).

have bpy units centered above and below the planes of the $\{Cu_8(CN)_8\}$ rings of the anionic networks. The bpy components of the cations are separated from the anionic layers by distances greater than sum of the van der Waals radii. In contrast, the planes of the rings of the cations composing the zigzag arrays are no longer parallel to the anionic network so as to avoid repulsive interactions of the anionic and cationic substructures by maintaining van der Waals contact distances of *ca.* 3.5 Å.[11] The Type II cations are subsequently significantly distorted, Fig. 4, from the conformation of the Type I cations.

The structure of compound **1** demonstrates the power of hydrothermal synthesis in the preparation of organic–inorganic composite materials. Not only are differential solubility problems avoided, reducing the tendency to phase segregate, but structurally more complex metastable phases are favored.[12] Compounds **1** and **2** also illustrate the rich diversity of structures that can be achieved with only minor variations of reaction conditions. In general, the structural complexity reflects the versatility of the organonitrogen component which may function as counter ion, ligand to the copper cyanide backbone or ligand in a coordination complex ion.[10] The role of the organic ligand as a component of a coordination complex cation, a recurring theme in metal oxide–organoamine chemistry, has now been extended to the metal halide[13] and metal pseudohalide phases,[10,14] where it is manifested in the large ring sizes of the copper cyanide networks which are required to accommodate the large binuclear cations in compound **2**. In addition, compound **1** demonstrates that such cations are non-rigid and capable of displaying a variety of conformations. These cations not only serve a charge compensating role but also participate in a synergistic fashion with the $[Cu_5(CN)_7]^{2-}$ framework in generating an inorganic microstructure based on both the $\{Cu_6(CN)_6\}$ rings and the larger $\{Cu_8(CN)_8\}$ rings. This observation suggests that cation dimensions in such structures are not determined by ring size, topology or interlamellar spacing of the anionic substructure, but rather function as agents for the kinetically controlled formation of a variety of structures.

Acknowledgements

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Notes and references

† IR spectra (cm^{-1}): 3436, (br, O–H stretch), 3122, 3091, 3055, 2778, 2688, 2612, 2545, 2473, 2428, 2119, (s, C–N stretch); 1725; 1596; 1501; 1282; 1143. TGA studies under an oxygen atmosphere show loss of the water of crystallization at *ca.* 165 °C and the successive loss of the organic components between 170 °C and 390 °C. Satisfactory C, H, N analyses were obtained.

‡ Crystal data for **1**: $C_{73.5}H_{48.5}Cu_{13.5}N_{25.5}O_{0.25}$, monoclinic, $P2/c$, $a = 21.6927(1)$, $b = 19.7886(2)$, $c = 17.5075(2)$ Å, $\beta = 98.12(1)°$, $V = 7440.07(1)$ Å^3, $Z = 4$, $M = 2150.67$, $D_c = 1.920$ Mg m^{-3}; $R_1 = 0.0458$; $wR2 = 0.1273$ (13015 reflections), $T = 150$ K, $\mu = 3.834$ mm^{-1}. CCDC reference number 186/1221.

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