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Robert D. Pike
William & Mary, rdpike@wm.edu

Kathryn E. deKrafft

Amanda N. Ley

Tristan A. Tronic

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Threaded structure and blue luminescence of $(CuCN)_{20}(Piperazine)_7$†

Robert D. Pike,*[a] Kathryn E. deKrafft,[a] Amanda N. Ley,[a] and Tristan A. Tronic[a]

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The structurally unique and highly luminescent 20:7 complex of CuCN with piperazine (Pip) was formed under aqueous conditions; its structure reveals two interpenetrated 2D sub-networks in 6:1 ratio: $(CuCN)_2$(Pip) and $(CuCN)_8$(Pip), the latter consisting of $Cu_{18}(CN)_{16}(Pip)_2$ macrocycles.

Copper(I) cyanide is recognized as forming a diverse array of metal-organic networks with bidentate bridging ligands (L).[1–9] Known $(CuCN)_n$L stoichiometries cover half-integer values, n = 1, 1.5, 2, 2.5, 3, 3.5, and 4. Metal-metal bonding (sometimes supported by cyano-bridging) is fairly common in these materials. The more copper-rich phases often show evidence of partially or fully independent CuCN chains within their structures. As part of an extensive study of luminescent metal-organic networks based on CuCN,[9] we herein report the formation of a copper-rich network having the unprecidented non-half-integer stoichiometry $(CuCN)_{20}(Pip)_7$ (Pip = piperazine, **1)** and showing intense visible luminescence.

Refluxing an aqueous suspension consisting of 4:2:1 CuCN:KCN:Pip produced a uniform cream powder which analyzed as $(CuCN)_{20}(Pip)_7$.‡ Hydrothermal (HT) synthesis using a 3:1:1 mixture (175 °C, 5 d) produced colorless prisms of **1** suitable for X-ray diffraction. Powder patterns of the reflux and HT products were found to be identical, excepting for the presence of some metallic copper in the HT sample. An X-ray structure of **1** was solved using an HT crystal and the calculated powder diffraction pattern was found to match the powder diffraction from the refluxed sample.§ The structure of **1** (see Figs. 1 and 2) contains twenty independent Cu atoms and twenty cyano groups, all of which are C/N site disordered. Since it is composed of two independent, interpenetrating sub-lattices in 6:1 ratio, **1** may be formulated as $6[(CuCN)_2(Pip)]•[(CuCN)_8(Pip)]$. Sub-lattice A is a simple 6^3 planar network of stoichiometry $(CuCN)_2$(Pip) which results from Pip-crosslinking of parallel $(CuCN)_\infty$ chains. All twelve Cu atoms in lattice A are three-coordinate, nevertheless the cyano–Cu–cyano angles are all >134°. The A sheets, which run parallel to the crystallographic a,b plane, are composed of tiled hexagonal $Cu_6(CN)_4(Pip)_2$ units. Sub-lattice B also consists of Pip-crosslinked $(CuCN)_\infty$ chains. However, the Pip units crosslink only two of every eight copper centers. The remaining metal atoms are two-coordinate. This arrangement produces a very large, rippled 2D network consisting of $Cu_{18}(CN)_{16}(Pip)_2$ rings. The CuCN chains in the B lattice are nearly linear along the six Pip-free units (a distance of about 24.4 Å), but they buckle at the crosslinks forming roughly 90° kinks in the B lattice sheets. Morevover, these kinked regions of the chains form helices.

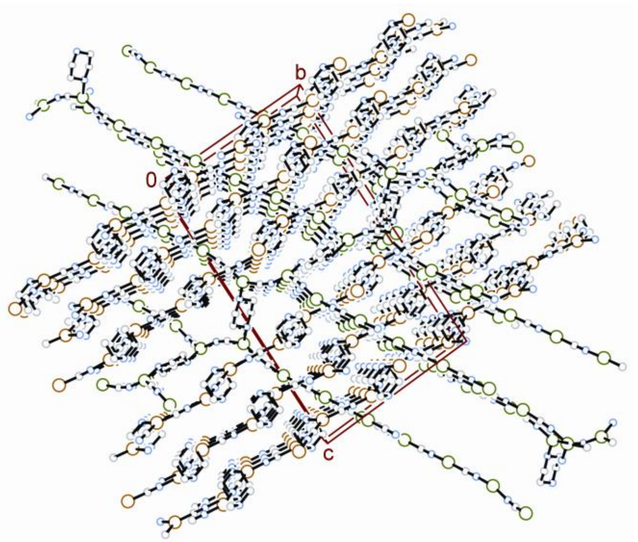

Fig. 1 Packing diagram of **1** showing interpenetrating sub-lattices. Cu atoms large circles, orange = sublattice A atoms and green = sublattice B atoms, N and C atoms small blue and grey circles, H atoms omitted for clarity. Distances for Cu–X (X = disordered C/N) = 1.843(5)–1.900(4) Å, distances for Cu–N(Pip) = 2.049(7)–2.144(4), distances for X≡X = 1.128(8)–1.168(6) Å, angles Cu–X≡X = 160.9(6)–178.8(4)°, and angles for X–Cu–X = 134.5(3)–143.6(2)° for 3-coordinate Cu atoms and 165.2(3)–179.76(19)° for 2-coordinate Cu atoms.

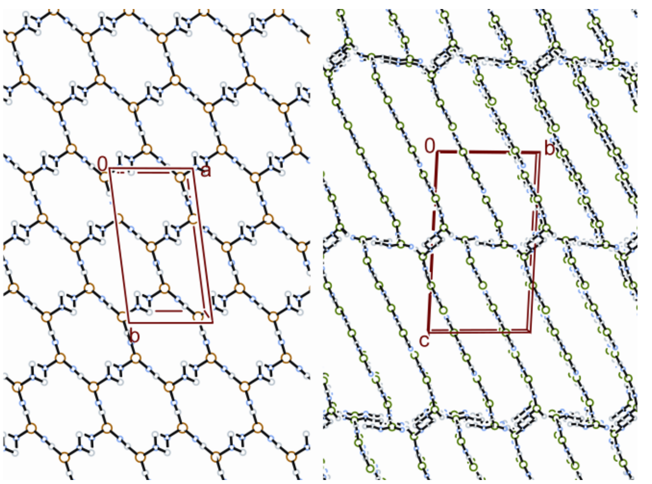

Fig. 2 Isolated views of **1** sub-lattices. Left: Sub-lattice A, right sub-lattice B. Cu atoms large orange and green circles, N and C atoms small blue and grey circles, H atoms omitted for clarity.

[a] *Department of Chemistry, College of William and Mary, Williamsburg, VA, USA. Fax: 757-221-2715; Tel: 757-221-2555; E-mail: rdpike@wm.edu*

† Electronic supplementary information (ESI) available: X-ray powder diffraction patterns for **1** (reflux and HT) and a thermal ellipsoid drawing showing Cu···Cu interactions. See DOI: XX.XXXX/XXXXXXX.

Sub-lattice B contains two crystallographically independent half Pip ligands. The lattice B Pip ligands lie roughly in line with the more numerous Pip ligands in lattice A. However, the B lattice Pip "chairs" are rotated by about 90° with respect to the A chairs and are tilted at a different angle as well. The thermal factors of the B Pip atoms are somewhat larger than those of the other Pip ligands, apparently due to the fact that the B Pip inhabits a fairly open region in the lattice. The large unit cell results from the long repeat unit of the B net. There are a total of ten Cu···Cu interactions that are close to the 2.8 Å van der Waals distance (Cu···Cu = 2.8156(10)–3.0378(11)). All of these weak interactions are between the two sub-networks and are unsupported by any ligand bridging.

Although there is no precident for the observed stoichiometry of **1**, analogies may be drawn to known species. Networks consisting of $(CuCN)_2L$ are known for many L, including Pip and N,N´-dimethylpiperazine (DMP).[2] While the 2:1 DMP complex forms hexagonal 6^3 sheets analogous to those of network A, in the 2:1 Pip complex, these sheets are crosslinked by μ_4-bridging cyano groups, producing a 3D network. Threading of $(CuCN)_\infty$ chains through 6^3 networks has previously been observed for $(CuCN)_3(Pyz)$ and $(CuCN)_n(Bpy)$ (Pyz = pyrazine, Bpy = 4,4′-bipyridine, n = 3.5, 4).[3–5] These interpenetrated materials may be formulated as $[(CuCN)_2(Pyz)]$•CuCN, $2[(CuCN)_2(Bpy)]$•3CuCN, and $[(CuCN)_2(Bpy)]$•2CuCN. Like **1** these compounds all contain 6^3 $(CuCN)_2L$ sheets. However, in contrast to **1**, the threaded $(CuCN)_\infty$ chains in these structures consist solely of two-coordinate Cu centers and lack L. Ours is the first example of two non-identical, intepenetrated CuCN-L lattices within a single network structure.

The common low temperature modification[10] of CuCN shows significant photoluminescence in the solid state at room temperature. As shown in Fig. 3, its excitation spectrum is fairly

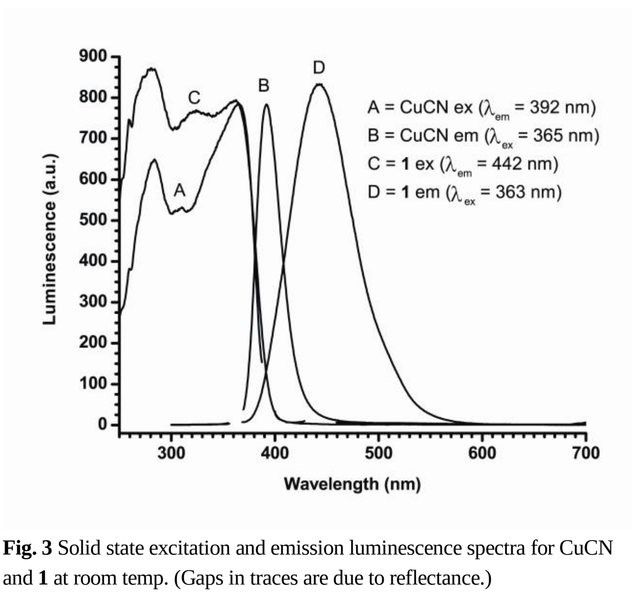

Fig. 3 Solid state excitation and emission luminescence spectra for CuCN and **1** at room temp. (Gaps in traces are due to reflectance.)

complex, showing maxima at 284, 311, and 365 nm. Its single emission band is centered at 392 nm, resulting in weak violet-colored visible luminescence since much of the output is in the near UV region. As revealed in Fig. 3, the luminescence intensity of **1** is roughly equal to that of CuCN itself. Moreover, it is apparent that the excitation spectrum of **1** (λ_{max} = 280, 324, 363 nm) is nearly identical to that of CuCN. This fact suggests very similar excitation mechanisms. However, the room temperature emission of **1** is both broader and red-shifted compared to that of CuCN. The λ_{max} = 442 nm for **1** places it completely in the visible range, leading to intense blue emission. This 50 nm increase in the Stokes shift from CuCN to **1** is likely associated with the increased vibrational modes that are imparted to the CuCN lattice through incorporation of the Pip crosslinks. The peak width at half-height values for CuCN and **1** are 28 and 71 nm, respectively. Emisson peak broadening in **1** probably reflects the more heterogeneous array of chemical environments found for the twenty unique Cu centers in **1**, versus those of the five independent Cu atoms in structure of low temperature CuCN.

Although many studies of copper(I) halide complexes have revealed luminescence behaviour in the solid state or in solution,[11–13] relatively few such examples of luminescence in CuCN complexes have been reported.[14–16] Many excitation mechanisms have been put forward to explain the observed luminescence of Cu(I) complexes. These include metal to ligand charge transfer (MLCT), halide to ligand charge transfer (XLCT), metal cluster centered transitions (CC), single metal centered transitions (MC) and ligand centered transitions (LC). In the cases of CuCN and **1** XLCT, CC, and LC transitions may be ruled out since metal-metal bonding is negligible and cyanide has a fairly large band gap. The 3d → π^*_{CN} MLCT in anionic complexes such as $[Cu(CN)_2]^-$ has been assigned to bands <250 nm,[17] and therefore is probably not important in the observed luminescence either. Further study is clearly needed, but it seems most reasonable and consistent with literature precedent to invoke MC transitions of the type 3d → (4p, 4s) as being responsible for the observed luminescence behaviour in **1**.

In conclusion, we have identified the first example of a CuCN-L network compound that contains two interpenetrating $(CuCN)_nL$ sub-lattices of differing stoichiometries (n = 2, 8). The product shows photoluminescence in the solid state at room temperature that is highly similar to that of CuCN itself, but with emission red-shifted by 50 nm, producing intense blue luminescence. Work is ongoing in our lab on this and related CuCN-based luminescent network materials.

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Notes and references

‡ Synthesis of **1**: Copper(I) cyanide (1.79 g, 20.0 mmol) and KCN (0.651 g, 10.0 mmol) were suspended in 50 mL H_2O and warmed. Pip was added (0.431 g, 5.0 mmol) and the resulting suspension was refluxed under N_2 overnight. Filtration afforded a suspended cream solid. (1.46 g, 0.608 mmol, 85.1%). IR (KBr pellet, cm^{-1}) 3243 (m), 2985 (w), 2907 (w), 2881 (m), 2855 (m), 2124 (s), 1447 (m), 1312 (s), 1275 (w), 1115 (m), 1098 (s), 989 (w), 868 (s), 625 (w). Anal. Calcd for $C_{48}H_{70}Cu_{20}N_{34}$: C, 24.80; H, 2.95, N 19.89. Found: C, 24.27; H, 2.97; N, 20.05. TGA Calcd for CuCN: 74.8. Found: 74.7. (175–245 ºC). HT crystal synthesis: CuCN (3.0 mmol), KCN (1.0 mmol), and Pip (1.0 mmol) were suspended in 5.0 mL H_2O in a 23 mL Teflon-lined Parr acid digestion vessel. After brief stirring, the vessel was sealed and heated at 175 ºC for 5 days. Filtration afforded colorless crystals, along with brown powder.

§ Crystal data for **1**: $C_{48}H_{70}Cu_{20}N_{34}$, *M* = 2394.18, triclinic, space group P–1 (no. 2), *a* = 8.4553(2), *b* = 15.7200(3), *c* = 27.6308(6) Å, α = 91.9900(10), β = 93.9660(10), γ = 97.2830(10)º, *U* = 3630.75(14), Z = 2, D_c = 2.190 g/cm^{-3}, *F*(000) = 2352, μ(Cu-K_α) = 6.591 mm^{-1}, λ = 1.54178 Å, T = 296(2) K. 63170 reflections measured, 13489 unique data (2θmax = 134.0º, Rint = 0.0399, numerical absorption correction). w*R*2 = 0.1398 for all data, conventional *R* = 0.0485 on reflections having $I > 2\sigma(I)$. CCDC 647769. For crystallographic data in CIF or other electronic format, see DOI: XX.XXXX/XXXXXXX Programs: Bruker SMART Apex II and SAINT+ control and integration software,[18] Bruker SHELXTL and WinGX for structure refinement and graphics.[19]

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