

Terpyridine copper^{II}–polycarboxylic acid architectures: formation of dimeric, helical, and cyclic nanostructures and their included-water molecule motifs

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New crystalline architectures have been prepared employing the propensity of terpyridine–Cu^{II} adducts to form coordination complexes with carboxylate moieties.

Crystal growth, design, and supramolecular self-assembly¹ of organic–inorganic hybrids² have repeatedly attracted considerable attention. The art of creating different superstructures by assembling similar components has met with great success,³ especially concerning nitrogen- and oxygen-containing ligands capable of metal coordination.⁴ The rational control of molecular geometry has yielded promising results for assembling new and robust, higher-order, molecular architectures.⁵

The pseudo-octahedral coordination⁶ of Ru-, Os-, and Fe-based bis(2,2':6',2''-terpyridine) complexes has been widely investigated because of their thermal and chemical stabilities as well as electron transfer properties; however to the best of our knowledge, no reports describe terpyridine–metal adducts singularly complexed to polyligating species. Terpyridine coordinated to transition metals in the 2⁺ oxidation state (*i.e.* Cu^{II}, Co^{II}, Ni^{II}, Mn^{II}, *etc.*) commonly binds carboxylate ions in a penta-coordinate fashion⁷ involving three metal–N bonds and two *cis*-oriented sites^{2a,2b} (angle: ~ 90°). We herein report the self-assembly of a 2,2':6',2''-terpyridine–Cu^{II} adduct [Cu(tpy)] with an aromatic carboxylate (Fig. 1) and the important role that included water molecules play in crystallization.

Four different structures were prepared (60–80%) using different methods. Dimer **1** (Fig. 2) was obtained by mixing terpyridine, Cu(BF₄)₂, and 1,4,5,8-naphthalene-tetracarboxylic acid (H₄NTC)

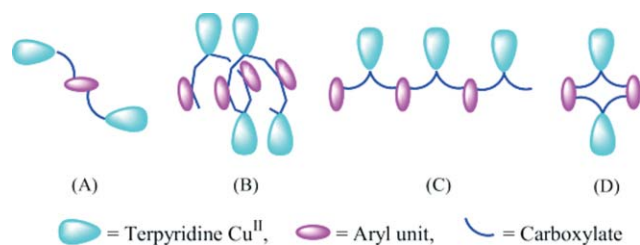


Fig. 1 Four different structures of Cu(tpy) associated with carboxylates: (A) Dimer; (B) Helix; (C) Linear; and (D) Macrocylic.

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or its dianhydride (NTCA) under aqueous basic conditions. X-ray diffraction analysis (–100 °C) revealed that the 1 and 5 carboxylates of the H₄NTC were coordinated to two Cu(tpy) moieties while the 4 and 8 carboxylic acid groups were uncomplexed and deprotonated thus affording an overall neutral complex. A single water molecule occupies the fifth coordinating site. De Munno, Lloret and co-workers⁸ previously reported a similar association of Cu(tpy) with benzenedicarboxylic acid, but unlike dimer **1**, the described molecule was cationic owing to fewer carboxylate moieties. In our case, the Cu–Cu, Cu–OOC and Cu–OH₂ distances were found to be 10.931, 1.907 and 2.229 Å, respectively, and the O–Cu–O angle (102.83°) for each coordinating center was found to be identical; however, the O_{water}–Cu–N and O_{COO}–Cu–N (for the N of the central pyridines) angles were quite different (95.32° and 160.68°, respectively). The plane of the naphthalene moiety was found to be perpendicular to the plane of terpyridines.

We recently reported the formation of a neutral achiral helical chain⁹ with a 1 : 1 ratio of left and right twists (**2** in Fig. 3) by using 1,3,5-benzenetricarboxylic acid as the terpyridine adduct connector. Compared to **1**, the O–Cu–O angles of **2** were found to be 90.85° and 85.15°, respectively, while the O₁–Cu–N and O₃–Cu–N (for the N of the central pyridine) angles were 109.75° and 159.31°, respectively. It is well known that water molecule *H*-bonding can play an important role in intermolecular interactions of organic, inorganic, and biological systems.¹⁰ X-ray analysis of crystals of **2** revealed hydrophilic, helical channels encapsulating three water molecules (O–O distances: 2.902 Å on average) per asymmetric unit that facilitate the formation of a 2D network.

The neutral, linear structure (**3** in Fig. 4) was prepared by heating 3,5-pyridinedicarboxylic acid and Cu(tpy) to 100 °C for 12 h. The pale green hexagonal crystals collected after standing for two days at 25 °C revealed a 1D framework with Cu(tpy) moieties bridging the carboxylates. Interestingly, the nitrogen in 3,5-pyridinedicarboxylic acid remained uncomplexed affording an

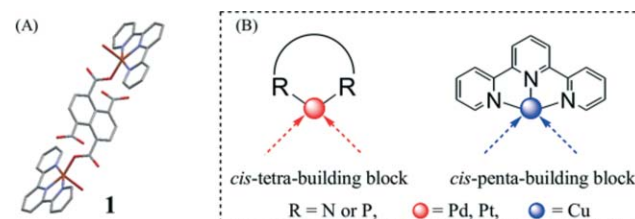


Fig. 2 A: Crystal structure of dimer **1**. B: Structural drawing of two building blocks.

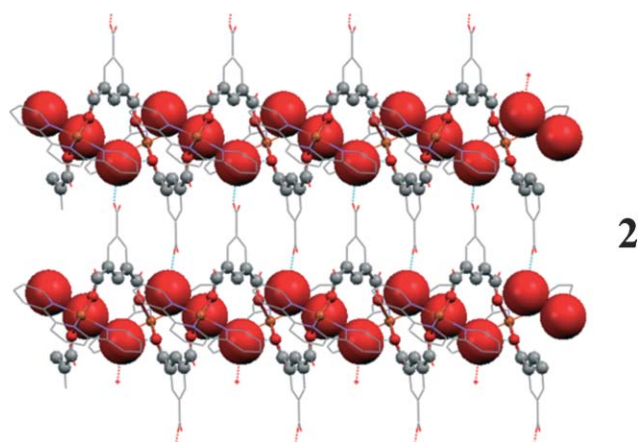


Fig. 3 Helical crystal structure of **2**: Water molecule oxygen packing in the helical channels (large red spheres).

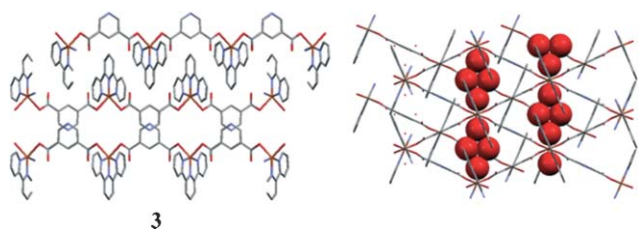


Fig. 4 Crystal structure of **3**: Left: side view; Right: top view showing the rhombohedral water molecule packing (represented by the spherical red oxygens) in the cavities.

additional complexation site. The Cu–Cu distance was found to be 10.174 Å. The Cu(tpy) planes were shown to be parallel with one another and perpendicular to the pyridine planes. The O–Cu–O angle was found to be 89.39°, but the O₁–Cu–N and O₃–Cu–N angles were the same (135.31°, referring to the central pyridine N) in contrast to the O₁–Cu–N and O₃–Cu–N angles of **1** and **2**, which were unequal. The π – π interactions between the planar terpyridine (face-to-face separation of \sim 3.457 Å) presumably facilitated the stacking of the linear chains (Fig. 4, left side). *H*-bonding between the rhombohedral, 4 H₂O clusters, and the carboxylates further assists in network construction. No *H*-bonding was observed between adjacent clusters (Fig. 4, right side). The O–O distances (resulting from the packing of the water molecules) were found to be the same (2.790 Å), and the rhombohedral angles in the tetrakis cluster were 57.97° and 122.03°.

The cyclo-dimer **4** was prepared by stirring 3,5-pyridinedicarboxylic acid and Cu(tpy) in water at 25 °C until a translucent green solution was obtained (A, Fig. 5). X-ray diffraction analysis of the green cubic crystals revealed a neutral macrocycle. The nitrogens on the two pyridine diacids remained uncomplexed and the Cu(tpy) planes were perpendicular to the ring formed by the complexation of the 3,5-pyridinedicarboxylic acid. From the side view, the asymmetric nature of the ring became evident (B, Fig. 5). The Cu–Cu distance was found to be 7.916 Å and the O–Cu–O angle was 87.80°. The two O–Cu–N angles (referring to the central ring) were 104.86° and 167.34°, respectively. A helical water molecule chain¹¹ (Fig. 5, C) was observed in the channel formed as a result of π – π stacking between the terpyridine planes. Ring

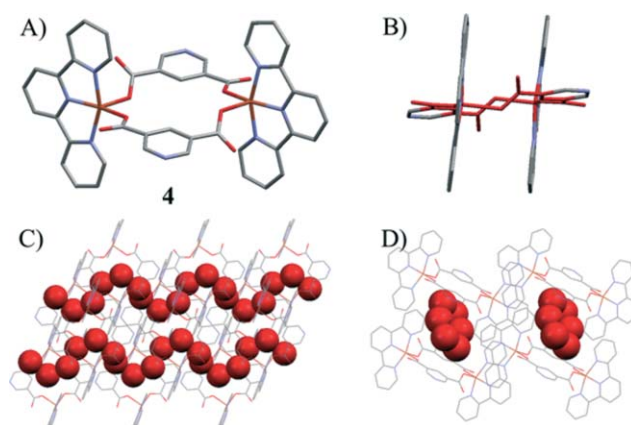


Fig. 5 Crystal structure of macrocycle **4**: A) one asymmetric unit, B) side view of asymmetric ring, C) side view of helical water chain, D) top view of water molecules occupying the channels (water molecules are simplified in C and D by depiction with red, space-filling oxygen atoms).

asymmetry presumably contributes to the water chain's helical shape due to the zig-zag manner of *H*-bonding interactions between water and the carboxylates. Notably, the adjacent O–O distances of 2.735–2.810 Å (2.78 Å on average) compare well with that of I_h- and I_c-type ice (2.74 Å; where, I_h and I_c denote hexagonal and cubic ice, respectively),¹² which suggests strong *H*-bonding within the water chain.

In conclusion, four different structures derived from the self-assembly of Cu(tpy) and aromatic carboxylic acids (naphthalene-tetracarboxylic acid, benzenetricarboxylic acid,⁹ and 3,5-pyridinedicarboxylic acid) were analyzed by X-ray diffraction. The molecular packing patterns of the enclosed water molecules associated with these complexes were also studied. The water molecules assumed various geometries based on the cavities and channels formed upon the complexation of the carboxylates with the Cu^{II} ions. The free carboxylates in **1** and **2** as well nitrogens in **3** and **4** have the potential for complexing other metals (*i.e.* Pd, Pt, Zn, *etc.*) resulting in new building blocks for the construction of a 3D network¹³ and cages.^{2,14} This work gives rise to a promising method for controlling the architecture of crystals and is currently being applied to the other terpyridine–transition metals. Their potential for bridging the nitrogen-containing units to form new multi-dimensional networks, which could find applications in the area of smart materials and nanoscale devices, is currently under investigation.†

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Notes and references

† **General procedure for crystal synthesis. 1:** A mixture of terpyridine (10 mg, 43 μmol) and Cu(BF₄)₂·4 H₂O (13.25 mg, 43 μmol) was stirred in water at 25 °C to obtain a translucent green solution, then 1,4,5,8-naphthalene-tetracarboxylic acid (H₄NTC) (6.5 mg, 21.4 μmol) [or its dianhydride (NTCA) and NaOH (3.5 mg, 8.75 μmol)] in deionised water (8 ml) was added and the mixture sonicated for 30 min. The solution was then stirred at 90–100 °C for 12 h. Light-green crystals were collected (80%) after cooling to 25 °C and standing for 2 days. Crystal data for **1** (C₄₄H₂₆Cu₂N₆O₁₀): Triclinic, *P*-1, *a* = 7.198(4) Å, *b* = 12.339(7) Å, *c* = 12.865(8) Å, β = 84.562(10)°, *V* = 1129.0(11) Å³, *Z* = 1, ρ = 1.362 Mg/m³,

$\mu = 1.003 \text{ mm}^{-1}$, $F(000) = 470$. Final R indices (for 280 parameters) [$I > 2\sigma(I)$] were $R1 = 0.0773$, and $R1 = 0.0960$, $wR2 = 0.2712$ for all 5058 data. **3**: Using the general procedure for the preparation of **1**, 3,5-pyridine-dicarboxylic acid was used as the polycarboxylate to obtain (62%) **3**, as green crystals. Crystal data for **3** ($\text{C}_{88}\text{H}_{56}\text{Cu}_4\text{N}_{16}\text{O}_{22}$): Orthorhombic, $Fddd$, $a = 49.567(17) \text{ \AA}$, $b = 18.394(6) \text{ \AA}$, $c = 8.701(3) \text{ \AA}$, $\beta = 90^\circ$, $V = 7933(5) \text{ \AA}^3$, $Z = 4$, $\rho = 1.627 \text{ Mg/m}^3$, $\mu = 1.149 \text{ mm}^{-1}$, $F(000) = 3952$. Final R indices (for 153 parameters) [$I > 2\sigma(I)$] were $R1 = 0.0766$, and $R1 = 0.0851$, $wR2 = 0.1778$ for all 16212 data. **4**: Using the general procedure for the preparation of **1**, stirring the mixture at 25°C , 3,5-pyridine-dicarboxylic acid was used as the polycarboxylate to obtain **4** (78%), as green crystals. Crystal data for **4** ($\text{C}_{44}\text{H}_{28}\text{Cu}_2\text{N}_8\text{O}_{14}$): Triclinic, $P-1$, $a = 9.263(3) \text{ \AA}$, $b = 10.844(3) \text{ \AA}$, $c = 12.754(4) \text{ \AA}$, $\beta = 93.110^\circ$, $V = 1066.3(6) \text{ \AA}^3$, $Z = 1$, $\rho = 1.587 \text{ Mg/m}^3$, $\mu = 1.077 \text{ mm}^{-1}$, $F(000) = 518$. Final R indices (for 307 parameters) [$I > 2\sigma(I)$] were $R1 = 0.0608$, and $R1 = 0.706$, $wR2 = 0.1703$ for all 8969 data. CCDC 269332–269334. See <http://dx.doi.org/10.1039/b505327g> for crystallographic data in CIF or other electronic format.

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