

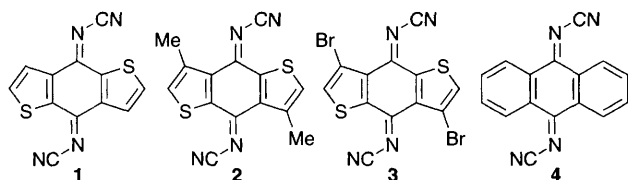
A novel coordination polymer derived from thiophene-fused DCNQI and CuI: a new family of DCNQI-based conducting copper complexes

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Thiophene-fused DCNQI compounds yield conducting CuI complexes built up of a unique three-dimensional supra-molecular coordination structure in which the zigzag ladder CuI polymers are bridged by the π -stacked acceptors as a bidentate ligand.

The radical-anion salts of copper with *N,N*-dicyanoquinone-diimines (DCNQIs), particularly in the form of their 2,5-disubstituted benzoquinone derivatives, have aroused wide interest because of their extremely high electrical conductivities.¹ In Cu(DCNQI)₂ salts, the DCNQI π -acceptor molecules are stacked, forming one-dimensional conduction bands. The Cu atoms are tetrahedrally coordinated by the terminal N atoms of the N-cyano group of the DCNQI molecules, so that one-dimensional DCNQI columns are connected three-dimensionally through Cu atoms. As π -expanded derivatives of DCNQI acceptors, we have recently prepared thiophene-fused DCNQI **1**, and found that this acceptor forms a conducting complex with copper(I) iodide of formula 1:2CuI.² Unfortunately, however, all our attempts to grow single crystals in 1:2CuI suitable for an X-ray analysis were unsuccessful.



We envisaged that the failure of crystallization to give single crystals could be attributed to the presence of configurational isomers with respect to =N-CN orientations;† coexistence of isomers in solution is considered to be disadvantageous in forming single crystals. We thus designed thiophene-fused DCNQIs bearing substituents at the β and β' positions of the condensed thiophene rings, *i.e.* DCNQI derivatives such as **2** and **3**. The β -substituents could exert buttressing effects to fix the CN group on the opposite side of the substituent, yielding exclusively *syn-syn* isomers as depicted and so increase the chance of isolation of single crystals. Here, we demonstrate unambiguously a new family of DCNQI-based conducting coordination polymer complexes and their novel three-dimensional architecture composed of organic layers of stacking π -acceptor molecules and inorganic layers of CuI ladder polymers.

The thiophene-fused DCNQIs **2** and **3** were prepared by the reaction of bis(trimethylsilyl)carbodiimide with the corresponding precursor quinone.³ The cyclic voltammograms of these acceptors exhibited two reversible redox waves. The data measured in benzonitrile are as follows: **1** $E_{1/2}^1 = +0.03$, $E_{1/2}^2 = -0.55$, **2** $E_{1/2}^1 = -0.07$, $E_{1/2}^2 = -0.60$; **3** $E_{1/2}^1 = +0.12$, $E_{1/2}^2 = -0.47$ V vs. Ag/AgCl.

It is known that the reaction of DCNQIs and CuI yields the radical salts Cu(DCNQI)₂,⁴ whereas for both **2** and **3** the same reaction afforded complexes of the type DCNQI-2CuI, as black fine needles. For 2:2CuI single crystals were obtained and therefore the electrical conductivity was measured on a single

crystal by a four-probe method and the room-temperature conductivity of 2:2CuI is 7.6×10^{-3} S cm⁻¹ and the temperature-dependent conductivities down to 200 K revealed that this complex is a semiconductor with an activation energy of 0.18 eV. On the other hand, the electrical conductivity of 3:2CuI, measured on a compressed powder sample at room temperature, is 8.2×10^{-3} S cm⁻¹.

The crystal structure of 2:2CuI is shown in Fig. 1‡ and the numbering scheme and selected structural parameters are shown in Fig. 2. The copper atoms are in nearly regular tetrahedral geometry coordinated by three iodine atoms and the nitrogen atom of a CN group in **2**. Each iodine atom is

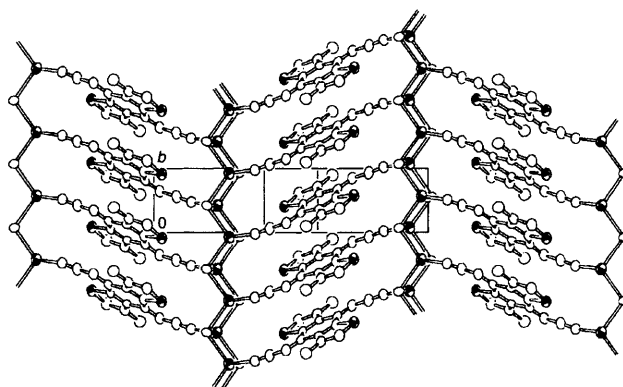


Fig. 1 Crystal structure of 2:2CuI, showing the CuI ladder and the stacking of molecules of **2**

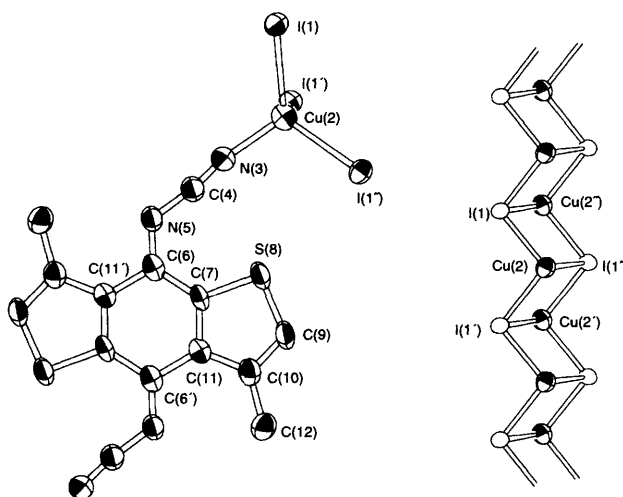


Fig. 2 Numbering scheme and selected bond lengths (Å) and angles (°): I(1)–Cu(2) 2.654(2), I(1')–Cu(2) 2.673(2), I(1'')–Cu(2) 2.681(2), Cu(2)–N(3) 1.960(13), N(3)–C(4) 1.13(2), C(4)–N(5) 1.33(2), N(5)–C(6) 1.293(19), Cu(2)⋯Cu(2') 2.896(3), Cu(2)⋯Cu(2'') 2.899(3); I(1)–Cu(2)–N(3) 115.0(4), I(1)–Cu(2)–I(1') 103.47(8), I(1)–Cu(2)–I(1'') 114.61(9), I(1')–Cu(2)–I(1'') 114.07(9), Cu(2)–I(1')–Cu(2') 65.82(7), Cu(2)–I(1'')–Cu(2'') 65.50(7), Cu(2')–I(1'')–Cu(2'') 103.47(8), I(1')–Cu(2)–N(3) 103.8(4), I(1'')–Cu(2)–N(3) 105.5(4)

alternately positioned to the copper atom, building up a zigzag ladder structure parallel to the *b* axis. Molecules of **2** bridge the CuI ladders as bidentate ligands by N-coordination of the CN groups to Cu. The π -acceptor molecules **2** are almost planar and stacked in a face-to-face arrangement with overlapping π -planes in the direction of the *b* axis. The interplanar distance of 3.56 Å is longer than that, 3.217 Å, found in Cu(Me₂DCNQI)₂.⁴

The Cu...Cu distance in the ladder is 2.89 Å, this being much shorter than the value, 3.88 Å, in Cu(Me₂DCNQI)₂⁴ and close to that, 2.56 Å, in metallic copper while the Cu...N distance is 1.96 Å. This value is similar to that found in Cu(Me₂DCNQI)₂.⁴ There are no short contacts less than the sum of the van der Waals radii between the chains; the inter-chain I...I distance is 4.18 Å and the S...I contacts are 3.95, 4.01 Å.

The X-ray powder diffraction pattern of 2·2CuI provides a strong indication of the layered structure associated with the coordination architecture. As shown in Fig. 3, the side-by-side arrangement of the CuI ladder polymers constitutes the layers of the inorganic component of CuI and these are aligned along the *c* axis alternately with the organic layers constituted by the stacking π -molecules. Thus, the X-ray powder diffraction exhibits a relatively sharp reflection at $2\theta = 7.15^\circ$ as well as sharp higher-order reflections. A set of these reflections affords a value of 12.35 Å for the basal spacing, corresponding to the interlayer distance.

The crystal engineering of two- and three-dimensional coordination polymers of Cu^I is of great current interest⁵ and there exist examples of coordination to the CuI ladder.⁶ The present organic-inorganic hybrid superstructure is the first example of a coordination polymer including a bridging ligand to CuI ladders.

The large, planar and rigid thiophene-fused DCNQI molecules would experience steric hindrance in tetrahedral four-coordinate geometry at copper in Cu(DCNQI)₂ type complexes, so that three molecules of iodine coordinate to copper in place of the π -acceptor molecules, resulting in release of steric hindrance and in the formation of the observed DCNQI·2CuI structures. Such consideration prompted us to investigate also a benzene-fused DCNQI, *i.e.* *N,N'*-dicyanoanthraquinonediimine **4**. Thus we have found that **4** also affords a complex of the type 4·2CuI, which exhibits a room-temperature conductivity of $4.3 \times 10^{-3} \text{ S cm}^{-1}$ as measured on a compressed powder sample.

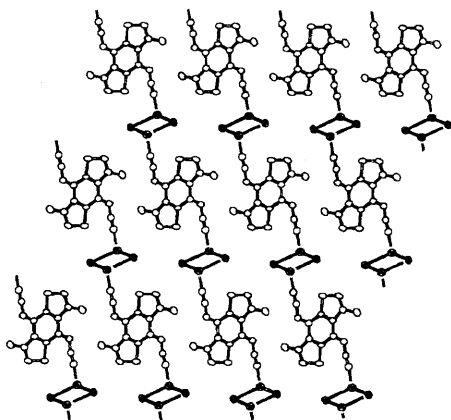


Fig. 3 Crystal structure of 2·2CuI viewed along the *b* axis showing the alternate layers of the stacking π -acceptor molecules and the CuI layers

Acceptor **4** has been documented,⁷ but no CuI complex has been described previously. We predict that other reported⁸ condensed-DCNQI derivatives can also afford CuI complexes.

The electrical transport properties in condensed-DCNQI·2CuI type complexes cannot be deduced at this stage. There may be several possibilities, since both the π -stacked organic columns and the inorganic CuI chains could participate in electron or hole transport, respectively, owing to their one-dimensional stacking and polynuclear chain structure, although the former mechanism would be less likely to occur because of the large face-to-face distance in the π - π stacking.

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Footnotes

† The NMR spectra of α,α' -diethyl derivative of the thiophene-fused DCNQI exhibited the presence of three isomeric species in a solution due to *syn-syn*, *syn-anti* and *anti-anti* configurational isomers. These signals coalesced at ca. 90 °C, indicating fast inversion of the CN group at the sp² nitrogen atom on the NMR timescale.

‡ Crystal data for C₁₄H₈Cu₂I₂N₄S₂: *M* = 677.26, monoclinic, space group *P*2₁/*a*, *a* = 16.647(2), *b* = 4.1826(2), *c* = 12.8187(15) Å, β = 105.786(11)°, *U* = 858.9(2) Å³, *Z* = 2, *D*_c = 2.618 g cm⁻³, Mo-K α (λ = 0.71073 Å), *T* = 295 K, μ (Mo-K α) = 0.679 mm⁻¹, crystal dimensions 0.3 × 0.12 × 0.01 mm, Data collection on a Rigaku AFC-5 four-circle diffractometer. $2\theta_{\text{max}}$ = 60°. Collection of data: $\omega(4 < 2\theta < 55)$ and $\omega-2\theta(55 < 2\theta < 60)$, 2996 reflections measured, 1596 independent of which 1500 were considered observed [*I* > 4.0 σ (*I*)]; 110 refined parameters. The structure was solved by Patterson methods and refined by block-diagonal least-squares analysis using the UNICS-III program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions. Final *R* = 0.0713, *R*_w = 0.0830 [*I* > 4 σ (*I*)]. Max./min. residual electron density in the final difference map: 2.978, -1.891 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/211.

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