

Self-assembly of a polynuclear ribbon: the structure of $\{[\text{Cu}_2(\text{CN})_2(\text{L})] \cdot \text{MeNO}_2\}_\infty$ [$\text{L} = 4,7\text{-bis}(2\text{-cyanoethyl})\text{-}1\text{-thia-}4,7\text{-diazacyclononane}$]

Alexander J. Blake,^a Jonathan P. Danks,^a Vito Lippolis,^a Simon Parsons^b and Martin Schröder^{*,a}

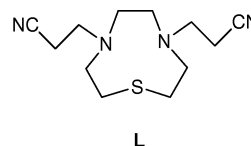
^a School of Chemistry, The University of Nottingham, Nottingham, UK NG7 2RD

^b Department of Chemistry, The University of Edinburgh, Edinburgh, UK EH9 3JJ

The compound $\{[\text{Cu}_2(\text{CN})_2(\text{L})] \cdot \text{MeNO}_2\}_\infty$ [$\text{L} = 4,7\text{-bis}(2\text{-cyanoethyl})\text{-}1\text{-thia-}4,7\text{-diazacyclononane}$] has been prepared by reaction of CuCN with L. The complex shows an unusual Cu^I—CN one-dimensional polymer capped by macrocyclic ligands.

The coordination chemistry of thia and mixed thia-aza crown ethers has been of great interest over the past decade.¹ This attention has focused mainly on the co-ordination chemistry of these ligands with transition-metal ions² and certain main-group elements.³ Binding studies of Cu^{II} centres with these ligands often has the goal of bioinorganic modelling and the understanding of the redox processes which involve the formation of tetrahedral or trigonal d¹⁰ Cu^I centres in biological systems. Complexes of Cu^I with CN[−] often contain $\mu_2\text{-}\kappa\text{C}:\kappa\text{N}$ bridging CN[−] units to give in some cases infinite —Cu^I—CN—Cu^I—CN— chains,⁴ in which the Cu atoms can be two-coordinate,⁵ three-coordinate^{6,7} or four-coordinate^{7–10} with the participation of one or more additional ligands. Nitrogen-based ligands such as NH₃, Et₂NH, Et₃N, N₂H₄, ethylenediamine, 4-methylpyridine, 1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline are normally used to stabilize the —(Cu^I—CN)_∞— polymeric chains by occupying the remaining two co-ordination sites on the Cu^I centres, and only recently a new series of polymeric copper(I) cyanide complexes of thiourea and substituted thioureas has been reported.¹¹ We report here the synthesis and crystal structure of the complex $\{[\text{Cu}_2(\text{CN})_2(\text{L})] \cdot \text{MeNO}_2\}_\infty$ where L is the mixed thia-aza pendant arm macrocycle 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane.^{†12}

[†] 4,7-Bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (L). Although this ligand has been reported¹² its coordination chemistry is unknown. A mixture of 1-thia-4,7-diazacyclononane (0.843 g, 5.78 mmol) and acrylonitrile (30 cm³) was stirred at 77 °C for 12 h. After cooling, the excess of acrylonitrile was removed leaving a yellow-orange oil which was passed through a silica gel column using THF as eluant. On removal of solvent a pale-yellow solid was obtained (1.21 g, 83% yield; mp 80–82 °C. Anal. found (calcd for C₁₂H₂₀N₄S): C, 57.42 (57.11); H, 8.26 (7.99); N, 21.93% (22.20%). ¹H NMR (CDCl₃) δ: 3.07–2.9 (m, 6H), 2.71 (s, 2H), 2.5 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (CDCl₃) δ: 119.28, 59.14, 56.27, 53.93, 31.38, 16.91. $\{[\text{Cu}_2(\text{CN})_2(\text{L})] \cdot \text{MeNO}_2\}_\infty$. A solution of 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (L) (30 mg, 0.119 mmol) and CuCN (10.7 mg, 0.119 mmol) in CH₃CN–MeOH (30 cm³, 1 : 1 v/v ratio) was stirred at 25 °C for 24 h and subsequently refluxed for 2 h under N₂. The solvent was removed and the residue taken up in MeNO₂. After filtration, a colourless solution was obtained and diffusion of Et₂O into it produced block-shaped colourless crystals (12 mg, 53.5% yield). Anal. found (calcd for C₁₅H₂₃Cu₂N₇O₂S): C, 36.10 (36.58); H, 4.23 (4.71); N, 19.43% (19.91%). FAB mass spectrum (3-NOBA matrix): *m/z* 341, 404; calcd for [CuCNL]⁺ and [Cu₂CN₂L]⁺: 341 and 404 respectively with the correct isotopic distributions. IR (KBr pellet): 2249m [ν(CN) nitrile groups of L] 2112s cm^{−1} [ν(CN) of bridging CN[−]].



Reaction of CuCN with L in MeCN–MeOH (1 : 1 v/v) affords a colourless solution from which a white powder can be isolated on removal of solvent. Recrystallisation of the product from MeNO₂–Et₂O gives colourless crystals of stoichiometry L(CuCN)₂·MeNO₂ in 54% yield.[†] In order to ascertain the structure of this compound, a single-crystal X-ray determination was undertaken.[‡]

The structure of the complex consists of infinite one-dimensional (zig-zag) —Cu^I—CN—Cu^I—CN— chains which run horizontally in Fig. 1. Each Cu^I centre within these chains is additionally bound to the N-atom of a further [Cu^I(L)CN] unit, and the whole network is planar with no significant

[‡] Crystal data for C₁₅H₂₃Cu₂N₇O₂S. *M* = 492.54, monoclinic, *P*2₁/*n*, *a* = 7.785(3), *b* = 18.186(5), *c* = 15.094(6) Å, β = 99.80(3)°, *V* = 2105.80(13) Å³, [from 2θ values for 49 reflections measured at ±ω (40 < 2θ < 44°), Cu–Kα radiation: λ = 1.54184 Å], *Z* = 4, *D*_{calc} = 1.55 g cm^{−3}, *F*(000) = 1008, *T* = 220(2) K, μ(Cu–Kα) = 3.627 mm^{−1}. Colourless block, 0.23 × 0.12 × 0.12 mm³. Stoe Stadi-4 diffractometer with Oxford Cryosystems open-flow cryostat¹³, ω–θ scans using on-line profile fitting,¹⁴ θ_{max} = 56.24°, 3077 absorption-corrected reflections (ψ scans, *T* = 0.382–0.521), 2652 unique (*R*_{int} = 0.022). Structure solution by automatic direct methods¹⁵ and refinement on *F*² using SHELXL-97,¹⁶ with non-H and H atoms having anisotropic and isotropic displacement parameters, respectively. H atoms were located from difference Fourier syntheses or introduced at calculated positions and thereafter incorporated into a riding model. The orientation Cu(1)—C(10)—N(11)—Cu(2) was established by competitive refinement against the Cu(1)—N(11)—C(10)—Cu(2) model. The remaining CN[−] anions [C(12)—N(13) and C(14)—N(15)] were found to be fully disordered about inversion centres and the positions and anisotropic displacement parameters of the C and N components at each site were constrained to be the same. A static disorder model was also investigated for N(44) but it offered no advantage over the model adopted. At final convergence, *R*₁ = 0.0664, *wR*₂ = 0.1733, *S* = 1.051 for 256 parameters and 1898 reflections with *I* ≥ 2σ(*I*) using the following weight scheme: *w* = 1/[σ²(*F*_o²) + (0.027*P*)² + 23.0*P*], *P* = (*F*_o² + 2*F*_c²)/3. Difference electron density features lay within the range 0.93 to −1.00 eÅ^{−3}. CCDC reference number 440/074.

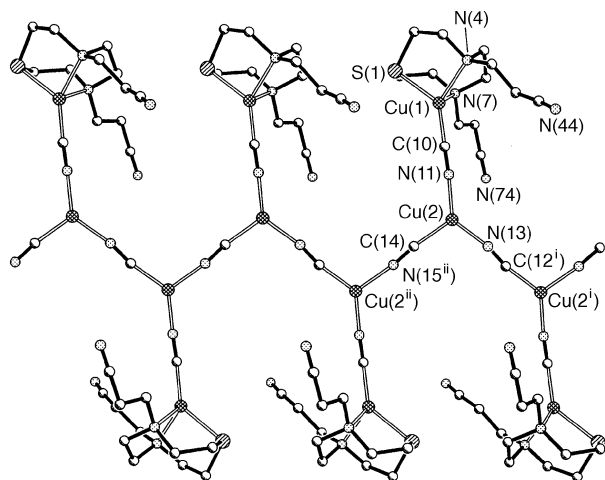


Fig. 1 View of structure of $[\text{Cu}_2(\text{CN})_2(\text{L})]_\infty$ showing the numbering scheme adopted. The MeNO_2 solvent molecules have been omitted for clarity. Only one component of each of the disordered cyanides is shown: $\text{Cu}(1) - \text{S}(1)$ 2.303(3), $\text{Cu}(1) - \text{N}(4)$ 2.131(7), $\text{Cu}(1) - \text{N}(7)$ 2.209(7), $\text{Cu}(1) - \text{C}(10)$ 1.861(10), $\text{Cu}(2) - \text{N}(11)$ 1.888(9), $\text{Cu}(2) - \text{N}(13)$ 1.888(10), $\text{Cu}(2) - \text{C}(14)$ 1.925(8), $\text{C}(10) - \text{N}(11)$ 1.158(11), $\text{N}(13) - \text{C}(12^i)$ 1.179(1), $\text{C}(14) - \text{N}(15^ii)$ 1.163(16) Å; $\text{N}(11) - \text{Cu}(2) - \text{C}(14)$ 120.8(4), $\text{N}(11) - \text{Cu}(2) - \text{C}(12)$ 131.4(4), $\text{Cu}(1) - \text{C}(10) - \text{N}(11)$ 170.6(8), $\text{Cu}(2) - \text{N}(11) - \text{C}(10)$ 171.1(8)°, i, $-x + 1, -y + 1, -z$; ii, $-x, -y + 1, -z$

apical interactions at the trigonal Cu^I centres. The complex therefore constitutes a rare example of a $-(\text{Cu}^I - \text{CN})_\infty$ —herring-bone polymer in which both trigonal and tetrahedral Cu^I are observed: the trigonal planar Cu^I centres lie within the polymer backbone chain, while the four-coordinate Cu^I centres are bound to the functionalised macrocycle, heavily distorted from ideal tetrahedral geometry by the conformational constraints of the ring system. Neither the terminal nitrile groups of the macrocyclic pendant arms nor the MeNO_2 of crystallisation interact with the Cu^I centres. The overall structure can therefore be regarded as a $[\text{Cu}_2(\text{CN})_2]$ polymer capped by L.

The CN^- bridging groups in the polymer backbone chain are fully disordered [average C—N bond distances 1.179(1) and 1.163(16) Å, see Fig. 1] whereas the CN^- donors bridging this chain to the $[\text{Cu}(\text{L})]^+$ units are fully ordered [$\text{C}(10) - \text{N}(11)$ 1.158(11) Å]. The $\text{Cu}(2) - \text{N}(11)$ bond distance [1.888(9) Å] is significantly shorter than that observed for the comparable three-coordinate Cu^I complexes $\text{KCu}(\text{CN})_2 \cdot \text{H}_2\text{O}$ and $\text{NaCu}(\text{CN})_2 \cdot \text{H}_2\text{O}$.^{6,9} [$\text{Cu} - \text{N}(\text{cyanide}) = 1.99 - 2.05$ Å]. Four-coordinate copper centres in previously reported complexes^{6–9} show $\text{Cu} - \text{C}(\text{cyanide})$ distances of 1.87–1.99 Å and $\text{Cu} - \text{N}(\text{cyanide})$ distances of 1.90–2.00 Å. In the present case, at tetrahedral $\text{Cu}(1)$, the $\text{Cu}(1) - \text{C}(10)$ distance is 1.861(10) Å, whereas $\text{Cu}(1) - \text{N}(4) = 2.131(7)$ and $\text{Cu}(1) - \text{N}(7) = 2.209(7)$ Å. The $\text{Cu}(1) - \text{S}(1)$ distance [2.303(3) Å] falls within the range of $\text{Cu} - \text{S}$ bond distances observed for copper(I) complexes^{1,17} (2.19–2.52 Å) and Cu^I —cyanide complexes¹¹ of thiourea and substituted thioureas (2.27–2.48 Å). The present complex is unique insofar¹⁸ as all previous examples of trigonal planar complexes of Cu^I with three CN^- ligands show two-dimensional sheet structures or one-dimensional polymeric chains having C-bonded terminal CN^- ligands. In the present case the co-ordination of the macrocycle to the terminal Cu^I centres prevents the growth of the herring-bone polymer into a two-dimensional sheet.

Diverse structural archetypes can be generated by the bridging action of the CN^- on a wide range of metal ions and in the presence of other ligands.¹⁹ The types of polymeric structure that result for Cu^I systems are frequently controlled by the nature of the co-ligands,^{5–11} but, to our knowledge,

macrocyclic molecules have never been used for this purpose. Studies are in progress to understand how functionalized mixed thia-aza crowns can be used for the regiospecific control of Cu^I —cyanide polymer growth.

Acknowledgements

We thank EPSRC for support.

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*Received in Cambridge, UK, 5th August 1998;
Letter 8/06163G*