Polycatenated copper(I) molecular ladders: a new structural motif in inorganic coordination polymers

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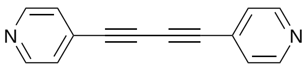
The complex $\{[Cu_2(MeCN)_2L_3](PF_6)_2\}_\infty$ [L = 1,4-bis(4-pyridyl)butadiyne] is prepared and characterised by X-ray diffraction studies which show an undulating polycatenated molecular ladder structure involving fully interwoven two-dimensional sheets.

The study of inorganic coordination polymers and their use in constructing solid-state architectures has become an area of increasing interest.[1] Although the design of inorganic networks is less well developed than corresponding hydrogen-bonded systems,[2] recent examples have helped to extend the understanding of this rapidly expanding area.[1,3–8] Of particular interest in inorganic co-ordination polymers is the degree and nature of interpenetration or polycatenation[3] and to this end we have been investigating the effect of ligand functionality upon the construction of two- and three-dimensional arrays, and in particular adamantoid or super-diamondoid networks based upon copper(I) complexes.[4,5] We have established recently a degree of control over the assembly of these copper(I) adamantoid networks showing that the degree of interpenetration of independent networks can be increased or decreased by variation of the length[4] and steric bulk[5] of the linking ligand. During further investigations into such systems we have isolated a remarkable new structural motif for inorganic coordination polymers, a polycatenated undulating molecular ladder.



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The reaction of $[Cu(MeCN)_4]PF_6$ with 1,4-bis(4-pyridyl)butadiyne (L) in MeCN–CH_2Cl_2 yields a deep red solution from which red crystals of composition $\{[Cu_2(MeCN)_2L_3](PF_6)_2\}_\infty$ were isolated by layering with Et_2O.† The same product is isolated even in the presence of a large excess of ligand, with metal : ligand ratios of up to 1 : 4. X-Ray diffraction studies‡ of these crystals show that the compound exists as a network of molecular ladders in which the two independent Cu^I centres are each coordinated in a tetrahedral geometry to three ligands L, Cu–N 1.993(9)–2.114(10) Å, and one MeCN ligand, Cu–N 1.980(13), 1.997(12) Å, (Fig. 1). The ladder structure is generated *via* the 1,4-bis(4-pyridyl)butadiyne ligands which each bridge two Cu^I centres. This structure is particularly surprising as insoluble adamantoid networks have been previously observed from this type of reaction.[4–6] Molecular ladders have been observed for relatively few related systems although in all previous cases the metal junction of the ladder has been a pseudo-octahedral[7] or octahedral[8] centre generating what may be termed a flat ladder with all linking ligands coplanar.[7,8] In the case reported here the tetrahedral Cu^I centres allow the ladder to undulate. The large cavities between the rungs of the ladder encourage the inclusion of discrete symmetry-related ladders. Examples of molecular ladders based upon cobalt(II)-bipyridyl complexes exhibit no interpenetration.[8] Interpenetration of symmetry-related ladders has been observed although this interpenetration was found to be perpendicular to the orientation of the original ladder, generating a three-dimensional polycatenated structure.[7] In the example reported here the ladders are polycatenated to give a remarkable two-dimensional layer structure involving undulating ladders which interweave in a parallel fashion (Fig. 2). These two-dimensional layers are flattened by a distortion of the N(1)–Cu(1)–N(5) and N(1′)–Cu(2)–N(4) angles from tetrahedral to 128.4(4) and 124.9(4)°, respectively, allowing a significant flattening of each ladder. Each ladder is polycatenated by a further four ladders which weave through the first ladder so as to fill the spaces between the ladders' rungs giving a fully polycatenated sheet (Fig. 3). Potential π–π interactions between adjacent, symmetry-related ladders at a distance of 3.484 Å may presumably contribute to the stability of the observed structural motif. The two-dimensional sheets of interwoven ladders are separated by PF_6^- counter-anions and solvent molecules with the co-ordinated MeCN molecules pointing towards the next sheet in the crystal.

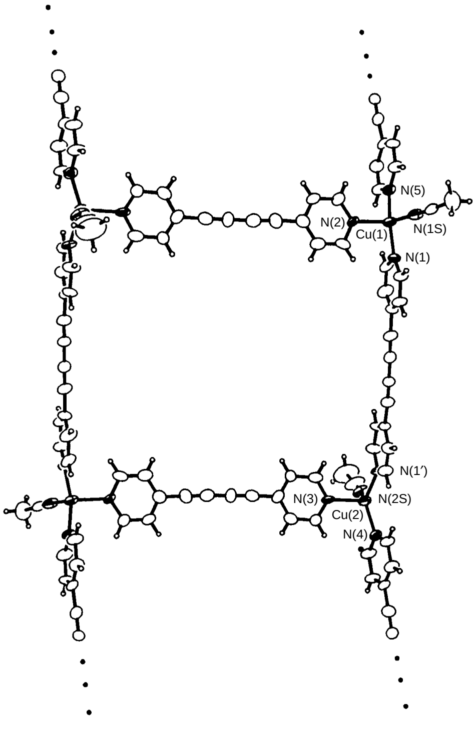

Fig. 1 A view of part of one infinite undulating ladder. Cu(1)–N(1S) 1.997(12), Cu(1)–N(1) 1.997(9), Cu(1)–N(5) 1.998(9), Cu(1)–N(2) 2.087(9), Cu(2)–N(2S) 1.980(13), Cu(2)–N(4) 1.993(9), Cu(2)–N(1′) 2.032(9), Cu(2)–N(3) 2.114(10) Å.

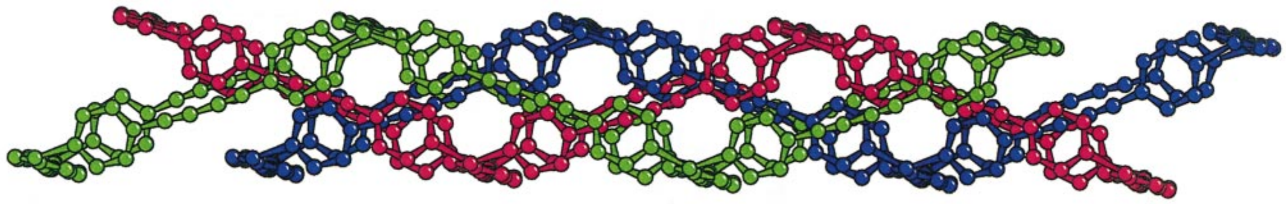

Fig. 2 A lateral view of three undulating ladders distinguished by colour showing their interweaving. The PF_6^- anions, solvent molecules and coordinated MeCN are omitted for clarity.

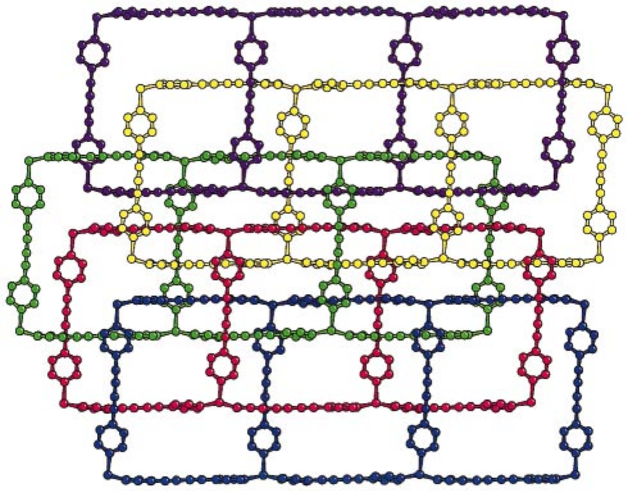

Fig. 3 An orthogonal view whose central area shows the interpenetration of five ladders, which are distinguished by colour. The PF_6^- anions, solvent molecules and coordinated MeCN are omitted for clarity.

In conclusion we have isolated a unique polycatenated undulating molecular ladder which forms interwoven two-dimensional sheets. We are currently investigating the factors that effect the formation of molecular ladders instead of the more common adamantoid networks in copper(I) bipyridyl arrays.

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Footnotes and References

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† *Experimental*: $\{[Cu_2(MeCN)_2\{1,4\text{-bis}(4\text{-pyridyl})\text{butadiyne}\}_3](PF_6)_2\}_\infty$. A solution of 1,4-bis(4-pyridyl)butadiyne (32 mg, 0.16 mmol) in MeCN (10 cm^3) was layered over a solution of $[Cu(MeCN)_4]PF_6$ (16 mg, 0.04 mmol) in CH_2Cl_2 (10 cm^3). Diffusion between the two phases over a period of days gave a homogeneous red solution. Diethyl ether was then diffused into the solution to give deep red crystals.

‡ *Crystal data* for $\{[Cu_2(MeCN)_2\{1,4\text{-bis}(4\text{-pyridyl})\text{butadiyne}\}_3](PF_6)_2\}_\infty\cdot0.5MeCN\cdot0.5Et_2O$: $C_{49}H_{35}Cu_2F_{12}N_{8.5}O_{0.5}P_2$, $M = 1167.88$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.789(6)$, $b = 15.139(6)$, $c = 16.192(8)$ Å, $\alpha = 110.59(5)$, $\beta = 91.36(4)$, $\gamma = 107.43(4)°$. $U = 2771(2)$ Å^3, $Z = 2$, $F(000) = 1177$, $D_c = 1.400$ g cm^{-3}, μ(Mo-Kα) = 0.907 mm^{-1}. A red tabular crystal (0.30 × 0.16 × 0.15 mm) was used for data collection on a Stoe Stadi-4 four-circle diffractometer (graphite-monochromated Mo-Kα radiation, ω–θ scans, $\theta_{max} = 22.5°$). No absorption correction was applied, 7210 unique reflections [$R_{int} = 0.0676$], of which 4256 had $I \geqslant 2\sigma(I)$, were used in all calculations. A correction for crystal decay (37%) was applied during data reduction. The structure was solved using direct methods[9] and all non-H atoms were located using subsequent difference-Fourier methods.[10] Both PF_6^- anions were found to be disordered, the first with each F atom split over two sites of occupancy 0.75 and 0.25, the second with the whole PF_6^- disordered over two equally occupied sites. The MeCN and Et_2O molecules were both found to have a half occupancy in their respective sites. Hydrogen atoms were placed in calculated positions and were allowed to ride on their parent atoms. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.2P)^2]$, $P = [\max.(F_o^2,0) + 2F_c^2]/3$ was adopted. At final convergence[10] R_1 [$I > 2\sigma(I)$] = 0.1232, wR_2 (all data) = 0.3699 for 649 parameters, $S = 1.219$, $(\Delta/\sigma)_{max} = 0.008$, $\Delta\rho_{max} = 0.94$ e Å^{-3}. The high value for R_1 is attributed to the effects of crystal decay. CCDC 182/608.

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