DALTON COMMUNICATION

A Cu(I) coordination polymer employing a nonsteroidal aromatase inhibitor letrozole as a building block †

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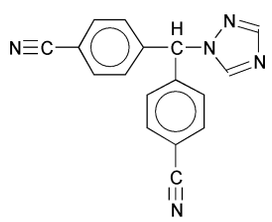
The reaction of $[Cu(I)(MeCN)_4](BF_4)$ with letrozole (1-[bis(4-cyanophenyl)methyl]-1,2,4-triazole, LTZ) affords a quite unusual 3-D coordination polymer in which for the first time LTZ demonstrates its coordinating ability as a tetradentate ligand.

In recent times highly symmetric bridging ligands have attracted great attention, mainly because of their ability to serve as building blocks in the construction of supramolecular assemblies such as squares,[1] rectangles,[2] honeycomb networks,[3] diamondoid networks and highly symmetric coordination cages.[4] Typically such structures involve commonly used ligands such as tetra(4-cyanophenyl)methane,[5] tetra(4-cyanophenyl)-silane,[6] 1,3,5-trimesic acid, 1,3,5,7-adamantane tetracarboxylate,[7] 1,3,5-tri(4-benzoic acid)benzene,[7] 1,2,3,4,5,6-hexaimidazolebenzene and 2,4,6-tri(4-pyridyl)-1,3,5-triazine.[7] More recently, Blake and co-workers have explored the use of 2,4′-bipyridyl derivatives as low symmetry building blocks in the construction of novel three-dimensional coordination polymers.[8] We have also employed this approach in the self-assembly of some interesting supramolecular architectures. In our search for other low symmetry ligands that may serve as appropriate bridging units we note that many organic drugs have the potential to act as building blocks, and we have been exploring their supramolecular chemistry.[9]

Letrozole (1-[bis(4-cyanophenyl)methyl]-1,2,4-triazole, abbreviated as LTZ) is a widely used nonsteroidal aromatase inhibitor[10] that has four potential donor atoms and therefore may serve as a low symmetry building block in a supramolecular assembly. We note that many organic compounds used in medicine do not have a purely organic mode of action; some are activated or biotransformed by metal ions while others have a direct or indirect effect on metal ion metabolism, however to the best of our knowledge, there is no report of any metal complex with LTZ. Herein we report the reaction of letrozole with $[Cu(I)(MeCN)_4](BF_4)$ to afford a 3-D coordination polymer with reversible guest molecular absorption–desorption: $\{[Cu(I)(LTZ)](BF_4)\cdot CHCl_3\}_n$ (**1**).

Compound **1** was synthesized in the solvothermal reaction between $[Cu(I)(MeCN)_4](BF_4)$ and LTZ.‡ The presence of cyano groups in **1** was confirmed by one weak peak at 2250 cm^{-1} in the IR spectrum, compared to one strong peak at 2250 cm^{-1} found in free LTZ. A very strong broad peak at *ca.* 1100 to 1020 cm^{-1} suggested the presence of uncoordinated BF_4^- anions in **1**. To study the thermal stability of compound **1**, thermogravimetric analyses (TGA) were performed on polycrystalline samples which indicated that one weight loss step occurred between 35 and 182 °C (22.03% loss), corresponding to the removal of one chloroform molecule per formula unit (21.53%). Most important is the fact that no weight loss was recorded between 182 and 250 °C, suggesting that the host is a stable molecular network. Our experimental results indicate that the host cavity can include chloroform molecules to regenerate **1**. (Identical X-ray powder diffraction patterns were obtained for samples of **1** before and after the removal of chloroform guest molecules. In addition, the quantitative GCMS results confirm that the desolvated network can absorb the same amount of chloroform as contained in **1**.) The host decomposes above 250 °C.



LTZ

The three-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction investigation.§ The local coordination environment around the Cu(I) ion can be best described as a slightly distorted tetrahedron (Fig. 1) in which the four coordinating N atoms (two triazole ring N atoms and two 4-cyanophenyl group N atoms) come from four different LTZ ligands. In addition, each LTZ ligand in **1** acts as a tetradentate bridging ligand that links to four Cu(I) ions. The resulting polymer extends in three dimensions as shown in the ESI.†

In order to appreciate the connectivity of complex network structures it is often useful to represent structural units by nodes and then examine the connectivity of these nodes. The choice of chemical unit to be represented by a node is not always clear but once the choice has been made the internal connections of the chemical unit that a node represents are irrelevant in describing the topology. It would seem sensible in the structure presented to have the organic ligands represented by a single node and the copper atoms represented by a second node. From a topological perspective both of these nodes are four connecting. The connectivity of the structure may be understood in terms of sheets that extend in the *a*–*c* plane. In Fig. 2 the very large spheres represent Cu atoms while the slightly smaller spheres are C3 atoms, which from a topological perspective represent the ligand. It should be emphasised that the selection of a point that represents the node is arbitrary since topology is not concerned with the position of a node, only its connections. It can be seen that within this sheet each Cu centre links to three ligands and each ligand links to three copper centres thus creating a 6,3 sheet. A 6-membered ring within the sheet is highlighted. 6,3 sheets are observed in other 4-connecting structures such as diamond but structures

† Electronic supplementary information (ESI) available: a 3-D microporous perspective view of **1**. See http://www.rsc.org/suppdata/dt/b1/b104880p/

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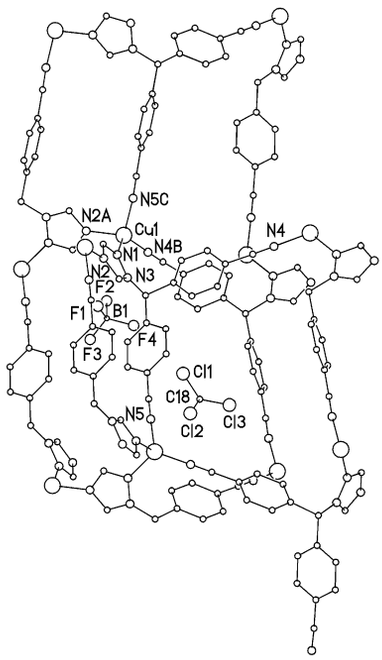

Fig. 1 A representation of one cage-like coordination polymer of **1**. H atoms are omitted for clarity.

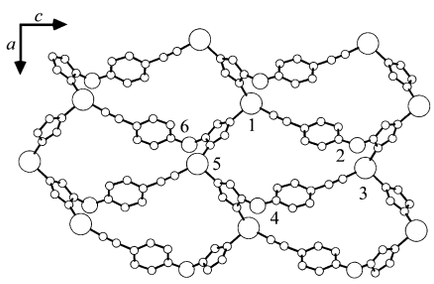

Fig. 2 A topological perspective representation in the *a*–*c* plane. The open circles represent Cu (large) and C3 (small), respectively.

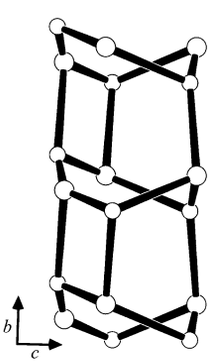

Fig. 3 A cage-like net representation of **1**.

can differ depending upon the connectivity between sheets. In Fig. 3, near vertical connections, that are in reality benzonitrile units, extend in the *b*-direction linking adjacent sheets by bridging C3 and Cu atoms. In structures such as wurtzite and zinc blende the vertical connections alternate between up and down on adjacent atoms. In this coordination polymer the alternation is less regular resulting in the formation of 4-membered rings between adjacent sheets. We are grateful to a referee for pointing out that the four-connected net is the same as found in the mineral variscite ($AlPO_4 \cdot 2H_2O$)[11] and has the topological symbol 4.6^5c.[12]

A common feature of coordination polymers based upon symmetric ligands is the presence of voids and channels within the networks that are also symmetric. As with its high symmetry counterparts, voids within this coordination polymer are clearly apparent (Fig. 1 (or ESI †)) and are occupied by BF_4^- anions and chloroform molecules, however in this case the voids and channels are irregular in shape. These voids may be considered to lie between the sheets which extend in the *a*–*c* plane and are held apart by benzonitrile "pillars".

In conclusion, it has been demonstrated that LTZ can coordinate to metal ions as a tetradentate chelating agent. Apart from providing a new insight into the reaction of LTZ with metal ions the work has also demonstrated the potential for the use of low symmetry ligands in the generation of coordination polymers. Such materials with irregular channels and voids may have important application in the selective absorption and desorption of guest molecules.

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‡ Preparation of compound **1**. Solvothermal (1.5 ml benzene and 0.5 ml $CHCl_3$) treatment of $[Cu(I)(MeCN)_4](BF_4)$ (0.2 mmol) and LTZ (0.2 mmol) for three days at 100 °C afforded a colorless plate crystalline product (one pure phase). The yield of **1** was about 40% based on LTZ (found: C, 38.71; H, 2.21; N, 12.81. Calc.: C, 38.92; H, 2.16; N, 12.61%). IR (KBr, cm^{-1}): 3500(w), 3100(vw), 2250(w), 1605(m), 1520(m), 1420(w), 1300(m), 1100(br, vs), 1027(br, vs), 890(w), 820(w), 796(w), 750(m), 650(w), 5279(m).

§ Crystal data for **1**. $C_{18}H_{12}BCl_3CuF_4N_5$, orthorhombic, *Pbca*, $a = 8.9646(3)$, $b = 22.8924(9)$, $c = 23.9497(9)$ Å, $V = 4915.0(3)$ Å^3, $Z = 8$, $M = 555.03$, $D_c = 1.500$ Mg m^{-3}, $R_1 = 0.0822$, $wR_2 = 0.2535$ (3092 reflections), $T = 150$ K, $\mu = 1.260$ mm^{-1}, $S = 1.083$. CCDC reference number 164957. See http://www.rsc.org/suppdata/dt/b1/b104880p/ for crystallographic data in CIF or other electronic format.

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