Control of copper(II) coordination geometry *via* supramolecular assembly of ligands in the solid state

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The high density and strength of intermolecular hydrogen bonding between amine and sulfonamide units in the complex [Cu(Tstn)$_2$] [TstnH = *N*-(3-aminopropyl)-4-methylbenzenesulfonamide] give rise to energetically unfavourable coordination geometries at the copper centres in the solid state, in a manner analogous to the entatic state forced on metal active sites in metalloenzymes through secondary and tertiary protein structures.

The blue copper sites, present in several protein environments, exhibit a number of characteristics, derived from unusual electronic structures, that distinguish them from small molecule, copper(II) complexes.[1,2] These characteristics arise from distorted coordination geometries at the metal centre. The mismatch between the coordination environment supplied by the protein (determined by its amino acid sequence and hydrogen bonded structure), and that preferred by the metal centre (determined by electronic and steric effects) leads to this metastable 'entatic' or 'rack' state.[3,4] Entatic states have been modelled in small molecules by using rigid, predisposed[5] or sterically hindered ligands.[6] Although hydrogen bonded systems have been widely studied due to their potential to control solid state geometries[7] their application in imposing 'entatic states' in simple metal complexes has not been described previously.

In the system presented here we have used an unhindered ligand to engineer a high density of hydrogen bond donors and acceptors into a copper(II) complex, which lead to a large number of intermolecular interactions in the solid state. The copper(II) complex [Cu(Tstn)$_2$] exists in two crystalline forms which differ only in the disposition of intermolecular hydrogen bonds, but which have distorted copper coordination geometries that differ markedly from each other and from that seen in solution.

Reaction of TstnH, **1**, with copper acetate in boiling methanol gives a deep blue solution which, on evaporation at ambient temperature, deposits a dark blue crystalline compound, **2,** identified as [Cu(Tstn)$_2$].† If evaporation is prevented and the solution is instead left to stand at ambient temperature in a sealed vessel, it deposits a bright green crystalline compound, **3**, with the same molecular formula, [Cu(Tstn)$_2$]. In solution (DMF) the electronic and electrospray mass spectra of **2** and **3** are identical, suggesting that a single species is present. The compounds can be interconverted by dissolution in hot methanol; evaporation produces **2**, whilst crystallization on cooling and standing produces **3**, regardless of the starting complex. The marked difference in colour and in the measured solid state visible spectra, in the FTIR spectra and in the melting behaviour of the two solids led us to determine X-ray crystal structures for both to define the origin of these differences.‡

The asymmetric unit of the blue compound, **2**, contains two almost isostructural but independent [Cu(Tstn)$_2$] molecules (weighted rms deviation 1.062 Å) in which the ligands chelate the metal through deprotonated sulfonamide and amine nitrogens (Fig. 1). The coordination geometry (Table 1) at copper is highly distorted square planar (dihedral angles between the chelate planes 36.4 and 34.5° in the two independent molecules). All the amine protons form intermolecular hydrogen bonds (Table 2) to sulfonamide oxygens resulting in zigzag

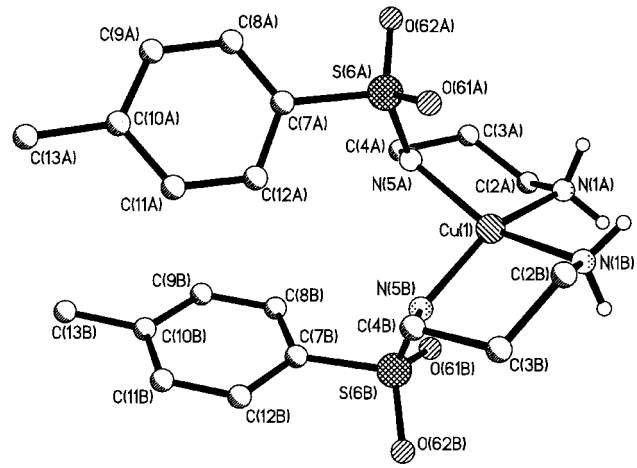

Fig. 1 Molecular structure of **2**. Only amine hydrogens are shown. Selected bond distances and angles for **2** are given in Table 1.

Table 1 Selected bond distances (Å) and angles (°) in **2** and **3**

	2	**3**		**2**	**3**
Cu1–N1A	2.023(7)	2.001(5)	N1A–Cu1–N1B	91.8(2)	95.01(16)
Cu1–N1B	2.013(7)	2.009(5)	N1A–Cu1–N5A	91.2(3)	93.3(2)
Cu1–N5A	1.970(8)	1.946(6)	N1A–Cu1–N5B	154.5(4)	138.3(2)
Cu1–N5B	1.954(8)	1.959(6)	N1B–Cu1–N5A	153.7(4)	137.1(2)
S6A-O61A	1.448(7)	1.445(4)	N1B-Cu1-N5B	90.5(3)	93.7(2)
S6A-O62A	1.449(7)	1.463(5)	N5A-Cu1-N5B	97.9(2)	107.33(18)

Table 2 Hydrogen bonded distances (Å) and angles (°) in **2** and **3**

	H···O	N–H···O	N···O
2			
N1A–H1A1···O61D	2.170	172.6(9)	3.075(12)
N1A–H1A2···O62B	2.068	170.5(9)	2.969(12)
N1B–H1B1···O61B	2.181	172.9(9)	3.086(11)
N1B–H1B2···O62D	2.072	173.1(8)	2.977(11)
N1C–H1C1···O62C	2.178	168.3(9)	3.075(11)
N1C–H1C2···O62A	2.052	163.2(9)	2.934(12)
N1D–H1D1···O61A	2.139	172.7(9)	3.044(12)
N1D–H1D2···O61C	1.996	170.4(9)	2.898(12)
3			
N1A–H1A1···O62A	2.086	153.1(6)	2.927(6)
N1A–H1A2···O62B	2.344	141.2(5)	3.106(6)
N1B–H1B1···O62B	2.058	151.9(5)	2.893(6)
N1B–H1B2···O62A	2.405	140.4(5)	3.160(6)

Note: the N-H distances were fixed at 0.91 Å. H-bonds were assigned using the Platon program[13] to interactions of the oxygen and nitrogen atoms that were < 3.12 Å.

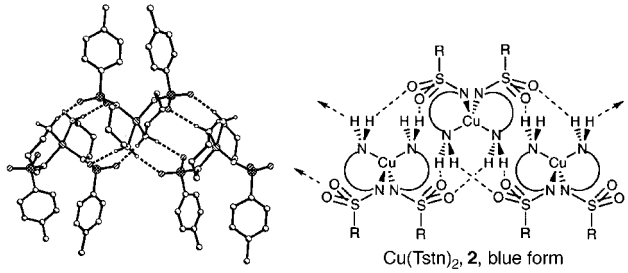

Fig. 2 Hydrogen bonded interactions in the solid state structure of **2** and a schematic representation of these interactions. Selected distances are given in Table 1.

chains of the complex extending through the structure (Fig. 2).

The asymmetric unit of the green compound, **3**, contains a single [Cu(Tstn)$_2$] molecule (Fig 3). The copper centre has a more nearly tetrahedral geometry; the dihedral angle between the two chelate planes is 58.4° and the N1–Cu–N5 chelate angles are larger, 93.3(2) and 93.7(3)°, than in **2** (average 90.9°). One of the oxygen atoms on each sulfonamide group forms two hydrogen bonds to amine protons. All of the amine protons are therefore involved in hydrogen bonds and each complex has eight S=O···H–N interactions, four as the donor and four as the acceptor. This results in the formation of a linear one dimensional hydrogen bonded polymer of [Cu(Tstn)$_2$] molecules (Fig. 4). Both **2** and **3** are very insoluble materials, dissolving only very slowly in polar solvents, reflecting the large number of intermolecular interactions. The number of hydrogen bonds that each molecule is involved in is the same in each structure. However, the mean of the O···N distances is shorter in **2** and the mean of the O···H–N angles is closer to 180°, suggesting that the hydrogen-bonded interactions are stronger than those in **3**. A survey of the CSD[8] reveals that the majority of copper(II) N_4 complexes with 1,3-diaminopropane based ligands are square planar[9] and deviation from this geometry is only observed with very bulky ligands.[6] The significant distortion toward the energetically unfavourable tetrahedral geometry observed in **2** and **3** appears to be a consequence of the system seeking the lowest free energy in the solid state *via* formation of very stable hydrogen bonding networks favoured by the ligands. This offers the intriguing possibility of controlling the electronic and magnetic properties of metal centres in the solid state using simple ligands designed to provide a matrix with unusual coordination sites for metals. Whilst such an approach is analogous to the entatic state[3] binding sites in proteins, unlike these, the unusual geometries are unlikely to be preserved in solution.

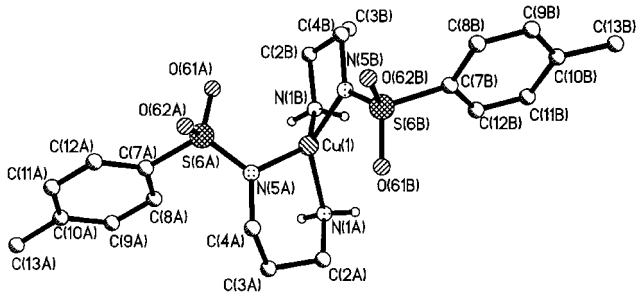

Fig. 3 Molecular structure of **3**. Only amine hydrogens are shown. Selected bond distances and angles are given in Table 1.

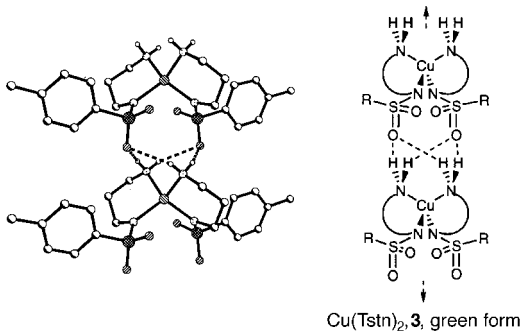

Fig. 4 Hydrogen bonded interactions in the solid state structure of **2** and a schematic representation of these interactions. Selected distances are given in Table 1.

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Notes and references

† *Experimental procedures*: **1**: this was prepared by a modification of the method described by Kirsanov and Kirsanova.[10]

2: A solution of **1** (0.228 g, 1 mmol) in boiling methanol (10 mL) was added to a solution of copper acetate hydrate (0.1 g, 0.5 mmol) also in methanol (10 mL). Immediately a dark, ink blue solution was obtained. The solution was filtered hot then allowed to cool to room temperature. Evaporation of solvent at ambient temperature over 24 h gave dark blue crystals. These were collected by filtration, washed with methanol (3 × 5 mL), then diethyl ether (2 × 5 mL) and dried *in vacuo* (22 mg, 20% yield). Crystals suitable for X-ray diffraction were obtained by evaporation of a saturated methanol solution of the complex; mp 170 °C, decomp. 200 °C (Found: C, 46.39; H, 5.60; N, 10.60. Calc. for $C_{20}H_{30}N_4CuO_4S_2$: C, 46.36; H, 5.84; N, 10.81%); UV–VIS [λ_{max}/nm (ε dm^3 mol^{-1} cm^{-1})]: dmf, 620 (135); reflectance, 495; MS (FAB, nba) *m/z* [Cu(Tstn)$_2$]$^+$ 518.

3: This complex was prepared in an identical manner to **2**. However, instead of evaporating the dark blue solution it was left to stand in a sealed vessel at ambient temperature for 48 h giving bright green crystals. These were collected by filtration, washed with methanol (3 × 5 mL), then diethyl ether (2 × 5 mL) and dried *in vacuo* (24 mg, 22% yield). Crystals suitable for X-ray diffraction could be obtained using this method; mp (18 °C decomp.) 200 °C (Found: C, 46.36; H, 5.91; N, 10.79. Calc. for $C_{20}H_{30}N_4CuO_4S_2$: C, 46.36; H, 5.84; N, 10.81%). UV–VIS [λ_{max}/nm (ε dm^3 mol^{-1} cm^{-1})]: dmf, 620 (135); reflectance, 510. MS (FAB, nba) *m/z* [Cu(Tstn)$_2$]$^+$ 518.

‡ *Crystal data:* both structures were solved by Patterson methods (DIRDIF)[11] and refined against F^2 (SHEXL-97).[12] **2**: $C_{20}H_{30}N_4CuO_4S_2$, M = 518.14, monoclinic, space group $P2_1/c$, a = 15.019(6), b = 24.783(10), c = 12.873(8) Å, β = 101.43(4)°, U = 4696(4), Z = 8, D_c = 1.466 g cm^{-3}, T = 220(2) K, μ (Cu-K$_\alpha$) = 3.26 mm^{-1}, wR_2 = 0.1923 (8543 independent reflections), R = 0.0612 [$F > 4\sigma(F)$].

3: $C_{20}H_{30}N_4CuO_4S_2$, M = 518.14, monoclinic, space group C2/c, a = 32.427(7)), b = 6.1076(15), c = 23.254(5) ≈, β = 96.30(3)°, U = 4577.6(19), Z = 8, D_c = 1.504 gcm^{-3}, T = 220(2) K, μ (Mo-Kα) = 1.171 mm^{-1}, wR_2 = 0.1157 (4050 independent reflections), R = 0.0524 [$F > 4\sigma(F)$]. CCDC 182/1246. See http://www.rsc.org/suppdata/cc/1999/1107/ for crystallographic files in .cif format.

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