

Secondary coordination sphere controlled reversible geometry reorganisations in copper(II) complexes†

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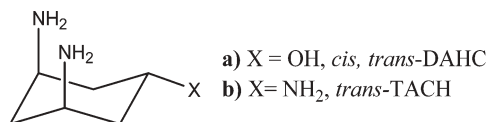
Received (in Cambridge, UK) 13th May 2004, Accepted 12th July 2004

First published as an Advance Article on the web 20th August 2004

Reversible geometry reorganisations are demonstrated by *cis*-3,5-diamino-*trans*-hydroxycyclohexane (*cis,trans*-DAHC) copper(II) fluoride complexes, with the concentration of water in the mother liquor controlling interconversion between blue crystals of 5-coordinate *syn*-[Cu(DAHC)₂F](F)·2CH₃OH·H₂O and red crystals of 4-coordinate *anti*-[Cu(DAHC)₂](F)₂·2H₂O.

The ability of copper(II) complexes to undergo structural reorganisation as a result of a mismatch between the coordination environment supplied by the ligand and that preferred by the metal centre (determined by electronic and steric effects) can lead to interesting metastable states.¹ Indeed the formation of such metastable or 'entatic' state, common to blue copper sites, has been observed in many proteins.² Similar reversible changes of coordination geometry have been observed in the small molecule complexes of several metal cations,^{3–6} and the consequent alterations in physical properties such as colour^{4–6} and magnetism⁶ are well documented. Often, such changes are induced by external stimuli including temperature,³ type of solvent^{4,6} and electrochemically or photochemically driven changes in oxidation state.⁵

In the system presented here, crystals of two simple, four and five coordinate copper(II) complexes of the ligand *cis,trans*-DAHC, interconvert *via* an unusual reversible structural reorganisation (*cis,trans*-DAHC was prepared as an analogous ligand to *cis,trans*-1,3,5-triaminocyclohexane, which itself forms a variety of discrete multinuclear complexes and coordination networks).⁷ This process involves the release or coordination of a fluoride ion coupled with rotation of one of the ligands through 180°, and occurs through a solid–solution–solid transformation controlled by the concentration of water in the mother liquor. The driving force for the transformation appears to be extremely subtle, and is governed by a delicate balance of metal–ligand, secondary coordination sphere and solvent interactions. Notably, most examples of solvent driven interconversion do not result in interchange of crystalline material, and involve changing the bulk solvent.



Blue crystals of *syn*-[Cu(DAHC)₂F](F)·2CH₃OH·H₂O (**1**)‡ were produced in a 35% yield by diffusion of diethyl ether into a methanolic solution of *cis,trans*-DAHC (0.54 mmol) and copper(II) fluoride (0.28 mmol), prepared by dissolving the ligand and copper(II) fluoride in methanol (20 ml, 0.05% water) and reducing to 3 ml in volume. Addition of a small amount of water (5 μl, 0.28 mmol) to crystals of **1** in their mother liquor (1 ml) resulted in conversion within 10 h to crystals of red *anti*-[Cu(DAHC)₂](F)₂·2H₂O (**2**)†§ isolated in a yield of 24%. This transformation could be reversed by diffusion of diethyl ether into **2** redissolved in dry methanol (distilled from magnesium). The entire process was captured photographically (Fig. 1), showing that the

transformation proceeds by dissolution of **1** and recrystallisation as **2**. It is interesting to note that compound **2** can also be synthesised directly from methanol containing a higher percentage of water.

The structure of the complex cation in **1** (Fig. 2) shows near ideal square pyramidal geometry, with the *cis,trans*-DAHC ligands occupying the equatorial plane at an average Cu–N distance of 2.0275(14) Å and the copper centre located 0.0647(9) Å to the fluorine atom side of the N₄ plane. The DAHC ligands are arranged *syn* to each other. Weaker coordination of the axial fluoro ligand is indicated by the longer Cu–F bond length of 2.2944(10) Å.

In the solid state, the cations are arranged in 2D hydrogen bonded layers running parallel to the crystallographic *bc* plane, with a minimum interlayer distance of about 2.40 Å (measured hydrogen atom to hydrogen atom). An intricate hydrogen bonded network leads to formation of the 2D layers (Fig. 3). Cations are stacked parallel to the crystallographic *c* axis, with the fluoro ligands accepting two hydrogen bonds from the hydroxyl groups of the next cation in the stack and a further hydrogen bond from a water molecule. To connect the 1D stacks into 2D layers, solvent molecules and fluoride counterions fit between the stacks and link them *via* hydrogen bonds. The fluoride anions accept five hydrogen bonds in a pyramidal geometry, four are from amines in the cation stacks on either side and the fifth is donated by a water molecule. A full summary of the hydrogen bonding interactions and their lengths is displayed in Table 1.

Four coordinate compound **2** (Fig. 2 and 4) has near ideal square planar geometry, with an average Cu–N distance of 2.0191(10) Å and *anti* arrangement of the DAHC ligands; note both fluoride

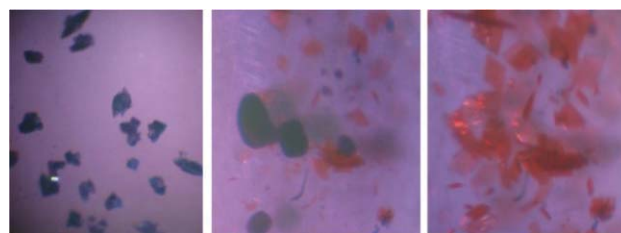


Fig. 1 Transformation of crystals from **1** to **2**, 10 min (LHS), 5 h (middle) and 8 h (RHS) after addition of water. The middle and RHS photos are of the same position, showing dissolution of **1** and recrystallisation as **2**.

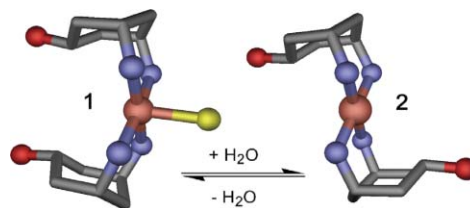


Fig. 2 Representation of the crystal structures of *syn*-[Cu(DAHC)₂F] in **1** and *anti*-[Cu(DAHC)₂]²⁺ in **2**. Hydrogen atoms are omitted. Carbon atoms are grey, oxygen red, nitrogen blue, fluorine yellow and copper is copper. This colour scheme is retained in all figures.

† Electronic supplementary information (ESI) available: full experimental details. See <http://www.rsc.org/suppdata/cc/b4/b407229d/>

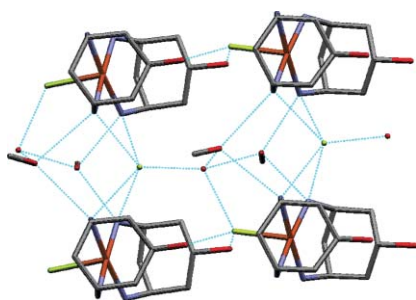


Fig. 3 Hydrogen bonding in a layer of *syn*-[Cu(DAHC)₂F](F)·2CH₃OH·H₂O (**1**). Hydrogen atoms are omitted for clarity and hydrogen bonds are shown heavy atom to heavy atom.

Table 1 Summary of hydrogen bonding interactions per formula unit in the two complexes. ESDs ≤ 0.0020 Å

Interaction	Complex 1		Complex 2	
	Number	Average D...A length/Å	Number	Average D...A length/Å
RNH ₂ ...F	4	2.8365	4	2.7920
OH ₂ ...F	1	2.5969	2	2.5919
ROH...F	0	—	2	2.5449
OH ₂ ...F(Cu)	1	2.6941	0	—
ROH...F(Cu)	2	2.6153	0	—
RNH ₂ ...OH ₂	0	—	4	2.9697
MeOH...OH ₂	2	2.7515	0	—
OH ₂ ...HOR	0	—	2	2.8053
RNH ₂ ...HOMe	4	3.0055	0	—
Total (to F)/overall average	14(8)	2.8138	14(8)	2.7808

ions are non-coordinated and are situated *ca.* 3.9 Å away from the copper centre. Again, the cations are arranged in closely packed 2D hydrogen bonded layers, this time running parallel to the crystallographic *ab* plane, with a minimum interlayer distance of about 2.69 Å. These 2D layers are built up from 1D stacks of cations that bisect the plane of the crystallographic *a* and *b* axes through the origin. Hydrogen bonds generate the stacks by linking the amines of one cation to the hydroxyls of another, *via* fluoride ions and water molecules. Further hydrogen bonds to counterions and solvent molecules link the stacks into layers. The clearest difference to the hydrogen bonded network of **1** is the replacement of a mixture of 5-coordinate hydrogen bonded fluoride ions and 3-coordinate fluoro ligands with 4-coordinate fluorides. These fluorides each accept two hydrogen bonds from amines, one from water and one from the ligand hydroxyl group.

Detailed study of the two structures suggests driving forces for the reversible transformation. This is because in **1**, the electrostatic interactions appear dominant as demonstrated by the shorter Cu–F contact. However, in **2**, the stability comes from the stronger hydrogen bonding interactions. In Table 1 it can be seen that while the two networks contain an equal number of hydrogen bonding

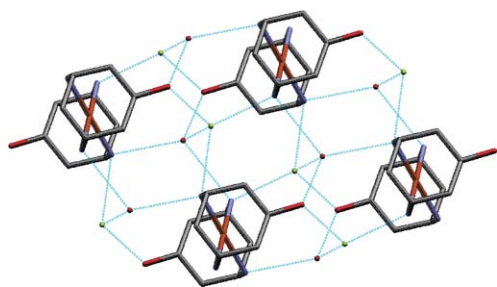


Fig. 4 Hydrogen bonding in a layer of the *syn*-[Cu(DAHC)₂](F)₂·2H₂O (**2**). Hydrogen atoms are omitted for clarity and hydrogen bonds are shown heavy atom to heavy atom.

interactions, in **2** they are generally shorter, implying stronger bonds and greater stability (this analysis is supported by the D–H...A angles, which are closer to ideality in **2**). Therefore, the reversible reorganisation may be the result of a fine balance between the stability of the hydrogen bonded network and the geometrical preferences of the metal centre. Departure of the fluoro ligand from **1** implies a reduction in stability, which is perhaps compensated by a more stable network and slightly shorter Cu–N bonds in **2**.

The interconversion of **1** and **2** was also examined by UV–vis spectroscopy, which indicated that the dissolved species are either identical or interchange rapidly (the peak positions of **1** and **2** are identical to within 3 nm), with the concentration of water controlling which form is more favourable in the solid state. Although this effect of water can be explained by its ability to hydrogen bond to anions, preventing coordination,⁸ it is more surprising that the change can occur after the complex has already crystallised. In addition, the tight interlayer separation of the 2D hydrogen-bonded network in **1** implies that conversion from **1** to **2** is triggered by the additional water molecules hydrogen bonding to fluorides on the crystal surface, leading to dissolution.

In conclusion, two simple complexes have been shown to undergo an interconversion controlled by an extremely subtle change in their surrounding environment. This appears to be due to a balance between the geometrical preferences of the metal centre and the stability of the hydrogen bonded network. Further studies will be conducted to fully understand the driving forces and mechanism of this reversible transformation. JF thanks the EPSRC and DL the Leverhulme Trust for funding.

Notes and references

‡ Analysis of C₁₂H₃₀CuF₂N₄O₃ (**1**, MeOH removed): calcd (found) %: C 37.94 (38.14), H 7.96 (8.63), N 14.75 (14.51). FTIR (KBr disc) cm⁻¹: 3420 s, 3201 s, 3040 s, 2946 s, 2896 s, 1614 m, 1368 m, 1226 m, 1075 s, 919 m. UV–vis (dry MeOH) nm (L mol⁻¹ cm⁻¹): 356 (1837), 577 (80). Crystal data for *syn*-[Cu(DAHC)₂F](F)·2CH₃OH·H₂O (C₁₄H₃₈CuF₂N₄O₅) (**1**): monoclinic, *Pc*, *a* = 10.2410(2) Å, *b* = 7.0340(1) Å, *c* = 14.9794(2) Å, β = 111.497(1)°, *V* = 1003.98(3) Å³, *Z* = 2, ρ_{calcd} = 1.468 g cm⁻³, μ(Mo–Kα) = 1.137 mm⁻¹, 12637 reflections measured, 3615 unique which were used in all calculations. Final *R*1 = 0.0210 and *wR*2 = 0.0525 (all data). Data were measured at 150(2) K on a Nonius KappaCCD diffractometer [λ(Mo–Kα) = 0.71073 Å], graphite monochromator. Structure solution and refinement were performed by using SHELXS-97 and SHELXL-97 *via* WinGX.⁹

§ Analysis of C₁₂H₃₂CuF₂N₄O₄ (**2**): calcd (found) %: C 36.22 (36.01), H 8.11 (7.94), N 14.08 (13.84). FTIR (KBr disc) cm⁻¹: 3417 s, 3197 s, 3029 s, 2929 s, 2894 s, 1614 m, 1367 m, 1224 w, 1074 s, 917 w. UV–vis (MeOH) nm (L mol⁻¹ cm⁻¹): 359 (1940), 581 (80). Crystal data for *anti*-[Cu(DAHC)₂](F)₂·2H₂O (C₁₂H₃₂CuF₂N₄O₄) (**2**): triclinic, *P1̄*, *a* = 7.0993(2) Å, *b* = 7.1315(2) Å, *c* = 10.0059(3) Å, α = 108.567(1)°, β = 92.233(1)°, γ = 112.912(1)°, *V* = 434.56(2) Å³, *Z* = 1, ρ_{calcd} = 1.521 g cm⁻³, μ(Mo–Kα) = 1.300 mm⁻¹, 7086 reflections measured, 1974 unique which were used in all calculations. Final *R*1 = 0.0197 and *wR*2 = 0.0524 (all data). Data collection and structure solution as for compound **1**. CCDC 239722 and 239723. See <http://www.rsc.org/suppdata/cc/b4/b407229d/> for crystallographic data in .cif or other electronic format.

- S. H. B. Gray and E. I. Solomon, in *Copper Proteins*, ed. T. G. Spiro, Wiley, New York, 1981, pp. 1–39.
- R. J. P. Williams, *Eur. J. Biochem.*, 1995, **234**, 363.
- R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.
- G. Pilloni, G. Valle, C. Corvaja, B. Longato and B. Corain, *Inorg. Chem.*, 1995, **34**, 5910.
- A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni and B. Ventura, *J. Am. Chem. Soc.*, 1997, **119**, 12114.
- (a) Y. Sato, S. Ohkoshi, K. Arai, M. Tozawa and K. Hashimoto, *J. Am. Chem. Soc.*, 2003, **125**, 14590; (b) W. Fujita and K. Agawa, *J. Am. Chem. Soc.*, 1997, **119**, 4563.
- G. Seeber, B. Kariuki and L. Cronin, *Chem. Commun.*, 2002, 2912; A. L. Pickering, G. Seeber, D.-L. Long and L. Cronin, *Chem. Commun.*, 2004, 136.
- L. Carlucci, G. Ciani and D. Proserpio, *Chem. Commun.*, 2004, 380.
- L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.