Novel supramolecular self-assembly of a transition-metal–organo network based on simultaneous coordinate- and hydrogen-bond interactions

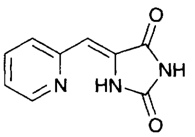
Mubarik M. Chowdhry, D. Michael P. Mingos, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY

The crystal structure of [Cu(pyhy)$_2$·2melamine] is reported; this supramolecular complex is simultaneously self-assembled *via* coordinate- and hydrogen-bond formation using superheating induced by microwave dielectric heating.

We have previously shown how the application of molecular recognition principles based on triple hydrogen bonding resulted in the crystal engineering of aggregates based on bifunctional transition-metal complexes and organic molecules containing complementary arrangements of hydrogen-bond donors and acceptors.[1] These systems are of great interest because the incorporation of transition-metal ions into such systems introduces magnetic, optical and conductive properties characteristic of these ions into materials with potential for nonlinear optical, conducting, and ferromagnetic properties. This work provides a new direction in the area of organic supramolecular chemistry[2] and builds on the elegant work of Whitesides,[3] Lehn,[4] and Hamilton[5] and their coworkers.

The didentate ligand 5-(2-pyridylmethylene)hydantoin (Hpyhy) has attracted our interest as a potential bifunctional ligand with the necessary hydrogen-bonding characteristics.[6] It has the appropriate conformation to form stable complexes with transition metals.[6] These complexes also retain the ability to form complementary hydrogen bonds with nucleotide and related bases through the C(O)–NH–C(O) moiety on the hydantoin ring.[7]



5-(2-pyridylmethylene)hydantoin (Hpyhy) (*Z*-conformation)

However, the ability of these complexes to form complementary triple hydrogen bonds with these bases is hampered by their poor solubilities. We have found that microwave dielectric heating which superheats the solutions by 70–100 °C improves their solubility characteristics significantly.

Here we report what we believe is the first example of a 'one-pot' self-assembly, by a combination of coordinate-bond formation and hydrogen bonding, of the co-crystallised transition-metal complex–organic molecule hydrogen-bonded network, [Cu(pyhy)$_2$·2melamine] **1**.

Complex **1** was obtained by partially dissolving Hpyhy (0.053 mmol) in MeOH (20 cm^3) followed by the addition of solid melamine (0.053 mmol) and $CuCl_2\cdot 2H_2O$ (0.026 mmol). The reaction mixture was heated in a microwave oven at 130 °C for 1 h in a sealed Teflon container. The solution was cooled slowly to room temperature and the resulting crystalline precipitate was filtered and air dried (Scheme 1). Crystals suitable for single-crystal X-ray diffraction studies were extracted from the precipitate. Conventional reflux techniques in ethanol failed to produce the hydrogen-bonded adduct and only the components were isolated.

$$CuCl_2\cdot 2H_2O + 2Hpyhy + 2melamine \xrightarrow{i} [Cu(pyhy)_2\cdot 2melamine]$$

Scheme 1 *Reagents and conditions*: MeOH, 130 °C, microwave irradiation, 1 h

In Fig. 1 the X-ray crystal structure of **1**† shows that the desired coordination and aggregation has been achieved with the copper atom being coordinated to two pyhy ligands which are in turn involved in an ADA≡DAD (A = hydrogen-bond acceptor, D = hydrogen-bond donor) arrangement with melamine molecules. The copper atom is, as expected in the light of previous metal complexes formed with pyhy,[6] coordinated to the N(1) and N(8) centres. The complex has crystallographic C_2 symmetry. The coordination geometry is intermediate between square planar and tetrahedral. The N(1)–Cu–N(1a) and N(8)–Cu–N(8a) angles are 152.7(1) and 134.2(1)°, respectively, *cf.* 160.3 and 158.0° in [Cu(pyhy)Cl(OH$_2$)]. The remaining N–Cu–N angles are in the range 93.6(1)–97.0(1)°. The Cu–N distances, Cu–N(1) 1.940(2), Cu–N(8) 2.046(3) Å, are very similar to those in the related [Cu(pyhy)Cl(OH$_2$)] complex [1.962(2) and 2.028(3) Å].[6] The pyridyl and hydantoin rings are almost coplanar (2° twist about the single-bond linkage) and the internal C(5)–C(6)–C(7) angle [127.5(3)°] and the associated non-bonded N(1)···N(8) separation (2.91 Å) are within the ranges previously observed.[6] The planes of the two coordinated ligands are twisted by *ca.* 53.0° to each other.

The triple hydrogen bonding between the hydantoin and melamine units comprises one short [N(3)···N(20) 2.77 Å], and two long [N(21)···O(4) 3.11, N(25)···O(2) 3.21 Å] linkages (**b**, **a** and **c**, respectively, in Fig. 1). The weakness of the outer two interactions (**a**, **c**) is a consequence of the slight geometric mismatch between the five-membered ring (ADA) on the pyhy ligand and the six-membered ring (DAD) on the melamine component. However, despite this mismatch the cooperative effect of the three hydrogen bonds results in the relatively shorter and stronger N(H)···N interaction. The hydantoin and melamine rings are approximately co-planar, there being a *ca.* 5° twist between them about the NH···N direction. The 1:2

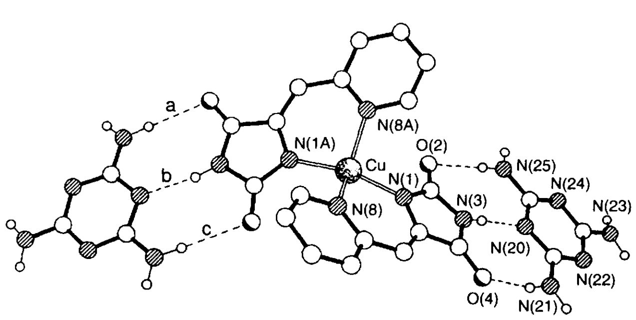


Fig. 1 Molecular structure of [Cu(pyhy)$_2$·2melamine] showing the distorted tetrahedral coordination geometry for the copper atom and the intermolecular hydrogen bonds between the complexed ligand pyhy and melamine. Selected bond lengths (Å): Cu–N(1) 2.046(3), Cu–N(8) 1.940(2). Hydrogen bonding geometries: N···N/O, H···N/O distances (Å), N–H···O/N angles (°): **a** 3.11, 2.23, 167; **b** 2.77, 1.87, 171; **c** 3.21, 2.31, 178.

[Cu(pyhy)$_2$·2melamine] triply hydrogen-bonded complex is cross-linked to adjacent complexes *via* pairs of additional N(H)···N hydrogen bonds (**e**, 3.00 Å) employing one of the non-utilised amino hydrogen atoms in one melamine molecule and the ring nitrogen atoms of another related by a crystallographic C_2 axis. The planes of adjacent hydrogen-bonded melamine rings are significantly tilted by 49° with respect to each other and this coupled with the twists of coordinated pairs of pyhy ligands results in hydrogen-bonded sheets which are wave-like in nature as shown in Fig. 2. The lines of hydrogen-bonded melamine molecules form the troughs and the vectors passing through the Cu centres form the crests. These centrosymmetrically related corrugated sheets (Fig. 3) are cross-linked *via* further NH···O hydrogen bonds (**d**, 2.91 Å) between one of the hydrogen atoms of the amino group not involved in 'sheet formation' in one layer and one of the hydantoin oxygen atoms in another and *vice versa*. The remaining amino hydrogen atom is not involved in any significant intra- or inter-complex hydrogen bonding. Lattice-translated sheets (in the crystallographic *b* direction) are loosely linked (3.19 Å) *via* secondary weak CH···O hydrogen bonds (H···O 2.40 Å, C–H···O 139°) between the *ortho*-pyridyl CH groups in one sheet and the hydantoin carbonyl oxygen atoms in another and *vice versa*.

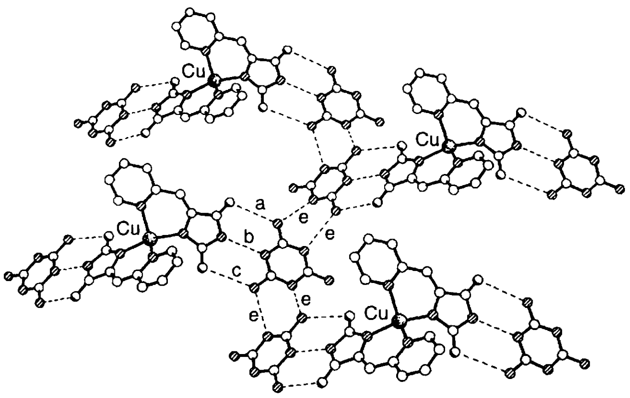


Fig. 2 Part of the hydrogen-bonded corrugated sheets formed by [Cu(pyhy)$_2$·2melamine] showing the intermolecular interactions between adjacent melamine units. The additional hydrogen-bond geometry **e**: N···N, H···N, distances, N–H···N angle, 3.00, 2.11 Å, 175°.

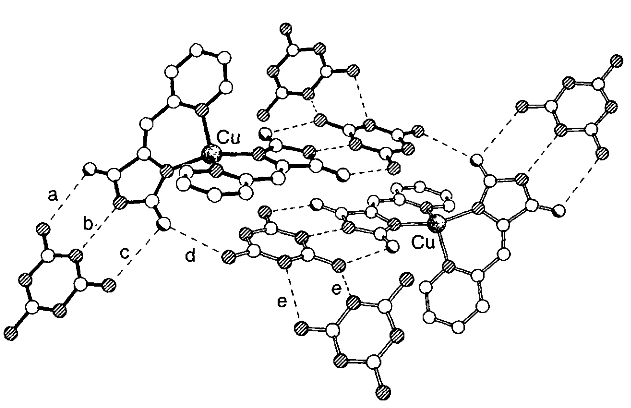


Fig. 3 Part of a pair of cross-linked hydrogen-bonded sheets. The additional hydrogen bond **d** has parameters N···O 2.91, H···O 2.01 Å, N–H···O 176°.

We have shown that, in a single step, the ligand Hpyhy fulfils its bifunctional role by generating a transition-metal complex as part of a multidimensional co-crystallised network, self-assembled by a combination of coordinate- and hydrogen-bond formation. In addition we have demonstrated that the same methodology can be extended to a range of substituted melamine derivatives.[7]

The EPSRC is thanked for financial support and BP plc for generously endowing D. M. P. M.'s Chair.

Footnote

[†] *Crystal data* for $C_{24}H_{24}CuN_{18}O_4·0.5H_2O$, M = 701.2, monoclinic, space group $P2/n$, a = 12.070(3), b = 7.694(2), c = 15.672(4) Å, β = 99.64(2)°, U = 1434.9(6) Å^3, Z = 2 (the molecule has crystallographic C_2 symmetry), D_c = 1.623 g cm^{-3}, μ(Cu-Kα) = 16.90 cm^{-1}, λ = 1.54178 Å, F(000) = 720. A green platy crystal of dimensions 0.02 × 0.11 × 0.14 mm was used. Data were measured on a Siemens P4 rotating anode diffractometer with graphite-monochromated Cu-Kα radiation (ω-scans). 2137 Independent reflections were measured ($2\theta \leqslant 120°$) of which 1838 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically by full-matrix least squares using absorption corrected data to give R = 0.041, R_w = 0.046 [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/14.

References

1 A. D. Burrows, C.-W. Chan, M. M. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329 and references therein.

2 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; M. Mascal, *Contemp. Org. Synth.*, 1994, **1**, 31; J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383; D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229 and references therein; D. B. Amabilino, J. F. Stoddart and D. J. Williams, *Chem. Mater.*, 1994, **6**, 1159.

3 J. A. Zerkowski, C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 9025; C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1991, **113**, 712; J. A. Zerkowski, C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1992, **114**, 5473; C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 905; C. T. Seto, J. P. Mathias and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 1321.

4 J.-M. Lehn, M. Mascal, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 479; J.-M. Lehn, M. Mascal, A. DeCian and J. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1992, 461.

5 S. K. Chang and A. D. Hamilton, *J. Am. Chem. Soc.*, 1988, **110**, 1318; S. J. Geib, S. C. Hirst, C. Vincent and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1991, 1283; F. Garcia-Tellado, S. J. Geib, S. Goswami and A. D. Hamilton, *J. Am. Chem. Soc.*, 1991, **113**, 9265; E. Fan, S. A. Van Arman, S. Kincaid and A. D. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 369; S. J. Geib, C. Vincent, E. Fan and A. D. Hamilton, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 119.

6 M. M. Chowdhry, A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1995, 1521.

7 M. M. Chowdhry and D. M. P. Mingos, unpublished work.

Received, 28th December 1995; Com. 5/08398B