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Synthesis and structure of a copper(II) melamine complex, $[Cu(C_3H_6N_6)(\mu\text{-}OCH_3)(ONO_2)(HOCH_3)]_2$, with direct Cu–melamine coordination

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The title compound, which was obtained by an *in situ* conversion of diacetylmelamine to melamine in the presence of copper(II) nitrate, appears to be the first structurally characterised example of a melamine complex with direct metal–melamine bonding; complexes are linked *via* N–H···O and O–H···N hydrogen bonds to form sheets.

Melamine, first obtained by Liebig in 1834,[1] and its derivatives have long had very extensive industrial applications. More recently, attention has also focused on the use of melamine to form supramolecular networks by hydrogen bonding either to other organic molecules or to organic ligands coordinated to metal ions.[2] Although metal complexes with melamine have been reported,[3] so far as we are aware,† there has been no X-ray structurally characterised example of a compound containing a direct coordinate bond between melamine and a transition metal ion. We report here the structure of a copper(II) complex with direct bonding of melamine to the metal ion.

Diacetylmelamine[4] (0.2 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.2 mmol) were refluxed in methanol (10 cm^3) for *ca.* 5 minutes. The resulting solution was filtered and allowed to stand at room temperature for a week, during which time bluish-green crystals $\{([Cu(C_3H_6N_6)(\mu\text{-}OCH_3)(ONO_2)(HOCH_3)]_2\mathbf{1})\}$ suitable for X-ray characterisation had formed (52% yield). X-Ray analysis‡ on this product revealed that the reaction had resulted in the conversion of the diacetylmelamine to melamine, presumably by the well-known metal catalysed solvolysis of amides, which is particularly strong for copper(II),[5] and formation of the binuclear complex (**1**) shown in Fig. 1.

The complex has crystallographic C_i symmetry, the two copper centres being linked symmetrically [Cu–μ-O 1.933(2) and 1.932(2) Å] by the oxygen atoms of two methoxide bridges; the non-bonded Cu···Cu separation is 3.0016(8) Å. The coordination geometry at each copper centre is distorted square pyramidal, the basal plane comprising the two bridging methoxide oxygen atoms, a nitrate oxygen atom and a ring nitrogen atom of a coordinated melamine molecule; the apical coordination site is occupied by a weakly bonded methanol molecule [Cu–O(7) 2.426(2) Å]. The atoms comprising the basal coordination plane are coplanar to within 0.08 Å and the copper atom is displaced by only 0.14 Å out of the plane in the direction of the apical methanol oxygen atom, reflecting the weakness of that linkage. The plane of the melamine ligand is rotated by *ca.* 67° out of the basal coordination plane, an orientation that is clearly in part a consequence of a pair of intra-complex N–H···O hydrogen bonds (**a** and **b** in Fig. 1) and a minimis-

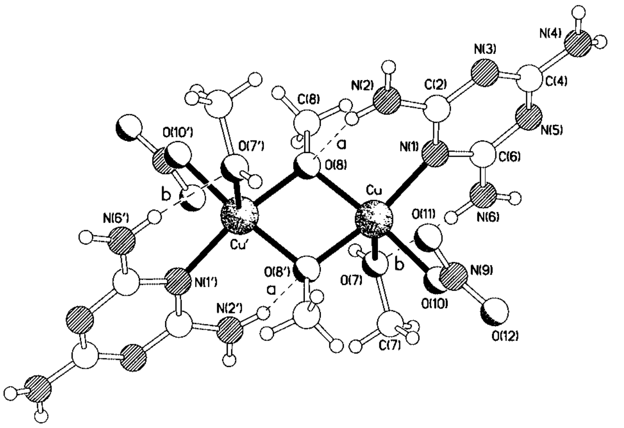

Fig. 1 The molecular structure of **1**. Selected bond lengths (Å) and angles (°) are: Cu–N(1) 2.010(2), Cu–O(8) 1.933(2), Cu–O(8′) 1.932(2), Cu–O(10) 1.996(2), Cu–O(7) 2.426(2); N(1)–Cu–O(8) 93.88(9), O(8)–Cu–O(8′) 78.10(9), O(8′)–Cu–O(10) 95.32(9), N(1)–Cu–O(10) 93.88(9). Hydrogen bonding geometries: **a**, N···O, H···O 2.89, 2.10 Å, N–H···O 146°; **b**, 2.94, 2.04 Å, 174°.

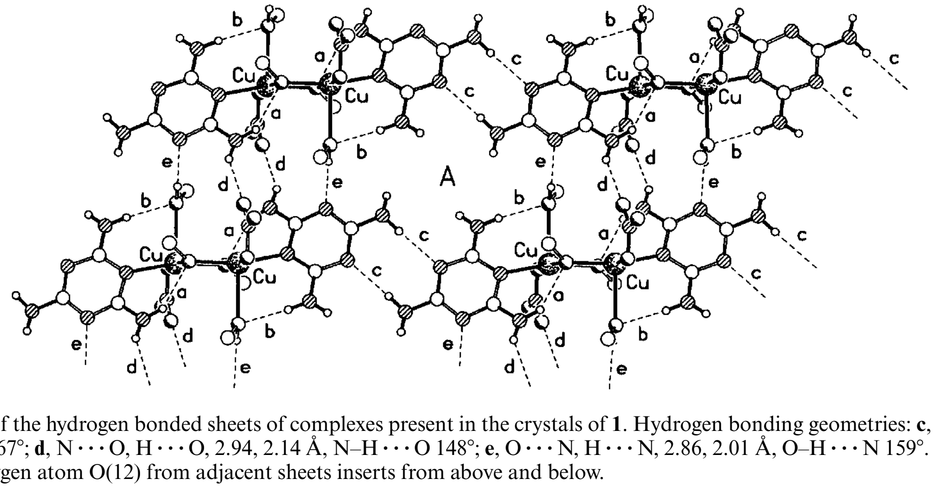

Fig. 2 Part of one of the hydrogen bonded sheets of complexes present in the crystals of **1**. Hydrogen bonding geometries: **c**, N···N, H···N, 3.05, 2.16 Å, N–H···N 167°; **d**, N···O, H···O, 2.94, 2.14 Å, N–H···O 148°; **e**, O···N, H···N, 2.86, 2.01 Å, O–H···N 159°. **A** represents the region where the nitrate oxygen atom O(12) from adjacent sheets inserts from above and below.

ation of steric interactions. This complex, we believe, presents the first example of a structurally characterised melamine compound with direct melamine–transition metal bonding. The Cu–N distance [2.010(2) Å] is at the short end of the range found for *e.g.* copper–pyridine bonds in five-coordinate complexes,[6] but it is comparable to those seen in copper(II) complexes with 2,6-dimethylpyridine (2,6-Me_2py), where the Cu–N distances range typically between 1.997 Å in Cu(2,6-$Me_2py)_2Br_2$[7] and 2.046 Å in Cu(2,6-$Me_2py)_2(CH_3CO_2)_2$.[8]

It is interesting that there is a noticeable asymmetry in the two external angles at N(1) with that proximal to the shorter hydrogen bond (**a**, to the methoxide oxygen) being contracted [117.6(2)°], whereas that proximal to the weaker hydrogen bond (**b**, to the methanol oxygen) is expanded [126.4(2)°]. There is also a small pyramidalisation at the nitrogen atom, which lies 0.011 Å out of the plane of its substituents.

Centrosymmetrically related pairs of dimers are linked *via* N–H···N hydrogen bonds (**c**, in Fig. 2) between one of the hydrogen atoms of the amine group *para* to the coordinated nitrogen atom in one molecule and the ring nitrogen atom N(5) of another, and *vice versa*, to form tapes. These tapes are then cross-linked by N–H···O and O–H···N hydrogen bonds (**d** and **e** in Fig. 2) to form extended, slightly corrugated sheets. Adjacent sheets are mutually offset and very weakly linked *via* N–H···O hydrogen bonds [N···O 3.18 Å, H···O 2.39 Å] between amine hydrogen atoms and nitrate oxygen atoms, O(12), which are inserted from above and below into the 'vacant' region indicated by **A** in Fig. 2.

In view of the serendipitous synthesis of this crystalline product, the apparent absence hitherto of other fully structurally characterised, directly coordinated melamine complexes may simply reflect difficulties on obtaining suitable crystalline products by a more direct approach.

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Notes and references

† A search of the April 1999 release (517) of the Cambridge Crystallographic Database[6] revealed no examples.

‡ Crystal data for **1**: $C_{10}H_{26}N_{14}O_{10}Cu_2$, $M = 629.5$, triclinic, $P\bar{1}$ (no. 2), $a = 7.861(1)$, $b = 7.938(1)$, $c = 10.487(1)$ Å, $\alpha = 89.94(1)$, $\beta = 81.78(1)$, $\gamma = 70.11(1)°$, $V = 608.33(7)$ Å^3, $Z = 1$ (the complex has crystallographic C_i symmetry), $D_c = 1.718$ g cm^{-3}, μ(Cu-Kα) = 28.5 cm^{-1}, $F(000) = 322$, $T = 293$ K; blue rhombs, 0.40 × 0.37 × 0.25 mm, Siemens P4/PC diffractometer, ω-scans, 1957 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically (the hydrogen atoms were refined isotropically subject to O–H and N–H distance constraints) using full matrix least-squares based on F^2 to give $R_1 = 0.036$, $wR_2 = 0.092$ for 1859 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 126°$] and 192 parameters. CCDC reference number 186/1588. See http://www.rsc.org/suppdata/dt/1999/2899/ for crystallographic files in .cif format.

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