Modification of supramolecular motifs: perturbation of the structure of an extended hydrogen-bonded biuret array by interaction with an intercalated copper complex and methanol molecules†

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The almost planar sheets formed by hydrogen bonding between biuret molecules become significantly more folded when intercalated bis{di(methoxycarbimido)amine}-copper(II) bromide, methanol and acetonitrile molecules are introduced into the lattice; an examination of the crystal structure suggests that selective control of the perturbation of the biuret sheets may be possible through appropriate variation of the intercalating species.

Crystal engineering, involving the self-assembly of discrete or extended structures using supramolecular interactions, particularly hydrogen bonding, is an expanding area of interest in chemistry.[1] The assembly of organic molecular solids, the aggregation of metal complexes and organic molecules, and the self-association of metal complexes have all been demonstrated to yield interesting supramolecular entities.[2] These molecular assemblies have potential applications in a number of areas of materials science, including use as non-linear optical materials. For many such applications the possibility of fine tuning an assembly is a desirable goal, and this might be accomplished by varying the molecular components through the substitution of atoms or groups. As an example, a hydrogen acceptor carbonyl group could be changed to a hydroxy group that can function both as a donor and acceptor.[3] A second approach is to insert small molecules or ions into the molecular lattice, such that the original motif is perturbed but not entirely disrupted. In this communication we report a modification of the well-known 'sheet' structure that occurs in crystals of biuret, by the intercalation of a metal complex.

The structure of biuret hydrate was established by Hughes, Yakel and Freeman[4a] who showed that the biuret molecules lie in slightly buckled sheets, each molecule having one intramolecular hydrogen bond and being joined to three neighbouring molecules by N · · · H6O hydrogen bonds. The sheets contain holes bounded by six biuret molecules and these holes align to form channels running through the structure. It is in these channels that water molecules lie in zigzag chains. The geometry of the sheet has been reported to vary a little with the extent of hydration of the crystal.[4b] We describe here the formation of crystals which contain sheets of biuret molecules assembled in the same general manner as in biuret hydrate, but in which there is a significantly increased corrugation of the sheet structure.

The labile complex, bis(biuret)copper(II) bromide, **1**, was prepared from biuret and copper(II) bromide[5] and bis{di(methoxycarbimido)aminato}copper(II), **2**, was prepared by the addition of methanol to dicyanimide in the presence of zinc chloride followed by the displacement of zinc by copper(II) using an ammoniacal solution of copper(II) sulfate.[6] A solution of **1** in methanol was mixed with a solution of **2** in acetonitrile. Blue crystals suitable for X-ray crystallography grew from the mixture on cooling the latter at −18 °C in a freezer; yield, 20%.‡

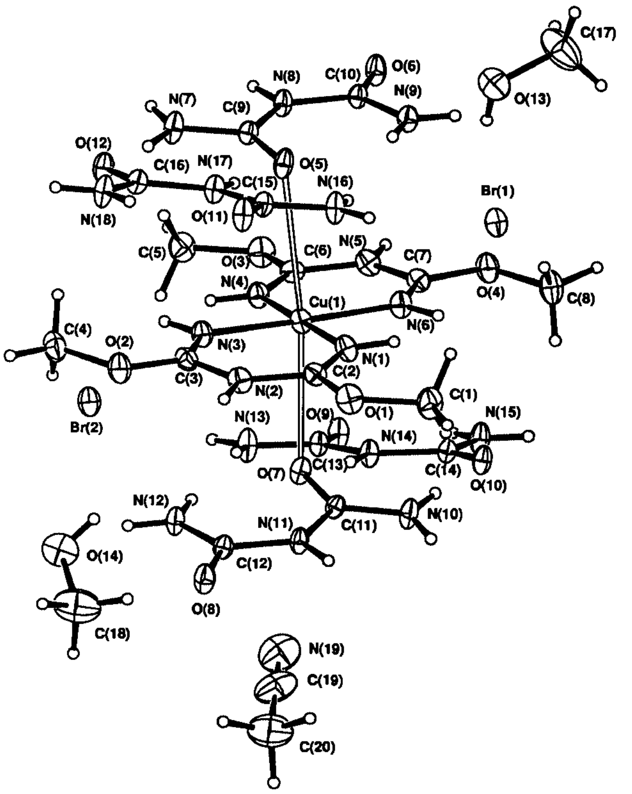

Fig. 1 ORTEP[7] depiction of the asymmetric unit contents of the bis{di(methoxycarbimido)amine}copper(II) bromide/biuret structure (methanol and acetonitrile solvate), with atomic displacement ellipsoids shown at the 25% level.

An ORTEP[7] depiction and the numbering scheme for the asymmetric unit components of the structure are given in Fig. 1. The crystal structure shows that complex **1** has disassembled in the reaction mixture and that the neutral complex **2** has gained two protons, one each on N(2) and N(4), to form bis{di(methoxycarbimido)amine}copper(II) dications, **3**. Two biuret molecules weakly coordinate to complex **3**, with the O(5)–Cu(1) and O(8)–Cu(1) bond lengths being 2.972(3) and 2.777(3) Å, respectively, and with an O–Cu–O bond angle of 173.2(1)°. The asymmetric unit also contains two methanol solvate molecules and an acetonitrile molecule with a 0.8 site occupancy, thus the new product has the formulation $[Cu(C_4H_9N_3O_2)_2(C_2H_5N_3O_2)_2]Br_2{\cdot}2C_2H_5N_3O_2{\cdot}2CH_3OH{\cdot}0.8CH_3CN$.§

The biuret molecules have been incorporated into the structure in sheets similar to those found in biuret hydrate. The biuret hydrate structure has sheets of hydrogen-bonded biuret molecules stacked in the (2,0,0) planes; the least squares plane of the molecule forms a dihedral angle of 7.3(1)° with the stacking plane. The present structure has biuret molecules and bromide ions stacked in the (0,0,0) and (0,0,2) planes, together

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/a9/a909359a/

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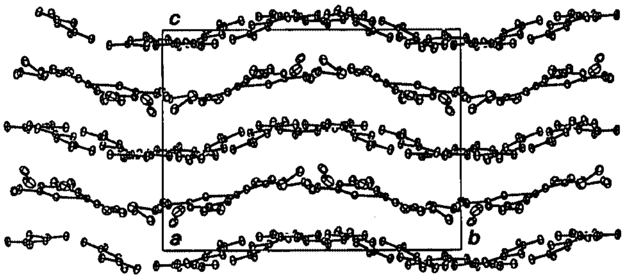

Fig. 2 ORTEP projection down the *a* axis of the unit cell of the bis{di(methoxycarbimido)amine}copper(II) bromide/biuret structure, showing the wave-like appearance of the layers in the structure.

with inter-leaved layers of complex **3** and solvate molecules in the (0,0,4) planes. The least squares planes of the two non-co-ordinated biuret molecules form dihedral angles of 3.1(1) and 7.6(1)° with the stacking plane, whereas the co-ordinated biuret molecule planes form dihedral angles of 20.1(1) and 25.2(1)° with the stacking plane.

In both the biuret structure and the structure of its adduct with **3**, the net effect of the inclined molecule planes is that the sheets have a corrugated or wave like appearance (Fig. 2). The 'amplitude' of the 'waves' in the biuret structure is approximately 0.4 Å, and in its adduct with **3** about 0.8 Å. In both cases the 'wavelength' is the length of the *b* axis, which is 17.78(2) Å for the biuret unit cell and 18.1222(7) Å for the unit cell of the adduct species. In the latter structure the non-co-ordinated biuret molecules can be regarded as forming flattened wave peaks and troughs, with the co-ordinated biuret molecules defining the wave faces and backs.

The equatorial co-ordination least squares plane of complex **3** forms dihedral angles of 13.2(1) and 18.6(1)° with the least squares plane of the two axially co-ordinated biuret molecules and 8.2(1) and 7.0(1)° with the least squares planes of the two non-co-ordinated biuret molecules. The inclination of the co-ordinated biuret molecules with respect to the copper co-ordination plane reduces contact with the equatorial ligands of complex **3**. The tilting of the non-co-ordinated biuret appears to arise similarly as a result of moderate hydrogen bonding to the co-ordinated biuret. The N(7) to O(12) and N(17) to O(5) donor–acceptor distances are 2.866(4) and 2.868(4) Å, and the N(14) to O(7) and N(10) to O(10) distances are 2.849(4) and 2.899(4) Å, respectively. It seems likely that the intercalation and co-ordination of complex **3** is responsible for (or significantly contributes to) the increased amplitude of the waves in the biuret sheets, relative to that found in biuret hydrate.

In the biuret hydrate structure, holes in the biuret sheets define channels occupied by the water molecules, and similar channels contain the bromide ions and solvate molecules in the present structure (Fig. 3). Like the water molecules in biuret hydrate, the bromide ions have a zigzag pattern along the channels, with Br to Br separations of 7.03 and 7.24 Å (clearly, much too long for any interaction) and a Br–Br–Br zigzag angle of 140.8°. The holes in the biuret sheets in this structure are slightly more open than those in biuret, presumably to accommodate the bromide ion, and the hole boundary is more ruffled. There are eight hydrogen bonds per molecule in the biuret hydrate structure, and only six in the adduct structure, with the intermolecular O(1) to N(1) distance increasing from 3.16 to 3.35 Å. The arrangement of the holes with respect to the *b* axis (the 'wavelength' axis) is also different in the two structures.

There are a number of hydrogen bonds to each bromide ion. A similar assembly of hydrogen bond donors around a halide ion is also observed in biguanide hydrochloride and in some self-assembling cages which use bromide or chloride ions as a template.[8] Each methanol molecule is hydrogen bonded to a bromide ion in the biuret layer and to a methoxycarbimido ligand in the complex **3** layer, and so provides a further link between the layers.

In conclusion, we have shown that the topology of the biuret sheet structure can be perturbed without significant disruption by the intercalation of a co-ordinating biuret complex. Based on the above, it appears feasible to control the extent of the perturbation by variation of the nature of the intercalation agent.

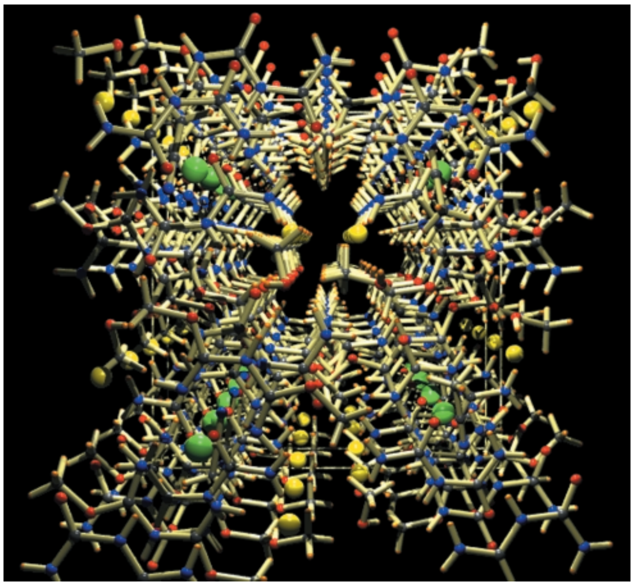

Fig. 3 Perspective projection down the *c* axis of the unit cell of the bis{di(methoxycarbimido)amine}copper(II) bromide/biuret structure, showing the channels in which the bromide and solvate molecules reside.

Acknowledgements

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Notes and references

‡ Crystal data: $C_{19.60}H_{48.40}Br_2CuN_{18.80}O_{14}$, M 994.93, orthorhombic, space group $P2_12_12_1$ (no. 19), a 17.1111(7), b 18.1222(7), c 13.4364(5) Å, V 4166.5(3) Å^3, μ(Mo-Kα) 2.521 cm^{-1}, $2\theta_{max}$ 56, N 44202, N_{ind} 9808 (R_{merge} 0.036), N_{obs} 8080 ($I > 2\sigma(I)$), residuals $R1(F)$ 0.0378, $wR2(F^2)$ 0.0986. Data were collected on a Bruker SMART 1000 CCD diffractometer. The structure was solved with SIR97 and refined with SHELXL97. Experimental details (including a discussion of the possibility of a centrosymmetric structure), atomic coordinates, thermal parameters and bond lengths and angles have been deposited. CCDC reference number 186/1781. See http://www.rsc.org/suppdata/dt/a9/a909359a/ for crystallographic files in .cif format.

§ Microanalysis of this product agreed with this formulation (found: C, 23.54; H, 5.13; N, 26.54. Calculated: C, 23.65; H, 4.87; N, 26.47%).

1 S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357.
2 A. D. Burrows, C.-W. Chan, M. M. Chowdhery, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, 329; J. E. McGrady and D. M. P. Mingos, *J. Chem. Soc., Perkin Trans. 2*, 1995, 355; A. Houlton, D. M. P. Mingos and D. J. Williams, *Transition Met. Chem.*, 1994, **19**, 653; C.-W. Chan, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Polyhedron*, 1996, **15**, 1753.
3 S. Kashino, S. Nakashima and M. Haisa, *Acta Crystallogr., Sect. B*, 1978, **34**, 2191; H. L. Ammon, S. K. Bhattacharjee and K. R. Henery-Logan, *Acta Crystallogr., Sect. C*, 1983, **39**, 355.
4 (*a*) E. W. Hughes, H. L. Yakel and H. C. Freeman, *Acta Crystallogr.*, 1961, **14**, 345; (*b*) B. M. Craven, *Acta Crystallogr., Sect. B*, 1973, **29**, 1525.
5 A. W. McLellan and G. A. Melson, *J. Chem. Soc. A*, 1967, 137.
6 G. Rembarz, E. Fischer, K.-Ch. Röber, R. Ohff and H. Crahmer, *J. Prakt. Chem.*, 1969, **311**, 889; G. Götz and H. U. Kibbel, *Z. Chem.*, 1975, **15**, 278.
7 (*a*) C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976; (*b*) S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp (Editors), Xtal 3.6 System, University of Western Australia, 1999.
8 S. R. Ernst, *Acta Crystallogr., Sect. B*, 1977, **33**, 237; R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258; R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 229.

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