Effects of non-molecular forces on molecular structure in tris(thiourea)-copper(I)

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Intermolecular-hydrogen bonding interactions have been shown to result in a shortening of the copper–copper distance by 0.274 Å to 2.5526(5) Å in $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ in comparison to three structures of the same cation in the absence of significant intermolecular interactions.

We have recently begun a programme of research into the synergistic interaction between molecular and crystal structure, especially in systems exhibiting a symmetry mismatch.[1,2] A number of complex, solid-state arrays have been generated as a result of non-complementary hydrogen bonding between metal aqua ions and crown ethers. In particular, the donor–acceptor system $[UO_2Cl_2(H_2O)_3]\cdot$15-crown-5 exhibits a structure involving a total of sixteen unique metal complex–crown ether pairs.[1] This kind of study is particularly rewarding in the case of labile systems because the overall crystal composition and indeed molecular stoichiometry is frequently governed by the imperative to maximise hydrogen-bonding interactions. Furthermore, multiple, strong hydrogen-bonding interactions may have a considerable effect upon molecular geometry. For example, interaction of hydrated NiX_2 (X = NO_3, ClO_4 or Br) with 18-crown-6 results in three very different species; $[Ni(H_2O)_5(NO_3)]_2[NO_3]_2\cdot$2(18-crown-6),[3] $[Ni(H_2O)_6]_2[ClO_4]_4\cdot$2(18-crown-6) and $[Ni(H_2O)_6]_3[NiBr_2(H_2O)_4]Br_6\cdot$4(18-crown-6)$\cdot 2H_2O$, the compositions being dependent entirely on the formation of strong hydrogen-bonding interactions within the crystalline solids.[2] Significant distortions away from the ideal octahedral geometry are noted in each case. We now report the extension of these investigations to hydrogen-bond donors other than aqua complex ions.

Along with $[CuCl_2]^-$, tris(thiourea)copper(I) chloride is one of the few water-soluble forms of Cu^I which do not disproportionate to Cu^{II} and Cu metal. Although labile in solution, $[Cu\{SC(NH_2)_2\}_3]Cl$ **1** exists as an infinite co-ordination polymer in the solid state[4] incorporating a single S-bound thiourea bridge from one metal centre to the next. Inter-chain interactions consist of NH ··· Cl and NH ··· S hydrogen bonds with N ··· Cl/S distances in the range 3.25–3.40 Å. A survey of the Cambridge Structural Database[5] however, reveals that the $[Cu\{SC(NH_2)_2\}_n]^+$ moiety can adopt a variety of geometries depending on the identity of the counter anion. Thus the hydrated sulfate, perchlorate and tetrafluoroborate salts exist as $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ **2** metal–metal bonded dimers.[6,7] Each dimer interacts with the anion *via* one or, at most, two hydrogen bonds NH ··· F/O 2.92–3.03 Å. The hydrated $[SiF_6]^-$ salt exhibits a polymeric structure incorporating six-membered Cu_3S_3 rings.[8] In the anhydrous form, $[SiF_6]^{2-}$ gives rise to discrete, mononuclear $[Cu\{SC(NH_2)_2\}_4]^+$ **3** tetrahedra,[9] while the hydrogen phthalate anion results in units with NH ··· O hydrogen bonds of 2.909 Å.[10] Other related oligomeric and polymeric structures are also known.[5] Given the preponderance of hydrogen-bond donors in the form of thiourea NH_2 moieties in all these systems we decided to investigate the solid-state behaviour of **1** in the presence of crown ethers as hydrogen-bond acceptors. Accordingly, an equimolar mixture of $[Cu\{SC(NH_2)_2\}_3]Cl$ and 18-crown-6 was prepared in water.† Slow evaporation of this solution afforded large, colourless blocks of a complex of formula $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]Cl_2\cdot 2[SC(NH_2)_2]\cdot 2H_2O\cdot$2(18-crown-6) **4** which was subjected to analysis by X-ray crystallography.‡

The dicopper(I) cation in **4** (Fig. 1) ostensibly resembles the binuclear species of type **2** isolated in the presence of tetrahedral anions such as ClO_4^-, although contrasts sharply to the parent material **1**. Interestingly, however, the Cu–Cu distance in complexes of type **2** is in the narrow range 2.827–2.862 Å, with Cu–S–Cu angles of *ca.* 71–74° suggesting a relatively weak Cu–Cu interaction. In the case of **4**, in essentially the same cation, the Cu–Cu distance is compressed to a remarkable 2.5526(5) Å, with a resultant bond angle at the bridging sulfur of 63.646(14)°, clearly suggesting a much more significant metal–metal interaction. This effect is also apparent in the Cu–S bond lengths which are rather longer to the bridging sulfur atoms in **4** compared to **2**, and shorter to the terminal sulfurs. This marked difference in molecular structure is apparently due to the significantly greater number of intermolecular interactions in which the $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ cation takes part in **4**. Thus the dicopper cation is surrounded by a total of six crown ethers (which exist in two different con-

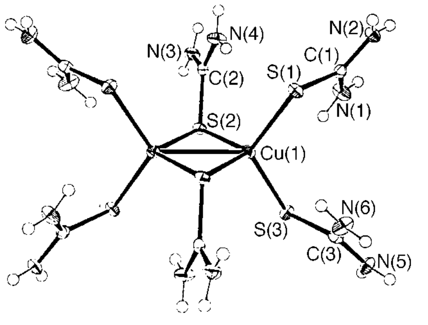

Fig. 1 The $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ cation in **4**. Selected bond lengths (Å) and angles (°): Cu(1)–S(3) 2.2752(5), Cu(1)–S(1) 2.2985(5), Cu(1)–S(2) 2.3988(5), Cu(1)–S(2′) 2.4417(5), Cu(1)–Cu(1′) 2.5526(5), Cu(1)–S(2)–Cu(1′) 63.646(14)

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† The salt $[Cu\{SC(NH_2)_2\}_3]Cl$ (0.20 g, 0.61 mmol) was dissolved in distilled water (5 cm^3) and added to a solution of 18-crown-6 (0.16 g, 0.61 mmol) in water (1 cm^3) to give a colourless solution. The resulting mixture was allowed to stand in air for *ca.* 2 weeks resulting in the gradual deposition of the product as large, colourless blocks in near quantitative yield.

‡ Crystal data for **5**: $C_{32}H_{84}Cl_2Cu_2N_{16}O_{14}S_8$, *M* 1371.61, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.1764(4)$, $b = 11.1352(4)$, $c = 13.5561(4)$ Å, $\alpha = 89.647(2)$, $\beta = 93.263(2)$, $\gamma = 99.868(2)°$, $U = 1510.94(9)$ Å^3, $Z = 1$, $\mu = 11.36$ cm^{-1}, $T = 100$ K. Reflections measured: 13 159, unique data: 5542 ($R_{int} = 0.032$), parameters: 407, $R1$ $[F^2 > 2\sigma(F^2)]$ 0.0303, $wR2$ (all data) 0.0783. CCDC reference number 186/1069. See http://www.rsc.org/suppdata/dt/1998/2601/ for crystallographic files in .cif format.

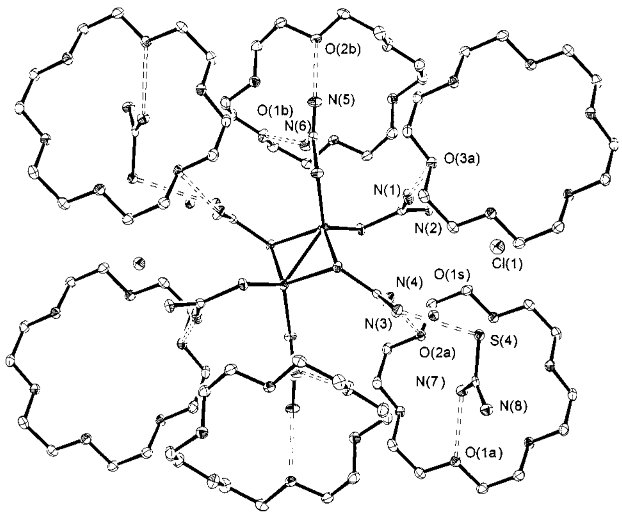

Fig. 2 The crystal environment of the $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ cation in **4**. Selected intermolecular contacts (Å): N(1)···O(3a) 2.991(2), N(2)···S(4) 3.350(2), N(3)···S(4) 3.305(2), N(4)···O(2a′) 3.017(2), N(5)···O(2b) 2.937(2), N(6)···O(1b) 2.915(2), N(7)···O(1a) 2.856(2), N(7)···O(2a) 3.013(2), N(8)···Cl(1) 3.278(2), N(8)···Cl(1″) 3.409(2)

formations) each of which form hydrogen bonds to four nitrogen atoms of the thiourea ligands, NH···O 2.991(2)–3.107(2) Å, Fig. 2. In addition, the remaining two N-atoms hydrogen bond to the solvent water, N(2)···O(1s) 2.986(2) Å, and the sulfur atom of the unco-ordinated thiourea molecule, N(3)···S(4) 3.305(2) Å. This extensive solid-state network is completed by interactions from the water molecule to the chloride anion 3.258(2) and 3.301(2) Å and from the NH_2 moieties of the unco-ordinated thiourea molecule to one of the crown ether ligands, N(7)···O(1A), O(2A) 2.856(2) and 3.013(2) Å, respectively. The unco-ordinated thiourea also hydrogen bonds with the chloride ligands, N(8)···Cl(1), Cl(1″) 3.278(2) and 3.409(2) Å. Finally, it is noteworthy that the C=S distance is very slightly shorter in the unco-ordinated thiourea than in the co-ordinated ligands; 1.718(2) *vs.* 1.724(2) Å (average).

The Cu^I centre in **4** would be expected to exhibit a low ligand-field splitting energy and hence there is no reason why it should necessarily obey the 18-electron rule. As a result the electronic environment about the metal centres is highly malleable, allowing the complex to undergo very large distortions in order to accommodate and maximise stabilising hydrogen-bonding interactions in the solid state. The sharp contrast between the co-ordination geometry of the $[Cu_2\{\mu\text{-}SC(NH_2)_2\}_2\{SC(NH_2)_2\}_4]^{2+}$ cation in **4** and the three closely related species **2** in which intermolecular hydrogen bonding is much less prevalent highlights the importance of a consideration of the overall crystal, as well as molecular structure, on molecular properties in the solid state.

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References

1 J. W. Steed, H. Hassaballa and P. C. Junk, *Chem. Commun.*, 1998, 577.
2 J. W. Steed, B. J. McCool and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, submitted.
3 P. C. Junk, S. M. Lynch and B. J. McCool, *Supramol. Chem.*, 1998, in the press.
4 Y. Okaya and C. Knobler, *Acta Crystallogr.*, 1964, **17**, 928.
5 April 1998 update, 181 309 entries: F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
6 M. van Meerssche, R. Kamara, J. P. Declerq and G. Germain, *Bull. Soc. Chim. Belg.*, 1982, **91**, 547.
7 F. Hanic and E. Durcanska, *Inorg. Chim. Acta*, 1969, **3**, 293.
8 A. G. Gash, E. H. Griffith, W. A. Spofford III and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1973, 256.
9 G. W. Hunt, N. W. Terry III and E. L. Amma, *Acta Crystallogr., Sect. B*, 1979, **35**, 1235.
10 M. B. Cingi, A. M. M. Lanfredi, A. Tiripicchio and M. Tiripicchio Camellini, *Acta Crystallogr., Sect. B*, 1977, **33**, 3772.

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