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A Dimer of Dimers and a Polymer of Tetramers: Structures of Copper Complexes involving 6-Fluoro-2-hydroxypyridine

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Two copper complexes of 6-fluoro-2-hydroxypyridine (Hfhp) have been synthesised and structurally characterised; the structures are related to those of the copper complexes formed with the analogous 6-chloro ligand but in this case ligand reorganisation leads to oligomerisation of di- and tetra-nuclear units.

In pursuit of controlled synthetic procedures for producing polynuclear homo- and hetero-metallic assemblies we have been exploring the co-ordination chemistry of ligands derived from 2-hydroxypyridine (2-pyridone) with first-row transition metals.[1-6] We have recently shown that homoleptic copper complexes of these ligands exhibit a strong structural dependence on the nature of the substituent in the 6 position, *e.g.* the complex with 6-chloro-2-hydroxypyridine (Hchp) is a dimer, $[Cu_2(chp)_4]$ **1**,[2] while that with 6-methyl-2-pyridone is hexanuclear.[1] In order to examine the effect of other derivatives of these ligands we have prepared complexes of 6-fluoro-2-hydroxypyridine (Hfhp), previously shown by Cotton and co-workers[7-11] to form novel dimeric complexes having 'polar' metal–metal bonds.

In a modification of the literature preparation of 6-bromo-2-hydroxypyridine,[12] Hfhp was prepared by base hydrolysis of 2,6-difluoropyridine, and the sodium salt was then obtained upon deprotonation with sodium methoxide. Solid Na(fhp) (12.6 mmol) was intimately ground with hydrated copper nitrate (6.1 mmol) in a pestle and mortar. The resulting paste was extracted with dichloromethane giving a dark green solution which was filtered to remove unreacted starting materials. Recrystallisation by addition of a hexane layer gave yellow-brown needles of $[\{Cu_2(fhp)_4\}_2]$ **2** (yield 61%)† the tetranuclear structure of which was revealed by a crystal structure determination (Fig. 1).‡

The complex consists of a dimer of dinuclear units linked by two μ-O atoms from fhp ligands. The four bridging fhp ligands within each dinuclear unit are arranged head-to-head, with all N atoms attached to one copper and all O atoms attached to the second, giving a dinuclear unit with approximate C_{4v} symmetry. In **1** four chp ligands are attached to two Cu atoms with approximate D_{2d} geometry. The rearrangement from **1** to **2** is attributable to the formation of additional axial Cu–O interactions which link the dimers in a tetranuclear array.

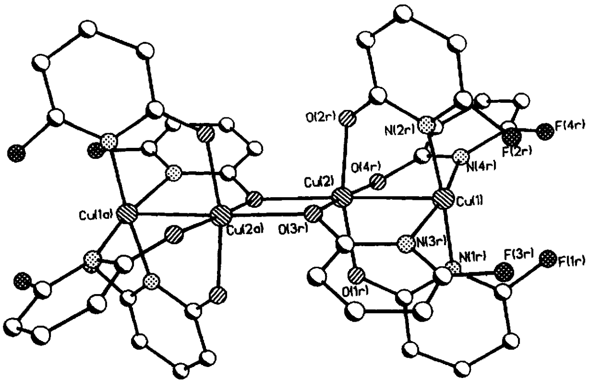

Fig. 1 Structure of **2** in the crystal. Selected bond lengths (Å) and angles (°): Cu(1)–N(1r) 1.986, Cu(1)–N(2r) 1.987, Cu(1)–N(3r) 2.034, Cu(1)–N(4r) 2.024, Cu(2)–O(1r) 1.968, Cu(2)–O(2r) 1.966, Cu(2)–O(3r) 1.971, Cu(2)–O(4r) 1.927, Cu(2)–O(3ra) 2.177 [av. estimated standard deviation (e.s.d.) 0.005 Å]; N(1r)–Cu(1)–N(2r) 175.0, N(1r)–Cu(1)–N(3r) 89.5, N(1r)–Cu(1)–N(4r) 90.7, N(2r)–Cu(1)–N(3r) 89.3, N(2r)–Cu(1)–N(4r) 89.4, N(3r)–Cu(1)–N(4r) 168.0, O(1r)–Cu(2)–O(2r) 164.4, O(1r)–Cu(2)–O(3r) 88.3, O(1r)–Cu(2)–O(4r) 91.3, O(2r)–Cu(2)–O(3r) 88.6, O(2r)–Cu(2)–O(4r) 89.6, O(3r)–Cu(2)–O(4r) 171.9, O(1r)–Cu(2)–O(3ra) 97.5, O(2r)–Cu(2)–O(3ra) 97.2, O(3r)–Cu(2)–O(3ra) 82.7, O(4r)–Cu(2)–O(3ra) 105.3 (av. e.s.d. 0.2°)

The two independent copper atoms in **2** have quite distinct co-ordination geometries; Cu(2) is bound to five O atoms, Cu(1) to four N atoms. The intra-dimer Cu–Cu distance in **2** of 2.5425(14) Å is significantly longer than that in **1** [2.4989(11) Å], presumably due to the presence of an axial ligand. The inter-dimer Cu–Cu distance is 3.116(2) Å.

Similar orientation of fhp ligands has been noted by Cotton and co-workers in complexes of the chromium triad,[7] ruthenium,[8,9] osmium[10] and rhodium.[11] In those cases the axial co-ordination site made available by isomerisation is occupied by either solvent molecules or chloride ligands. Here the absence of potential axial ligands leads to dimerisation, and hence a higher nuclearity assembly.

Recrystallisation of **1** from methanol–dichloromethane led to a tetrameric complex $[Cu_4(OMe)_4(chp)_4]$ **3**.[4] Similarly recrystallisation of **2** from methanol–CH_2Cl_2 gives a polymeric

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† Found: C, 43.1; H, 2.3; N, 9.8. Calc.: C, 41.7; H, 2.1; N, 9.7%.

‡ Crystal data for **2**: $C_{40}H_{24}Cu_4F_8N_8O_8$, $M = 1150.8$, tetragonal, space group $I4_1/a$, $a = 24.385(6)$, $c = 13.838(5)$ Å, $U = 8229$ Å^3 [from 2θ values of 37 reflections measured at ±ω ($24 \leq 2\theta \leq 28°$), $\lambda = 0.710\,73$ Å], $Z = 8$ (the molecule lies on an inversion centre), $F(000) = 4576$, $D_c = 1.86$ g cm^{-3}, $T = 150.0(2)$ K, yellow-brown needle, $\mu = 2.14$ mm^{-1}, dimensions 0.50 × 0.09 × 0.05 mm.

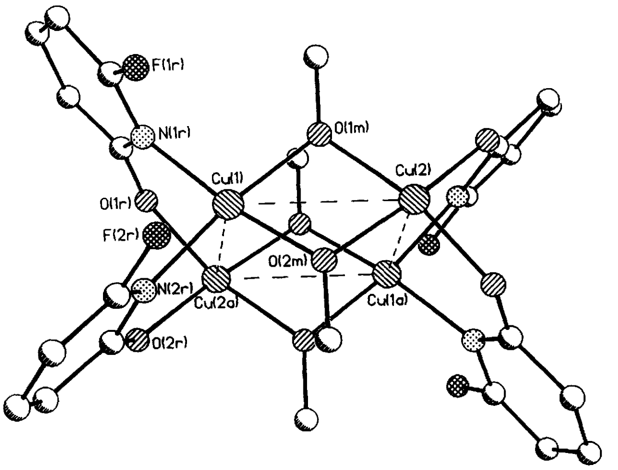

Fig. 2 The structure of the tetranuclear unit in **4**. Selected bond lengths (Å) and angles (°): Cu(1)–N(1r) 2.008, Cu(1)–N(2r) 2.004, Cu(1)–O(1m) 1.906, Cu(1)–O(2m) 1.914, Cu(2)–O(1m) 1.912, Cu(2)–O(2m) 1.936, Cu(2)–O(1ra) 1.913, Cu(2)–O(2ra) 1.954, Cu(2)–O(2rb) 2.452 (av. e.s.d. 0.006 Å); O(1m)–Cu(1)–O(2m) 75.9, O(1m)–Cu(1)–N(1r) 96.5, O(1m)–Cu(1)–N(2r) 170.3, O(2m)–Cu(1)–N(1r) 172.5, O(2m)–Cu(1)–N(2r) 94.5, N(1r)–Cu(1)–N(2r) 93.0, O(1m)–Cu(2)–O(2m) 75.3, O(1m)–Cu(2)–O(1ra) 167.0, O(1m)–Cu(2)–O(2ra) 98.3, O(2m)–Cu(2)–O(1ra) 92.9, O(2m)–Cu(2)–O(2ra) 170.4, O(1ra)–Cu(2)–O(2ra) 92.8, O(1m)–Cu(2)–O(2rb) 98.7, O(2m)–Cu(2)–O(2rb) 111.4, O(1ra)–Cu(2)–O(2rb) 90.4, O(2ra)–Cu(2)–O(2rb) 76.3 (av. e.s.d. 0.2°)

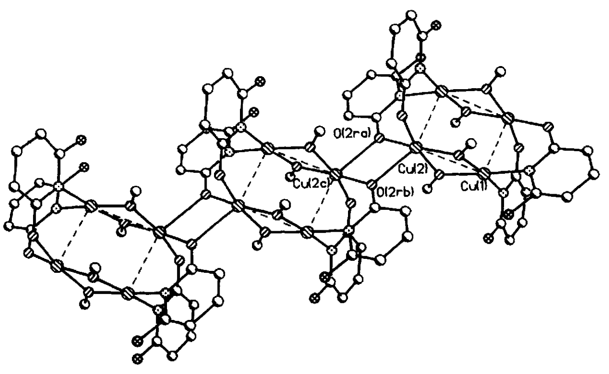

Fig. 3 The polymeric array of tetramers in **4**

complex $[\{Cu_4(OMe)_4(fhp)_4\}_n]$ **4** (yield 74%)† which contains a tetranuclear unit as a repeating motif (Fig. 2),‡ with a rectangular array of four copper atoms bridged alternately by two μ-O atoms from methoxide, or by two 1,3-bridging fhp ligands. The fhp ligands within the tetramer in **4** are arranged head-to-head, which now allows further inter-tetramer ligation of one of the copper atoms, leading to a polymeric array of tetramers (Fig. 3). The additional contact [Cu(2)–O(2rb) 2.452(6) Å] is longer than the other Cu–O and Cu–N bonds in the structure, but represents a significant interaction. The two copper sites in the asymmetric unit are therefore again quite distinct; Cu(2) is five-co-ordinate, bound to five O donors; Cu(1) is four-co-ordinate, bound by two N- and O-donor atoms. The Cu–Cu contacts within the tetramer are 2.874(2) Å for the edge bridged by fhp ligands and 2.997(2) Å for the edge bridged by methoxides; both of these contacts are slightly longer, by 0.05 and 0.03 Å respectively, than their equivalent contacts in **3**. The shortest inter-tetramer Cu–Cu contacts are much longer, at 3.479(2) Å, than the intra-tetramer Cu–Cu distances.

In contrast to the similarities observed in the structures of copper complexes of Hchp and 6-bromo-2-hydroxypyridine,[18] profound structural modifications occur upon ligation by Hfhp, allowing oligomerisation in **2** or polymerisation in **4**. The effect is presumably due to the small van der Waals radius of the fluorine atom and the shorter C–F bond, which allows arrangements to be adopted which would be sterically unfavourable for Cl or Br. This feature expands the scope of polynuclear metal complexes obtainable by the use of the versatile pyridone ligand system and confirms that control of the nuclearity of the resultant metal assemblies is possible through subtle modifications of the ligands.

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† Found: C, 34.8; H, 2.8; N, 6.6. Calc.: C, 34.9; H, 2.9; N, 6.8%.

‡ Crystal data for **4**: $C_{24}H_{24}Cu_4F_4N_4O_8$, $M = 826.6$, triclinic, space group $P\bar{1}$, $a = 7.528(2)$, $b = 9.443(4)$, $c = 10.959(4)$ Å, $\alpha = 95.13(2)$, $\beta = 103.85(3)$, $\gamma = 111.70(2)°$, $U = 689$ Å^3 [from 2θ values of 42 reflections measured at ±ω ($22 \leqslant 2\theta \leqslant 24°$), $\lambda = 0.710\,73$ Å], $Z = 1$ (the structure is polymeric; the formula corresponds to the repeat unit), $F(000) = 412$, $D_c = 1.99$ g cm^{-3}, $T = 150.0(2)$ K, dark blue lath, $\mu = 3.13$ mm^{-1}, dimensions 0.47 × 0.19 × 0.19 mm.

Data collection and processing for **2** and **4**: Stoë STADI-4 four-circle diffractometer with Oxford Cryosystems low-temperature device,[13] graphite-monochromated Mo-Kα X-radiation, for **2** ω–2θ scans with learnt-profile,[14] for **4** ω scans. All data corrected for Lorentz and polarisation effects and for absorption. Both structures solved by direct methods using SIR-92 (**2**)[15] or SHELXS 86 (**4**).[16] Both structures refined with all non-H atoms anisotropic to give: for **2**, with 307 parameters, $R1 = 0.0576$ for 2282 data with $F > 4\sigma(F)$, $wR2$ (on F^2) = 0.15 for all 3589 independent reflections ($2\theta \leqslant 50°$) [$w^{-1} = \sigma^2(F_o)^2 + (0.0535P)^2$]; for **4**, with 201 parameters $R1 = 0.0671$ for 1951 data with $F > 4\sigma(F)$, $wR2$ (on F^2) = 0.1872 for all 3184 independent reflections ($2\theta \leqslant 55°$) $\{w^{-1} = \sigma^2(F_o)^2 + (0.0978P)^2;\ P = \tfrac{1}{3}[\max.(F_o^2,0) + 2F_c^2]\}$. All refinements used SHELXL 93.[17]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxv–xxx.