Copper(II)-templated assembly of tetranuclear grid-like complexes from simple pyridine–pyrazole ligands

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Reaction of $Cu(O_2CMe)_2 \cdot H_2O$ with HL^1 [3-(2-pyridyl)pyrazole] or HL^2 [6-(3-pyrazolyl)-2,2′-bipyridine] and NH_4PF_6 followed by crystallisation of the crude products from dmf–ether affords $[Cu_4L^1_6(dmf)_2][PF_6]_2$ 1 and $[Cu_4L^2_4(dmf)_4][PF_6]_4$ 2 respectively, in which the deprotonated pyrazolyl groups act as bridging ligands and the 2 × 2 grid–like architectures are a result of the preference of the Cu^{II} ions for elongated square-pyramidal coordination geometries.

Recent developments in the specific, efficient syntheses by self-assembly processes of coordination complexes have afforded a variety of unusual topologies such as molecular helicates, grids, ladders, rings, and boxes.[1–6] Such complexes are of interest not only for their unusual structures and the simple synthetic methods used to prepare them, but also because they allow the preparation of high-nuclearity complexes in which several potentially interacting metal centres are linked in a well defined spatial array.

We describe here the syntheses and structures of the copper(ii) complexes of HL^1 [3-(2-pyridyl)pyrazole] and HL^2 [6-(3-pyrazolyl)-2,2′-bipyridine] in which the above principles have been used to prepare tetranuclear grid-like complexes. These complexes are of particular interest as they show (*i*) how the unusual stereoelectronic preferences of Cu^{II} can be harnessed to assemble complex high-nuclearity structures that are not accessible with other metal ions, and (*ii*) how simple polydentate ligands containing terminal pyrazolyl fragments are appealing components for use in supramolecular chemistry.

HL^1 (a known ligand)[7,8] forms simple mononuclear octahedral tris-chelate complexes with Ni^{II} and Zn^{II}.[9] We reasoned that this was unlikely with Cu^{II}. Reaction of HL^1 with $Cu(O_2CMe)_2 \cdot 2H_2O$ (3 : 2) in methanol at room temperature afforded a clear deep green solution from which a blue–green solid precipitated on addition of NH_4PF_6. This was recrystallised from dmf–ether to give crystals of **1**·2 dmf in *ca.* 90% yield. FAB mass spectrometry showed the presence of numerous peaks corresponding to polynuclear species [up to $Cu_4L^1_6$] and the elemental analysis was consistent with the empirical formula $[Cu_2L^1_3(dmf)][PF_6]$.The crystal structure of **1** (Fig. 1) shows that **1** is in fact $[Cu_4L^1_6(dmf)_2][PF_6]_2$.† There are two approximately planar $Cu_2(\mu\text{-}L^1)_2$ units, related by an inversion centre, in which each $[L^1]^-$ acts as a terdentate bridge linking the two metal centres; these units are stacked parallel and face-to-face (mean plane separation 3.2–3.5 Å), with additional

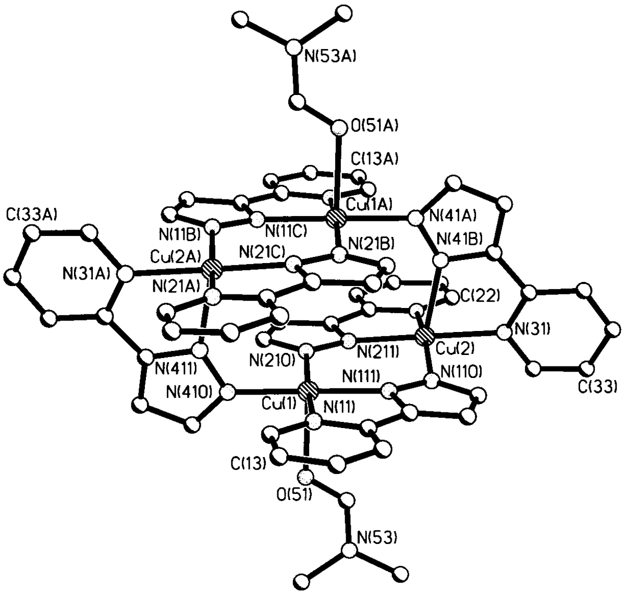

Fig. 1 Structure of the complex cation of **1**. Selected bond lengths (Å) and angles (°): Cu(1)–N(410) 1.977(2), Cu(1)–N(210) 1.980(2), Cu(1)–N(111) 1.982(2), Cu(1)–N(11) 2.064(2), Cu(1)–O(51) 2.339(2), Cu(2)–N(211(1.968(2), Cu(2)–N(110) 1.996(2), Cu(2)–N(31) 2.047(2), Cu(2)–N(21) 2.073(2), Cu(2)–N(411A) 2.198(2); N(11)–Cu(1)–N(111) 80.57(9), N(410)–Cu(1)–N(210) 91.57(9), N(210)–Cu(1)–N(111) 96.64(9), N(410)–Cu(1)–N(11) 90.51(9), N(410)–Cu(1)–N(111) 170.61(9), N(21)–Cu(1)–N(11) 168.85(9), N(211)–Cu(2)–N(110) 96.60(9), N(110)–Cu(2)–N(31) 90.31(9), N(211)–Cu(2)–N(21) 80.72(9), N(21)–Cu(2)–N(31) 91.31(9), N(211)–Cu(2)–N(31) 171.35(9), N(110)–Cu(2)–N(21) 165.66(9), N(31)–Cu(2)–N(411A) 78.44(9).

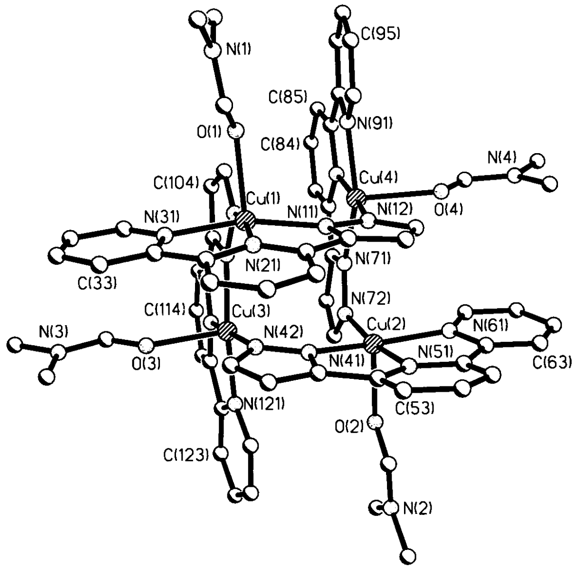

Fig. 2 Structure of the complex cation of **2**. Selected bond lengths (Å) and angles (°): Cu(1)–N(102) 1.949(5), Cu(1)–N(21) 1.957(5), Cu(1)–N(11) 2.001(5), Cu(1)–N(31) 2.050(5), Cu(1)–O(1) 2.243(4), Cu(2)–N(72) 1.951(5), Cu(2)–N(51) 1.954(5), Cu(2)–N(41) 2.012(5), Cu(2)–N(61) 2.049(5), Cu(2)–O(2) 2.271(4), Cu(3)–N(42) 1.952(5), Cu(3)–N(111) 1.956(5), Cu(3)–N(101) 2.010(5), Cu(3)–N(121) 2.056(5), Cu(3)–O(3) 2.229(4), Cu(4)–N(12) 1.949(5), Cu(4)–N(81) 1.961(5), Cu(4)–N(71) 2.012(4), Cu(4)–N(91) 2.041(5), Cu(4)–O(4) 2.227(4); N(102)–Cu(1)–N(21) 168.4, N(11)–Cu(1)–N(31) 157.6(2), N(51)–Cu(2)–N(72) 171.5(2), N(41)–Cu(2)–N(61) 156.8(2), N(42)–Cu(3)–N(111) 170.2(2), N(101)–Cu(3)–N(121) 156.4, N(12)–Cu(4)–N(81) 171.9(2), N(71)–Cu(4)–N(91) 156.1(2).

deprotonated ligands [L^1]$^-$ perpendicular to the two Cu$_2$(μ-L^1)$_2$ planes forming linking 'cross-pieces'. Two of the metals [Cu(1) and Cu(1A)] have additional dmf ligands attached, and therefore have a square-pyramidal N$_4$O environment in which the O ligands (dmf) are axial; Cu(2) and Cu(2A) have square-pyramidal N$_5$ environments in which one of the pyrazole donor atoms is in the axial position. In every case the axial ligand is significantly further from the metal [Cu(I)–O(51) 2.339(2) Å, Cu(2)–N(411A) 2.198(2) Å] than the four equatorial ligands (lengths in the range 1.97–2.07 Å), in keeping with the requirements of the Jahn–Teller effect.

HL^2 was prepared in exactly the same way as HL^1,[8] but starting from 6-acetyl-2,2′-bipyridine. HL^2 forms simple mononuclear octahedral complexes with many first-row metal ions.[9] Reaction of HL^2 with Cu(O$_2$CMe)$_2$·2H$_2$O (1 : 1) in methanol at room temperature followed by addition of aqueous NH$_4$PF$_6$ resulted in precipitation of a blue–green solid which was recrystallised from dmf–ether to give crystals of **2**·6dmf in *ca.* 80% yield. Electrospray mass spectrometry indicated the formation of a tetranuclear complex in solution, and the elemental analysis indicated the empirical formula [Cu(L^2)][PF$_6$], *i.e.* a 1 : 1 metal : ligand ratio. The crystal structure of **2** is in Fig. 2,† and shows that **2** is the tetramer [Cu$_4$L$^2_4$(dmf)$_4$][PF$_6$]$_4$ and has many structural similarities to **1**. The overall structure is that of a 2 × 2 grid, with two pairs of parallel, stacked [L^2]$^-$ ligands mutually perpendicular to each other. The stacking distances again are in the range 3.2–3.5 Å. Each metal ion is coordinated by the terdentate pocket of one deprotonated ligand [L^2]$^-$, one pyrazole donor atom which is acting as a bridge to a ligand attached to another metal ion, and a dmf ligand. The result is an elongated N$_4$O square-pyramidal geometry with the dmf ligand in the axial position; the axial bond lengths lie in the range 2.23–2.27 Å, in contrast to the equatorial ones which lie in the range 1.95–2.06 Å. The four metal ions are crystallographically independent but chemically very similar, and the complex has approximate S_4 symmetry (*cf.* the S_2 axis of **1** implied by its inversion centre).

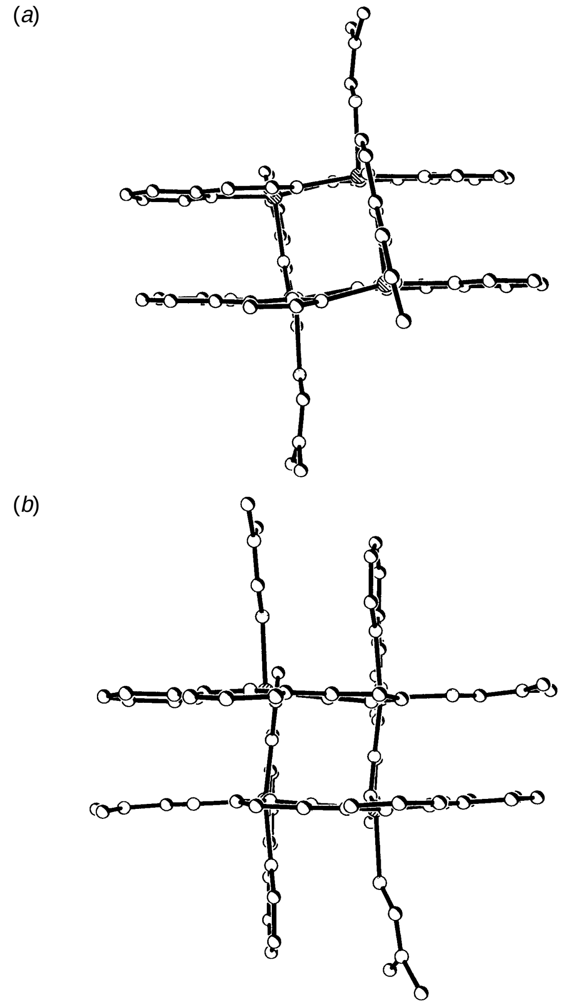

Fig. 3 Alternative views of the complex cations of **1** (*a*) and **2** (*b*) emphasising the grid-like structure and the aromatic stacking

The grid-like architecture of both complexes is emphasised in Fig. 3. Comparison with the simple mononuclear octahedral complexes that these ligands can also form[9] shows that assembly of these structures is directed principally by the stereoelectronic preference of the Cu$^{\text{II}}$ ions for elongated tetragonal geometry: to satisfy this requirement necessitates deprotonation of the pyrazole rings and bridging behaviour of the ligand. These structures are in interesting contrast to other grid- and ladder-like structures in which the necessary mutually perpendicular orientation of ligand strands is achieved by using ligands with bidentate compartments assembling around (pseudo-tetrahedral) Cu$^{\text{I}}$ or Ag$^{\text{I}}$ templates.[3,5,6]

Footnote

† *Crystallography*. Suitable crystals were mounted on a Siemens SMART diffractometer (graphite-monochromatised Mo-Kα X-radiation).

1·2dmf: C$_{60}$H$_{64}$Cu$_4$F$_{12}$N$_{22}$O$_4$P$_2$, M = 1701.4, green plates, crystal size 0.5 × 0.4 × 0.1 mm; triclinic, space group $P\bar{1}$; a = 10.410(2), b = 13.282(3), c = 14.170(2) Å, α = 85.254(10), β = 70.087(12), γ = 68.15(2)°; U = 1707.5(6) Å^3; Z = 1; D_c = 1.655 g cm^{-3}; F(000) = 864; μ(Mo-Kα) = 1.373 mm^{-1}. 8183 data were collected with 2θ_{max} = 50° at −100 °C, and merged to give 5820 unique data (R_{int} = 0.023).

2·6dmf: C$_{82}$H$_{106}$Cu$_4$F$_{24}$N$_{26}$O$_{10}$P$_4$, M = 2450.0, green needles, crystal size 0.7 × 0.15 × 0.1 mm^3; monoclinic, space group $P2_1/n$; a = 19.567(2), b = 26.313(3), c = 20.033(2) Å; β = 91.44(1)°; U = 10311(3) Å^3; Z = 4; D_c = 1.578 g cm^{-3}; F(000) = 5008; μ(Mo-Kα) = 0.987 mm^{-1}. 63 226 data were collected with 2θ_{max} = 55° at −100 °C, and merged to give 23 223 unique data (R_{int} = 0.079).

Both structures were solved by direct methods, and refined on all F^2 data using the SHELX suite of programs. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. For **1**·2dmf, R_1 = 0.036, wR_2 = 0.106. The complex is centrosymmetric so each asymmetric unit contains one half of the complex and one unique dmf molecule. For **2**·6dmf, R_1 = 0.079, wR_2 = 0.200. Each asymmetric unit contains one complete tetranuclear complex and six independent molecules of dmf. 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 182/323.

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