Controlled synthesis of heterotetranuclear complexes

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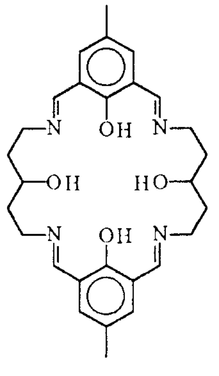
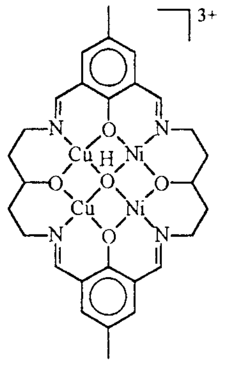
Template synthesis of a macrocyclic complex containing two copper(II) ions and two vacant coordination sites permits controlled access to a heterotetranuclear $Cu^{II}_2Ni^{II}_2$ complex without scrambling of the metal ions.

Heteronuclear complexes of the dinucleating 'Robson-type' macrocycles[1] have been known for many years.[2] Most commonly, these complexes are synthesised using ligands with dissimilar binding sites in either the final macrocyclic product or in a key non-cyclic intermediate in a stepwise synthesis. Here, we report a route for the controlled synthesis of heterotetranuclear complexes of a macrocycle with four identical binding sites.



H_4L^1



$[Cu_2Ni_2(L^1)OH]^{3+}$

Previous work using the ligand H_4L^1 has established the template formation of planar tetracopper(II)[3,4] and tetranickel(II)[5] complexes. The metal ions are separated by *ca.* 3 Å and interact through phenoxo and alkoxo bridges as well as through a central μ_4-OH ion. In tetracopper(II) complexes, the central μ_4-hydroxo moiety can be replaced by two 1,1-azido ligands to yield $[Cu_4(\mu\text{-}N_3)_2(L^2)(N_3)_2]\cdot 2MeOH$.[4] The geometry of the tetracopper(II) array is only slightly modified to allow the azide bridges to lie one on either side of the macrocyclic plane. Incorporation of a larger bridge might be expected to force the copper ions apart, disrupting the planarity of the complex.

Schiff-base condensation of 2,6-diformyl-4-methylphenol (dfmp) and 1,5-diamino-3-hydroxypentane (dahp) in the presence of $Cu(BF_4)_2\cdot 6H_2O$ and pyrazole (Hpyr) (mole ratios dfmp : dahp : Cu^{2+} : Hpyr = 1 : 1 : 2 : 1) in 1 : 1 methanol–ethanol, yielded a green powder. On recrystallisation by diethyl ether diffusion from acetonitrile containing excess pyrazole, two crystalline macrocyclic products were obtained. The major component (*ca.* 80%) consists of red–green dichroic crystals of formula $[Cu_2(\mu\text{-pyr})(H_3L^1)](BF_4)_2\cdot MeCN$ (**1**·MeCN), a minor amount (*ca.* 5%) of a dark green complex, $[Cu_4(\mu\text{-pyr})_2(L^1)](BF_4)_2$ **2** was also isolated. Both complexes have been characterised by single crystal structure analysis.†

The cation of complex **1**, $[Cu_2(\mu\text{-pyr})(H_3L^1)]^{2+}$, is a dicopper complex in which the copper ions are bridged by an alkoxo oxygen (O2) and a pyrazolate ion (Fig. 1). It can be viewed as resulting from the previously characterised $[Cu_4(L^n)(OH)]^{3+}$ core by loss of two copper ions and replacement of the central hydroxide by pyrazolate. The macrocyclic ligand is only monodeprotonated but, as observed in related systems,[6–8] the phenolic protons have transferred to the non-coordinated imine groups; these protons were located in the structure refinement. The cation thus has two vacant (if protonated) coordination sites, somewhat blocked by the presence of the pyrazolate ligand. The geometry at each copper ion shows a tetrahedral distortion from square planar which is necessary to accommodate the two-atom bridge. The Cu···Cu distance of 3.246(1) Å is somewhat shorter than the values found in other dicopper systems linked by the same two bridges (3.34–3.30 Å).[9,10] A marked twist in the saturated section of the macrocycle is similar to that observed in a non-cyclic structure with the same donor set[10] and is therefore likely to be imposed by the bridges rather than the cyclic nature of the ligand. Intermolecular π–π stacking involving both the macrocyclic π-systems is evident (interplanar distances 3.4–3.6 Å), as an intramolecular H–π interaction where the alcohol proton lies directly over the centre of the pyrazolate ring (H–ring centroid 2.18 Å). There are no significant interactions involving the acetonitrile solvate or BF_4^- anions.

The tetranuclear cation of **2** (Fig. 2) sits on a centre of inversion; bridging pyrazolate groups lie above and below the plane of the macrocycle, each linking a pair of copper ions which are also bridged by an alkoxo group. The mean planes of the pyrazolate ions are parallel, one on either side of the macrocycle, and are inclined at 46.4(2)° to the plane of the eight macrocyclic donors. The Cu(1)···Cu(2) and Cu(1)···Cu(1A) distances are 3.254(2) and 3.133(1) Å respectively, compared to 2.953(1) and 3.000(1) Å in the $[Cu_4(L^1)(OH)](NO_3)_3\cdot 3H_2O$ complex.[3] The copper ions are essentially four-coordinate, although Cu(2) interacts weakly [2.515(6) Å] with a fluorine atom of BF_4^-. Each pair of copper ions is displaced from the plane of the macrocyclic donors towards the coordinated

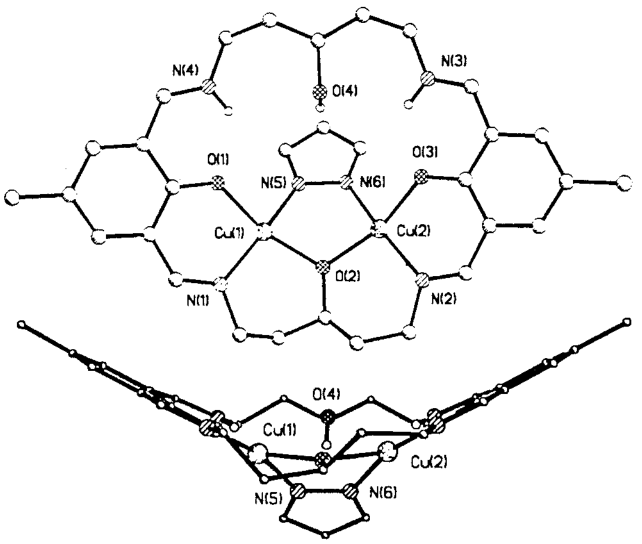


Fig. 1 Perspective views of the $[Cu_2(\mu\text{-pyr})(H_3L^1)]^{2+}$ cation; hydrogen atoms are omitted except for those bonded to oxygen or nitrogen atoms. Selected distances (Å) and angles (°): Cu(1)···Cu(2) 3.246(1), Cu(1)–O(1) 1.921(4), Cu(1)–N(1) 1.939(5), Cu(1)–O(2) 1.930(4), Cu(1)–N(5) 1.943(5), Cu(2)–O(3) 1.938(4), Cu(2)–N(2) 1.950(5), Cu(2)–O(2) 1.933(4), Cu(2)–N(6) 1.960(5); Cu(1)–O(2)–Cu(2) 114.4(2), Cu(1)–N(5)–N(6) 119.5(4), Cu(2)–N(6)–N(5) 118.3(4).

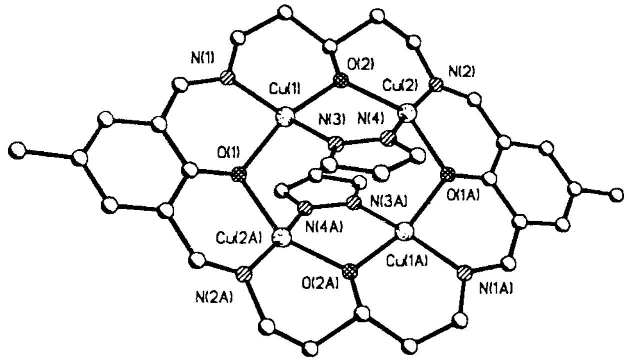


Fig. 2 Perspective view of the $[Cu_4(\mu\text{-pyr})_2(L^1)]^{3+}$ cation. Selected distances (Å) and angles (°): Cu(1)···Cu(2) 3.255(1), Cu(1)–Cu(2A) 3.133(1), Cu(1)–O(1) 1.949(5), Cu(1)–N(1) 1.945(7), Cu(1)–O(2) 1.918(6), Cu(1)–N(3) 1.954(6), Cu(2)–O(1A) 1.973(5), Cu(2)–N(2) 1.942(7), Cu(2)–O(2) 1.950(5), Cu(2)–N(4) 1.945(7); Cu(1)–O(1)–Cu(2A) 106.1(3), Cu(1)–O(2)–Cu(2) 114.6(2), Cu(1)–N(3)–N(4) 119.9(5), Cu(2)–N(4)–N(3) 118.4(5).

pyrazolate ligand and this arrangement causes the coordination geometry at copper to be substantially distorted towards tetrahedral. The resulting steric stress probably responsible for the formation of **1**, where the coordination geometry is more relaxed, as the major product.

Attempts to prepare a pure sample of the dinuclear complex **1**, using a ligand : Cu ratio of 1 : 2 rather than 1 : 4, have not proved successful to date. FAB and IR data are consistent with the suggestion that the initial green product contains the same complex as the crystals of **1** but recrystallised samples always contain a small amount of the tetranuclear complex **2**, suggesting an equilibration between **1** and **2** in solution. Clean samples of the tetranuclear complex can be obtained by treatment of $[Cu_4(L^1)(OH)](BF_4)_3$ with an excess of pyrazole in acetonitrile. In the solid state the two complexes can be distinguished from their IR spectra; **1** shows the expected split imine stretch (1637 and 1657 cm^{-1}) whereas **2** shows a single band at 1631 cm^{-1}. FAB mass spectra of the two complexes are also distinctly different; that of the initial green product shows peaks consistent with a dicopper complex **1**, while complex **2** clearly shows peaks due to tetracopper species.‡

In an attempt to fill the two vacant coordination sites of complex **1**, the crude dicopper complex was treated with an excess of nickel(II) acetate in 1 : 1 methanol–acetonitrile and refluxed overnight. The resulting green complex **3** was characterised from its FAB spectrum (Fig. 3). The spectrum is remarkably simple, showing only two significant clusters centered at *m/z* 807 and 748 which are assigned to $\{[Cu_2Ni_2(L^1)(OH)(MeCO_2)]^{2+}-H^+\}$ and $\{[Cu_2Ni_2(L^1)(OH)]^+-2H^+\}$ respectively; the isotope patterns in the clusters match those predicted.[11] Notably, there are no peaks attributable to scrambled tetranuclear complexes (*e.g.* containing Cu_4, $CuNi_3$, Cu_3Ni or Ni_4 cores) or to unreacted complex **1**. The absence of metal ion scrambling in the FAB, together with the marked preference of tetranickel(II) complexes for bridging acetate groups,[5,12] suggests the structure shown in the scheme, with the addition of an acetate bridge linking the nickel ions is likely to be correct, *i.e.* $[Cu_2Ni_2(L^1)(OH)(MeCO_2)](BF_4)_2$.

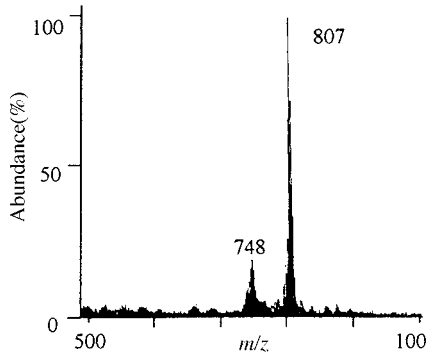


Fig. 3 FAB (SIMS) spectrum of the heterotetranuclear complex $[Cu_2Ni_2(L^1)(OH)(MeCO_2)](BF_4)_2$.

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Notes and references

† *Crystal data:* both data sets were collected ($4 < 2\theta < 50°$) using Mo-Kα radiation (λ = 0.71073 Å) at 153(2) K, corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods[13] and refined by full-matrix least squares on F^2.[14]

1·MeCN: $[Cu_2(\mu\text{-pyr})(H_3L^1)](BF_4)_2\cdot MeCN$, $C_{33}H_{41}B_2Cu_2F_8N_7O_4$, red block, 0.55 × 0.30 × 0.12 mm, monoclinic, a = 8.059(2), b = 21.760(4), c = 21.431(2) Å, β = 98.50(1)°, U = 3717(1)) $Å^{-3}$, space group $P2_1/c$, Z = 4, μ = 1.233 mm^{-1}, $F(000)$ = 1840. 7596 reflections, 6524 independent (R_{int} = 0.0476). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to oxygen and nitrogen were initially located from difference maps but all hydrogen atoms were then inserted at calculated positions. Refinement converged with $wR2$ = 0.1497, GOF = 1.012 (all data) and conventional $R1$ = 0.0591 (2σ data).

2 $[Cu_4(\mu\text{-pyr})_2(L^1)](BF_4)_2$, $C_{34}H_{38}B_2Cu_4F_8N_8O_4$, green plate, 0.37 × 0.30 × 0.05 mm, monoclinic, a = 8.446(1), b = 25.567(3), c = 9.034(1) Å, β = 96.23(1)°, U = 1939.3(4) $Å^{-3}$, space group $P2_1/c$, Z = 2, μ = 1.799 mm^{-1}, $F(000)$ = 1056. 3444 reflections, 3233 independent (R_{int} = 0.0743). Non-hydrogen atoms were refined with anisotropic thermal parameters, except for the minor component of a disorder in the saturated part of the macrocycle, and hydrogen atoms were inserted at calculated positions. Refinement converged with $wR2$ = 0.1465, GOF = 1.037 (all data) and conventional $R1$ = 0.0665 (2σ data). CCDC 182/1180. See http://www.rsc.org/suppdata/cc/1999/639/ for crystallographic files in .cif format.

‡ For the crude dicopper complex the main signals are clusters around the following masses (rel. abundance, assignment): 654 (100%, $[Cu_2(H_3L^1)(H_2O)_2]^+$); 616 (70%, $[Cu_2(H_3L^1)]^+$); 635 (20%, $[Cu_2(H_3L^1)(H_2O)]^+$). For the tetracopper complex: 963 (30%, $[Cu_4(L^1)(pyr)_2(BF_4)]^+$); 876 (100%, $[Cu_4(L^1)(pyr)_2]^+$); 895 (60%, $[Cu_4(L^1)(pyr)_2(H_2O)]^+$).

1 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.
2 See for example: R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W.R.Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; S. Ohtsuka, M. Kodera, K. Motoda, M. Ohba and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1995, 2599; T. Aono, H. Wada, Y. Aratake, N. Matsumoto, H. Okawa and Y. Matsuda, *J. Chem. Soc., Dalton Trans.*, 1996, 25; S. Mohanta, K. N. Nanda, L. K. Thompson, U. Florke and K. Nag, *Inorg. Chem.*, 1998, **37**, 1465.
3 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385.
4 V. McKee and S. S. Tandon, *J. Chem. Soc., Dalton Trans.*, 1991, 221.
5 J. E. Metcalfe, Ph.D. thesis, Queen's University, 1998.
6 S. S. Tandon and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1988, 19.
7 M. G. B. Drew, O. W. Howarth, G. G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1994, 3149.
8 M. G. B. Drew, C. J. Harding, V. McKee, G. G. Morgan, and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 1035.
9 H. Adams, N. A. Bailey, D. E. Fenton, R. Moody and J. M. Latour, *Inorg. Chim. Acta*, 1987, **135**, L1.
10 Y. Nishida and S. Kida, *Inorg. Chem.*, 1988, **27**, 447.
11 J. J. Manura and D. J. Manura, *Isotope Distribution Calculator*, SIS, 1996 *(http:/www.sisweb.com/mstools.htm).*
12 P. E. Kruger and V. McKee, *Chem. Commun.*, 1997, 1341.
13 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
14 G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997.

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