Synthesis and structure of a 2 Cu^{II} 2 Cu^{I} constellation ligated by the new biimidazole, bis(1-methyl-4,5-diphenylimidaz-2-oyl)carbinol

Rajiv Bhalla, Madeleine Helliwell and C. David Garner*

The Chemistry Department, University of Manchester, Oxford Road, Manchester, UK M13 9PL

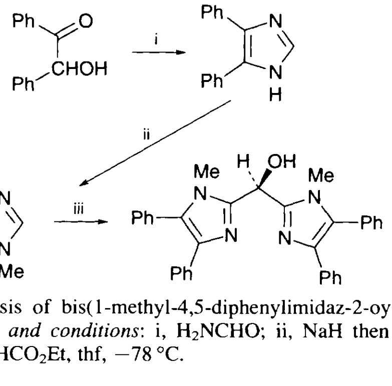
The new biimidazole, bis(1-methyl-4,5-diphenylimidaz-2-oyl)carbinol, BimOH, is synthesized and employed to form the novel tetrameric constellation $[Cu_4(BimOH)_2(BimO)_2]^{4+}$, involving an $(N_{im})_2Cu^{II}(OR)_2Cu^{II}(N_{im})_2$ centre with a Cu^{II}···Cu^{II} separation of 2.998(4) Å and two $Cu^{I}(N_{im})_2$ moieties *ca.* 5 Å from the Cu_2 centre, each with an N–Cu–N angle of 169.3(4)°.

The imidazole group of the amino acid histidine is a ubiquitous ligand for 3d transition-metal ions bound to proteins. Structural studies on copper-containing proteins including plastocyanin,[1] azurin,[2] haemocyanin,[3] Cu/Zn superoxide dismutase,[4] galactose oxidase,[5] nitrite reductase[6] and ascorbate oxidase[7] have revealed that there are at least two histidine residues bound to each copper centre. The existence of these centres in natural systems has stimulated extensive synthetic studies developing the new chemistry and illuminating the character of the natural systems.[8–12]

We have synthesized several new sterically hindered bi- and tri-imidazole ligands and investigated the manner in which they bind copper.[13,14] Herein we report the synthesis of bis(1-methyl-4,5-diphenylimidaz-2-oyl)carbinol BimOH (Scheme 1) and a product of its reaction with Cu^{I}.†

The reaction of BimOH with 1 equiv. of $[Cu(MeCN)_4][PF_6]$ in CH_2Cl_2 under Ar produced a green material **I** with relative composition Cu : ligand : $[PF_6]$ of 1 : 1 : 1. Recrystallization from CH_2Cl_2–MeOH (2 : 5 *v*/*v*) yielded green crystals of **I** which proved suitable for analysis by X-ray crystallography.‡ This revealed that **I** comprises (Figs. 1 and 2) a tetrameric copper constellation;[15] the asymmetric unit consists of half a molecule, the other half being generated by rotation about a twofold axis. Associated with each cation are four PF_6^- ions and two disordered MeOH molecules.

The two central copper atoms [Cu(1) and Cu(1A)] are each coordinated to two nitrogens from imidazole groups of different ligands [Cu(1)–N(1A) 1.99(1), Cu(1)–N(5) 1.943(8) Å]; two oxygen atoms bridge the central coppers [Cu(1)–O(1) 1.952(8), Cu(1)–O(1A) 1.936(7) Å], and another oxygen atom is weakly bound [Cu(1)–O(2) 2.44(1) Å]. The geometry of each central Cu may be described as square-based pyramidal with the furthest oxygen atom located at the apex. The other two copper atoms [Cu(2), Cu(2A)] are each coordinated to two imidazole nitrogens [Cu(2)–N(3) 1.88(1), Cu(2)–N(7) 1.85(1) Å] which originate from different ligands (Fig. 2). The geometry of these CuN_2 units is almost linear [N–Cu–N 167.9(4)°].



Scheme 1 Synthesis of bis(1-methyl-4,5-diphenylimidaz-2-oyl)carbinol, BimOH. *Reagents and conditions*: i, H_2NCHO; ii, NaH then MeI, thf; iii, BuLi then 0.5 HCO_2Et, thf, −78 °C.

The hydrogen atoms on O(2) and O(2A) were located by difference Fourier techniques consistent with the N(5)O(2)N(7) ligand (and its symmetry equivalent) being neutral (BimOH). Hydrogen atoms were not located on the oxygen atoms O(1) and O(1A) and thus their environment, and the arguments *vs.* the oxidation state of the Cu atoms, are all consistent with the N(1)O(1)N(3) ligand (and its symmetry equivalent) being deprotonated (BimO$^-$). Cu(2) and Cu(1) (and their symmetry equivalents) are assigned oxidation states of Cu^{I} and Cu^{II}, respectively. This is consistent with the nature and dimensions

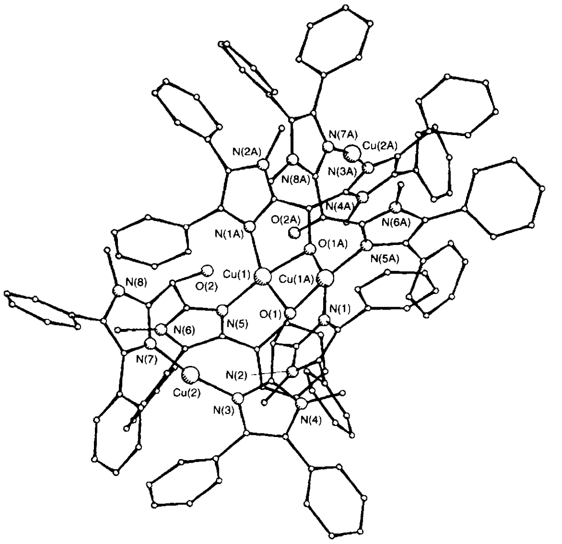


Fig. 1 PLUTO representation of the structure of the cation $[Cu_4(BimOH)_2(BimO)_2]^{4+}$ with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)···Cu(1A) 2.998(4), Cu(1)–O(1) 1.952(8), Cu(1)–O(1A) 1.936(7), Cu(1)–N(1A) 1.99(1), Cu(1)–N(5) 1.943(8), Cu(1)–O(2) 2.44(1), Cu(2)–N(3) 1.88(1), Cu(2)–N(7) 1.85(1), Cu(1)–Cu(2) 4.43, Cu(1)–Cu(2A) 5.73; O(1)–Cu(1)–O(1A) 75.8(3), O(1)–Cu(1)–N(1A) 158.4(3), O(1)–Cu(1)–N(5) 100.2(4), O(1A)–Cu(1)–N(1A) 83.2(4), O(1A)–Cu(1)–N(5) 169.3(4), (1A)–C(1)–N(5) 101.4(4), N(3)–Cu(2)–N(7) 167.9(4), Cu(1)–O(1)–Cu(1A) 100.9(3).

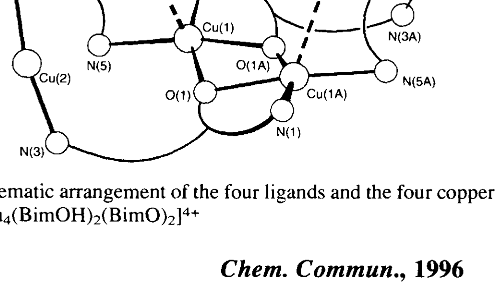


Fig. 2 Schematic arrangement of the four ligands and the four copper atoms within $[Cu_4(BimOH)_2(BimO)_2]^{4+}$

of the coordination spheres of copper centres[16–19] and the presence of a d–d band (λ_{max} = 688 nm in the solid state) indicating that at least one of the centres has an oxidation state of >I. Thus, the overall stoichiometry is charge balanced as 2 Cu^{2+}, 2 Cu^+, 2 BimOH, 2 $BimO^-$ and 4 PF_6^-.

The central $Cu^{II}(\mu\text{-}O)_2Cu^{II}$ portion of the cation deviates slightly from planarity; the angle between the planes O(1)Cu(1)O(1A) and O(1)Cu(1A)O(1A) is 155.4°. The $Cu^{II}\cdots Cu^{II}$ separation of 2.998(1) Å is reasonably small and this is consistent with a strong $Cu^{II}\cdots Cu^{II}$ interaction and the failure to detect an EPR signal for solid **I**.

The structure of the cation of **I** demonstrates a versatility of the coordinating ability of the new proligand reported herein. The neutral molecule (BimOH) coordinates to a Cu^I and a Cu^{II} centre *via* both imidazoles and the alcohol functionality; $BimO^-$ links two Cu^{II} centres *via* the alkoxide group and one imidazole binds to one of the Cu^{II} centres and the other to a Cu^I centre. There is sufficient flexibility in the ligand framework to allow the assembly of the tetracopper constellation with preferred geometries at the Cu^I and Cu^{II} centres.

We thank the University of Manchester for the award of a scholarship (R. B.), the funds provided by the EC Human Capital and Mobility Framework III MASIMO Network, and Drs. T. C. Higgs, J. McMaster and F. E. Mabbs for their valuable contributions.

Footnotes

† In a Schlenk tube, BimOH (200 mg, 0.40 mmol) and $[Cu(MeCN)_4][PF_6]$ (150 mg, 0.40 mmol) were dissolved in dry, degassed CH_2Cl_2 (20 cm^3) under Ar and stirred at room temp. for 2 h, during which time the solution became intense green. The volume was reduced by half and then carefully layered with Et_2O (40 cm^3) which yielded the pure green solid **I**. Yield = 120 mg, 42%.

‡ *Crystal data* for $[Cu_4(BimOH)_2(BimO)_2][PF_6]_4\cdot 2MeOH$: $C_{134}H_{118}Cu_2F_{24}N_{16}O_6P_4$, M_r = 2882.56, green block-like crystals (0.2 × 0.2 × 0.4 mm), monoclinic, space group *C*2/*c*, a = 25.606(8), b = 17.719(6), c = 33.666(7) Å, β = 106.18(2)°, U = 14670(8) $Å^3$, Z = 4, D_c = 1.305 g cm^{-3}, $F(000)$ = 5896, μ(Cu-Kα) = 17.86 cm^{-1}, 12227 reflections (11524 unique, R_{int} = 0.072) were collected at a temperature of 295 ± 1 K, using the ω–2θ scanning technique to a maximum value of 2θ value of 122°, on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54178 Å) and a 12 kW rotating anode generator. Data were corrected for Lorentz and polarization effects, decay (11.50% decline) and absorption effects, based on azimuthal scans of three reflections (transition factor ranging from 0.85 to 1.00). The structure was solved by the Patterson method (SHELXS 86[20]), which led to the location of most of the non-hydrogen atoms. The structure was developed using a combination of direct methods (DIRDIF[21]) and difference Fourier techniques. All non-hydrogen atoms of the cation and the $[PF_6]^-$ groups were refined isotropically, except those of the phenyl group C(61)–C(66), whose carbon and hydrogen atoms were constrained to form an idealistic C_6H_5 group [C–C = 1.40(2) Å, C–H = 0.95 Å], with the carbon atoms refined anisotropically. The methanol solvent molecules were disordered over two sites each with an occupancy of 0.5. Their carbon and oxygen atoms were refined isotropically. Most hydrogen atoms were included in idealised positions. The hydrogen atom attached to O(2) was found by difference Fourier methods. All hydrogen atoms were assigned isotropic thermal parameters 20% higher than those of atoms to which they were directly bonded. Full-matrix least-squares refinement was based on 5363 observed reflections [$I > 2\sigma(I)$] and 792 variable parameters, converging at R = 0.102, R_w = 0.114. The high R value is a result of the disorder present within the MeOH solvent molecules. Maximum and minimum peaks in a final difference map were 0.77 and −0.25 e^- $Å^{-3}$, respectively. 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 182/15.

References

1 J. M. Guss, E. A. Merritt, R. P. Phizackerly, B. Hedman, M. Murata, K. O. Hodgson and H. C. Freeman, *Science*, 1988, **241**, 806.
2 E. N. Baker, *J. Mol. Biol.*, 1983, **203**, 1071.
3 K. A. Magnus, H. Ton-That and J. E. Carpenter, *Chem. Rev.*, 1994, **94**, 727.
4 J. A. Tainer, E. D. Getzoff, K. M. Beem, J. S. Richardson and D. C. Richardson, *J. Mol. Biol.*, 1982, **160**, 181.
5 N. Ito, S. E. V. Philips, C. Stevens, Z. P. Oqel, M. J. McPherson, J. N. Keen, K. D. S. Yadav and P. F. Knowles, *Nature (London)*, 1991, **350**, 87.
6 J. W. Godden, S. Turley, D. C. Teller, E. T. Adman, M.-Y. Liu and J. LeGall, *Science*, 1991, **253**, 438.
7 A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gatti, A. Manchesini, R. Petruzelli and A. Finazzo-Agnó, *J. Mol. Biol.*, 1989, **206**, 513.
8 N. Kitajima, *Adv. Inorg. Chem.*, 1992, **39**, 1.
9 Z. Tyeklar and K. D. Karlin, *Acc. Chem. Res.*, 1989, **22**, 241.
10 E. Bouwman, W. L. Driessen and J. Reedijk, *Coord. Chem. Rev.*, 1990, **104**, 143.
11 T. N. Sorrell, W. E. Allen and P. S. White, *Inorg. Chem.*, 1995, **34**, 952.
12 S. Knapp, T. P. Keenan, Xiaohua Zhang, R. Fikar, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1990, **112**, 3452.
13 T. C. Higgs, M. Helliwell and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1996, in press.
14 J. McMaster, R. L. Beddoes, D. Collison, D. R. Eardley, M. Helliwell and C. D. Garner, *Chem. Eur. J.*, 1996, in press.
15 D. E. Fenton and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1993, 1349.
16 T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.*, 1983, **105**, 6013.
17 T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.*, 1982, **104**, 2053.
18 G. O. Tan, K. O. Hodgson, B. Hedman, G. R. Clark, M. L. Garrity and T. N. Sorrell, *Acta Crystallogr., Sect. C*, 1990, **46**, 1773.
19 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
20 G. M. Sheldrick, SHELXS-86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, C. Kreuger and R. Goddard, Oxford University Press, 1985, p. 175.
21 P. T. Beurskens, DIRDF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors, Technical Report 1984/1 Crystallographic Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands, 1984.

Received, 14th December 1995; Com. 5/08135A