Bimetallic Oxidation Catalysts. Oxygen Insertion into an Aryl–Hydrogen Bond of a Binuclear Copper(I) Complex

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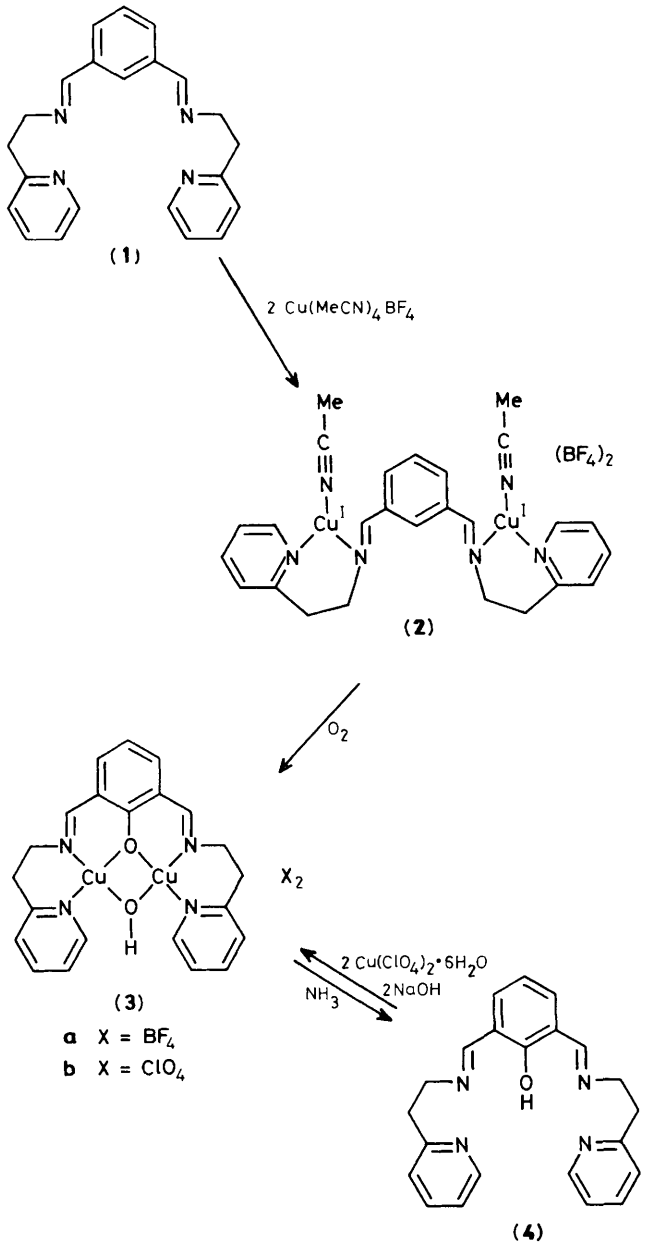
The binuclear copper(I) complex of 1,3-bis[*N*-(2-pyridylethyl)formimidoyl]benzene reacts with molecular oxygen to give a phenoxy- and hydroxy-bridged binuclear copper(II) complex; the structures of both complexes have been determined by *X*-ray crystallography.

It is well established that the biological action of many metalloproteins is associated with the occurrence of metal ions in pairs. Prominent members are proteins containing binuclear copper centres such as the oxygen transport protein hemocyanin[1] and the oxygenases, *e.g.*, tyrosinase.[2] Several potential mimics of binuclear copper sites in these enzymes as well as detailed structural studies of the co-ordination in copper complexes of binucleating ligands have appeared in recent years.[3,4] Karlin and co-workers[5] elegantly demonstrated the binding and activation of molecular oxygen with



Scheme 1

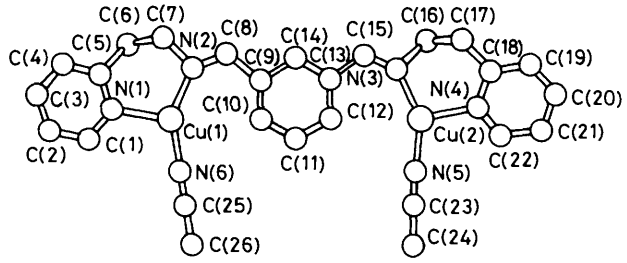


Figure 1. ORTEP diagram of (**2**). Selected bond distances (Å) and angles (°): N(1)–Cu(1) 2.066(10), N(2)–Cu(1) 1.978(11), N(6)–Cu(1) 1.915(12), N(3)–Cu(2) 1.955(11), N(4)–Cu(2) 2.086(11), N(5)–Cu(2) 1.895(12), Cu(1) · · · · Cu(2) 4.952(2); N(1)–Cu(1)–N(2) 103.3(4), N(1)–Cu(1)–N(6) 109.9(4), N(2)–Cu(1)–N(6) 143.9(5), N(3)–Cu(2)–N(4) 102.3(5), N(3)–Cu(2)–N(5) 149.4(5), N(4)–Cu(2)–N(5) 108.0(5).

binuclear copper complexes of bridged bis-2-(2-pyridyl)-ethylamine ligands. However the structural requirements for oxygen activation, and catalytic activity of binuclear copper centres are less well defined.

As a result of our investigation of bimetallic oxidation catalysts[6] we describe here the formation and structure determination of new catalytically active binuclear Cu^{I} and Cu^{II} complexes (**2**) and (**3**) and the hydroxylation of the arene moiety in (**2**) by molecular oxygen. With the aim of binding two Cu^{I} ions we synthesized 1,3-bis[*N*-(2-pyridylethyl)formimidoyl]benzene (**1**), a binucleating ligand in which two bidentate 2-(2-pyridyl)ethylimine units are separated by a *m*-xylyl bridge.† The binuclear Cu^{I} complex (**2**) was prepared as a yellow crystalline compound by adding (**1**), dissolved in tetrahydrofuran (THF), to a stirred suspension of $Cu^{I}(MeCN)_4BF_4$ in THF, followed by crystallization from CH_2Cl_2–MeOH (10:1), Scheme 1.‡

X-Ray analysis of this complex (Figure 1) revealed that each Cu^{I} is co-ordinated to three nitrogen donor atoms, two of which originate from the pyridylethylimine moiety and one from acetonitrile.§ The N_{imine}–Cu–N_{MeCN} angles [143.9(5) and 149.4(5)°] are large, and the Cu ions are well separated with a Cu(1)–Cu(2) distance of 4.952(2) Å. Distortion from planarity occurs mainly at only one of the Cu^{I} sites with Cu(1) 0.181 Å out of the N(1),N(2),N(6) plane and Cu(2) 0.045 Å out of the N(3),N(4),N(5) plane. The larger deviation at Cu(1) might be caused by an interaction with the pyridine nitrogen of a second dication as suggested by the structure analysis (Figure 1). The Cu–N bond lengths fall into the range generally found for 3-co-ordinated complexes except for the Cu–$N_{pyridine}$ bond lengths [2.066(10), 2.086(11) Å] which are unexpected in view of the 1.88—2.02 Å Cu^{I}–$N_{heterocyclic}$ distances common in 3-co-ordinated complexes.[5,7] A limited number of 3-co-ordinated Cu^{I} complexes containing unsaturated nitrogen ligands have been characterised and no

† Readily prepared from benzene-1,3-dicarbaldehyde and 2-(2-pyridyl)ethylamine.

‡ Satisfactory elemental analyses were obtained. One CH_2Cl_2 solvate molecule is present in (**2**).

§ *Crystal data*: complex (**2**), triclinic, space group $P\bar{1}$, 2 crystallographically independent molecules: a = 10.003(4), b = 10.979(2), c = 29.763(5) Å, α = 88.83(1), β = 81.38(2), γ = 89.91(2)°; Z = 4, D_c = 1.663 g cm^{-3}; U = 3220.9 Å^3; crystal dimensions 0.30 × 0.35 × 0.40 mm; λ(Mo-K_α) = 0.71073 Å; μ(Mo-K_α) = 15.6 cm^{-1}. Data were collected with graphite-monochromated Mo-K_α radiation on a CAD4F diffractometer and the structure was solved by direct methods (CAD4 SDP-programs, Enraf-Nonius Dreux & Associates). 3200 unique reflections with $I > 3.0\ \sigma(I)$ were used in full-matrix least-squares refinement, including H atoms with isotropic thermal parameters, to R = 0.076, R_w = 0.078 (non-hydrogen atoms were refined anisotropically).

Complex (**3a**), triclinic, space group $P\bar{1}$, Z = 2: a = 9.323(4), b = 10.449(2), c = 14.179(4) Å, α = 102.30(4), β = 102.43(2), γ = 101.84(2)°, D_c = 1.763 g cm^{-3}. 3384 Reflections with $I > 3.0\ \sigma(I)$ were collected on a Nonius CAD4F diffractometer. Some disorder was found in the C(21), C(22) part of the molecule; in a difference Fourier map without C(21) and C(22) four peaks with nearly the same electron density were located on positions with reasonably geometry. Carbon atoms C(211), C(212), C(221), C(222) introduced with a site occupation factor of 0.5 in these positions refined satisfactorily. H atoms, which were located on a difference Fourier map, were included in the final refinement with isotropic thermal parameters. The structure was solved using SHELX 86, and refined to R = 0.044 (non-hydrogen atoms were refined anisotropically).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

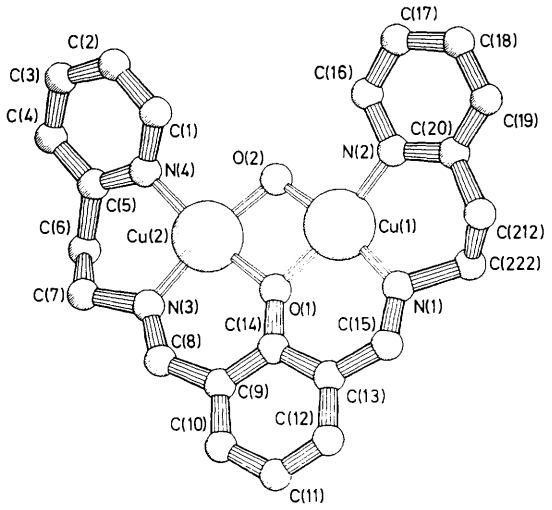


Figure 2. PLUTO diagram of (**3a**) showing one of the structures with disorder at C(21)–C(22). Selected bond distances (Å) and angles (°): Cu(1)–N(1) 1.933(6), Cu(1)–N(2) 1.996(5), Cu(1)–O(1) 1.968(4), Cu(1)–O(2) 1.909(4), Cu(2)–N(3) 1.939(5), Cu(2)–N(4) 1.991(5), Cu(2)–O(1) 1.967(4), Cu(2)–O(2) 1.911(4), Cu(1)–Cu(2) 2.990(2); N(1)–Cu(1)–N(2) 96.4(2), N(1)–Cu(1)–O(1) 90.7(2), N(2)–Cu(1)–O(1) 171.1(2), N(2)–Cu(1)–O(2) 95.3(2), N(1)–Cu(1)–O(2) 166.1(2), O(1)–Cu(1)–O(2) 78.3(2), N(3)–Cu(2)–N(4) 96.5(2), N(3)–Cu(2)–O(1) 91.8(2), N(4)–Cu(2)–O(1) 169.9(2), N(4)–Cu(2)–O(2) 93.6(2), O(1)–Cu(2)–O(2) 78.3(2), N(3)–Cu(2)–O(2) 169.9(2).

Cu^{I}–Cu^{I} interactions found;[5,7,8] to our knowledge (**2**) is the first example containing both bidentate and monodentate ligands.

Binuclear complex (**2**) is air stable for a few minutes in the crystalline state; however in solution in dimethylformamide (DMF) or acetonitrile it becomes very sensitive to air oxidation. Manometric oxygen uptake experiments showed a stoicheiometric reaction of (**2**) with molecular oxygen resulting in the formation of a green complex (**3a**). The crystalline dark-green binuclear Cu^{II} complex (**3a**) was obtained from EtOH–H_2O (Scheme 1).‡ *X*-Ray analysis of (**3a**) revealed incorporation of two oxygen atoms into the complex with one of the oxygen atoms formally inserted into the aryl–hydrogen bond of complex (**2**) whereas the other oxygen atom is incorporated into the hydroxy bridge (Figure 2).§ We suppose, in accord with earlier work,[5] that these oxygen atoms originate from molecular oxygen. Presumably molecular oxygen will bind to the two copper centres thereby bridging the two copper ions with a μ-1,1- or μ-1,2-peroxide intermediate. Rotation around both the aryl–imine carbon–carbon bonds brings the copper centres in close proximity allowing the formation of a binuclear Cu^{II} peroxo complex.

The geometry around each Cu^{II} ion in (**3a**) is slightly distorted square planar with a Cu^{II}–Cu^{II} separation of 2.990(2) Å. The latter is typical of binuclear copper complexes containing two one-atom bridging ligands,[5,7,9] and is considerably shorter than the Cu–Cu distance in oxyhemocyanine.[3] The Cu_2O_2 unit deviates from planarity with an O(1)–Cu(1)–O(2)–Cu(2) torsion angle of 9.3(2)°. The phenol ligand (**4**) could be liberated from complex (**3a**) with ammonia.[5] Complex (**4**) was prepared independently from 2-formylsalicylaldehyde, and the Cu^{II} perchlorate analogue (**3b**) was obtained from (**4**) by reaction with $Cu(ClO_4)_2.6H_2O$ (2 equiv.) and base. The products obtained by both routes had similar spectral data.[10] Cyclic voltammetric measurements on (**3b**) in acetonitrile under nitrogen showed no reversible oxidation–reduction sequence at the copper centres, presumably owing to reaction at the imine bond. Preliminary experiments showed that (**3a**) and (**3b**) are able to act as catalysts in the oxidations of α-hydroxy ketones to diketones and hydroquinones to quinones with molecular oxygen. Thus benzoin was quantitatively oxidized in a few minutes with oxygen to benzil using 5 mol % of (**3a**) in MeOH.

The insertion reaction of molecular oxygen with the aid of two Cu^{I} centres as described here is characteristic of some oxygenases, *e.g.* tyrosinase.[1,2] Karlin[5] was the first to discover this type of arene hydroxylation in the synthesis of a hemocyanin model system in which Cu^{I} ions are attached to tridentate bis-2-(2-pyridyl)ethylamine ligands separated by a *m*-xylyl bridge. Replacing the pyridine moieties in this complex by imidazole groups blocked the oxygen insertion completely.[7] Changes in their ligand system caused loss of oxygen insertion ability, which led to the conclusion that small electronic effects are crucial in determining whether or not this reaction occurs.[5,11] It is surprising that the binuclear Cu^{I} complex (**2**) containing one bidentate and one monodentate ligand attached to each Cu^{I} ion is able to bind molecular oxygen, this being followed by hydroxylation of the arene moiety. The findings described here might have consequences for the design of new ligand systems for binuclear copper enzyme models that mimic tyrosinase and hemocyanin.

Considering earlier results[11] it is shown that the aromatic hydroxylation with binuclear Cu^{I} complexes and molecular oxygen is not specific to a tridentate ligand system and does not as critically depend on the types of donor groups as previously suggested.

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