

Oxidative Nitrogen · · · Nitrogen Coupling of Nitriles at a Dicopper Site and the Structure of a Pentanuclear Copper-Triazolyl Complex containing Two-co-ordinate and Three-co-ordinate Copper(I)

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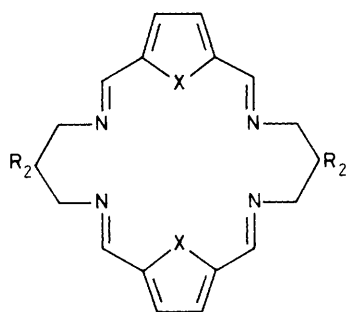
Reaction of a di-copper(II) complex of a macrocyclic ligand with acetonitrile in the presence of O₂ and H₂O affords a pentanuclear complex containing two-co-ordinate and three-co-ordinate copper(I) atoms linked *via* triply bridging 3,5-dimethyl-1,2,4-triazolate groups.

The rapidly growing interest in di- and poly-nuclear complexes arises partly from the awareness that pairs or clusters of metal ions are sometimes capable of mediating certain chemical reactions either better or differently than do isolated metal centres. Nature takes advantage of this fact in the use of many metalloproteins in which the active sites comprise pairs of metal ions in close proximity. We have previously stressed¹ the importance of a dinuclear site in some dicopper complexes of the macrocyclic ligand (**1a**) which are active catalysts for the oxidation of, *inter alia*, catechols to *o*-quinones; *cf.* the catecholase activity of the copper enzyme tyrosinase. We now report an unusual oxidative coupling reaction of aliphatic nitriles which also appears to require the agency of a dimetallic site.

The complexes [Cu₂(**1a**)(MeCN)₂][ClO₄]₂ (**2a**) and [Cu₂(**1b**)(MeCN)₂][ClO₄]₂ (**2b**) were prepared by treatment of Ba(**1a**)[ClO₄]₂·EtOH and Ca(**1b**)[ClO₄]₂·EtOH with a three-fold excess of [Cu(MeCN)₄][ClO₄] in MeCN-EtOH (2:3) at 60 °C in the absence of air. The structure of (**2a**) has previously been shown¹ to contain two three-co-ordinate Cu^I ions, 3.35 Å apart, each bonded to two imino nitrogens of the macrocycle and to one MeCN molecule; the structure of (**2b**) is presumed to be the same on the basis of its virtually identical properties. When the transmetallation was carried out at reflux temperature in 'wet' solvent (1–2% H₂O) with access to air the pentanuclear complexes [Cu₅(**1a**)₂(dmt)₂][ClO₄]₃ (**3a**) and [Cu₅(**1b**)₂(dmt)₂][ClO₄]₃ (**3b**) (dmt = 3,5-dimethyl-1,2,4-triazolate anion) were obtained in up to 55% yield. The

same products were obtained starting from (**2a**) and (**2b**). Separate experiments established the necessity of both H₂O and O₂ in the formation of the triazolate ring. Moreover, no triazolate was formed when [Cu(MeCN)₄][ClO₄] was used in place of the dinuclear complexes (**2a**) or (**2b**). The use of EtCN in the solvent mixture in place of MeCN afforded the corresponding pentanuclear complex of 3,5-diethyl-1,2,4-triazolate. The nature of the pentanuclear complexes (**3**) was determined by chemical analysis, i.r. and ¹H n.m.r. spectroscopy,[†] and in the case of (**3a**), (**3b**), and (**3c**)[‡] by their independent preparation in the absence of air and water *via* self-assembly from the complexes (**2**) (2 equiv.), pre-prepared Hdmt (2 equiv.), and [Cu(MeCN)₄][ClO₄] (1 equiv.). The structure of (**3b**) was determined by X-ray analysis.

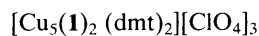
Crystal data for (**3b**): [Cu₅(**1b**)₂(dmt)₂][ClO₄]₃·1.7 C₂H₅OH, *M* = 1647.6, monoclinic, space group *C2/c*, *a* = 19.64(1), *b* = 13.12(1), *c* = 26.94(1) Å, β = 81.6(1)°, *U* =



(1)



(2)



(3)

a; X = O, R = H
b; X = O, R = Me
c; X = S, R = Me

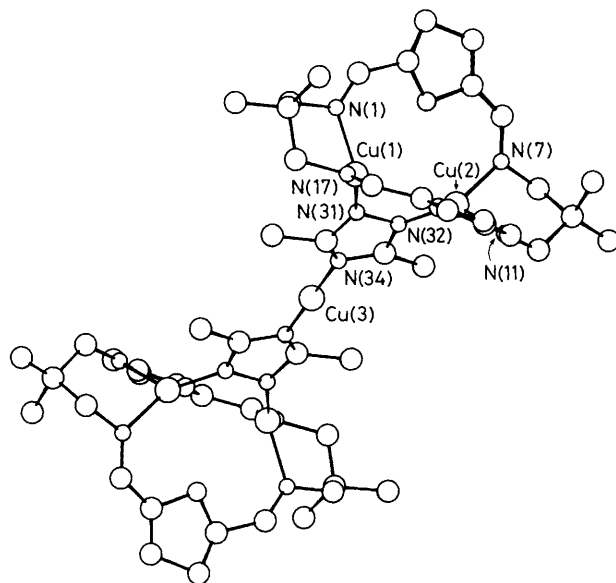


Figure 1. The structure of the pentanuclear [Cu₅(**1b**)₂(dmt)₂]³⁺ cation.

[†] All new complexes gave analyses (C,H,N) in agreement with the proposed formulae. In contrast to complexes (**2**) the ¹H n.m.r. spectra of (**3**) in CD₃CN reflect the inequivalence of the two faces of the macrocycle. Thus, for (**3b**), the ring CH₂ protons occur as a pair of doublets (*J*_{HH} = 12 Hz) at δ 3.50 and δ 4.42, and the CH₃ protons as a pair of singlets at δ 1.17 and δ 1.92.

[‡] Complex (**3c**) was prepared directly by a template method using Cu^I rather than by transmetallation from an alkaline earth metal complex as in the case of (**3a**) and (**3b**).

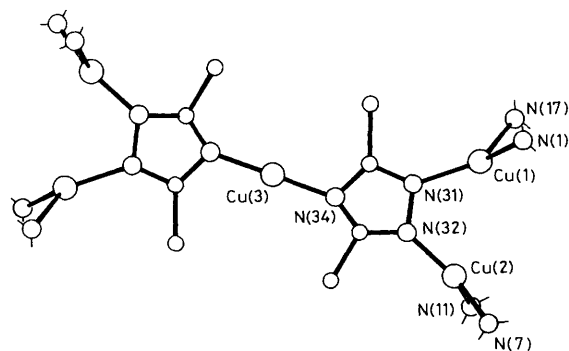


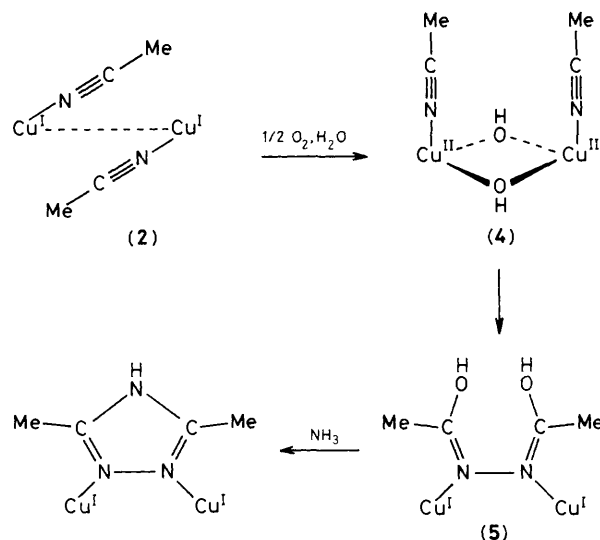
Figure 2. The co-ordination spheres of the copper atoms in (3b): bond lengths: Cu(1)-N(1) 1.95(3), Cu(1)-N(17) 2.10(3), Cu(1)-N(31) 1.97(3), Cu(2)-N(7) 1.90(3), Cu(2)-N(11) 2.04(3), Cu(2)-N(32) 1.80(2), Cu(3)-N(34) 1.85(3) Å.

6870.2 Å³, $D_c = 1.59$, $D_m = 1.54$ g cm⁻³, $Z = 4$. 1104 Reflections above background were collected by diffractometer and the structure refined (Cu and Cl anisotropically, C, H, O, and N isotropically) to R 0.10.§

The centrosymmetric cation is shown in Figure 1. A linearly co-ordinated copper atom Cu(3) is positioned on the centre of symmetry and links two Cu₂(1b)(dmt) moieties in which the copper atoms are three-co-ordinate and approximately planar, each bonded to two nitrogens of a macrocycle and one nitrogen of a triazolate ring. Cu(1) and Cu(2) each have a slight pyramidal distortion being 0.27 and 0.19 Å from the respective N₃ planes, these, in turn, being almost perpendicular to the triazolate ring plane with angles of intersection of 74.7 and 87.8°, respectively. The four nitrogen atoms of each macrocycle form a plane (maximum deviation 0.05 Å) with the two copper atoms 0.83 and 0.89 Å displaced to one side (towards the triazolate ring) and the two furan oxygen atoms 0.61 and 0.63 Å to the other. The Cu(1) ··· Cu(2) distance is 3.343(9) Å. The geometry of the co-ordination spheres is illustrated in Figure 2 together with the important dimensions. Presumably, the presence of the methyl substituents on the triazole ring prohibits any bonding to Cu(3) in the plane but there are some weak contacts (*ca.* 2.6 Å) to the disordered solvent ethanol in the axial direction.

The central two-co-ordinate copper atom Cu(3) in (3b) and (3c) may be replaced by Ag^I *via* the use of Ag[ClO₄] in place of [Cu(MeCN)₄][ClO₄] in the direct 'self-assembly' method of preparation to afford [AgCu₄(1b,c)₂(dmt)₂][ClO₄]₃ in good yield.

The oxidation of aliphatic nitriles *via* N ··· N coupling is, as far as we are aware, unprecedented. Its occurrence here on a dicopper complex known to contain co-ordinated nitrile ligands at adjacent copper centres is strongly indicative of a mechanism involving concerted nitrile-to-Cu^{II} electron transfer with concomitant N ··· N coupling at the dimetallic site. The proposed sequence of steps summarised in Scheme 1 incorporates this idea as well as the known facts relating to the reaction. The first step is seen as an aerobic oxidation of (2) to



Scheme 1

a di- μ -hydroxo-di-Cu^{II} species (4).¶ This is followed by intramolecular nucleophilic attack by the *cis*-co-ordinated OH⁻ groups at the nitrile carbon atoms, as observed by Schibler and Kaden² in the hydrolysis of some (mononuclear) complexes of tetra-azamacrocycles having pendant nitrile groups. A concerted nitrile-to-Cu^{II} electron transfer at both metal centres with accompanying coupling of the two adjacent nitrogens leads to the species (5). The NH₃ needed for the final ring-closure step is believed to come from a separate metal-promoted hydrolysis of acetonitrile, the intermediate hydrolysis product acetamide having been detected (*g.l.c.*) in the reaction mixture.

It is probably significant that the only previous report³ of the formation of a 1,2,4-triazole *via* N ··· N coupling is of the reaction of the sodium salt of an amidine (obtained from benzonitrile and sodium amide) with CuCl in 1,2-dimethoxyethane. Since the aggregation of simple Cu^I salts in poorly co-ordinating solvents is well known⁴ it seems likely that this reaction also proceeds by way of di- or poly-nuclear intermediates.

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§ The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ A di- μ -hydroxo-di-Cu^{II} complex of (1a) has been prepared and characterised (*ref.* 1). This complex may also be used as a starting material for the preparation of (3a).