

Bridging Phenoxo-ligands in Dicopper(I) Complexes: Synthesis and Structure of Tetrakis(isocyanide)-bis(μ -phenoxo)-dicopper(I) Complexes

Marco Pasquali,^a Paolo Fiaschi,^a Carlo Floriani,^{*a} and Amelia Gaetani-Manfredotti^b

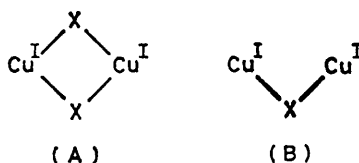
^a *Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy*

^b *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Università di Parma, 43100 Parma, Italy*

The reaction of CuCl with PhONa followed by the addition of RNC (R = cyclohexyl, *p*-tolyl) gave as thermally stable crystalline solids [$(\text{RNC})_4\text{Cu}_2(\text{OPh})_2$] containing a dicopper(I) unit doubly bridged by two phenoxo-groups [R = *p*-tolyl; Cu . . . Cu, 3.223(3) Å], with isocyanide ligands completing the tetraco-ordination around each copper [$\nu(\text{C-N})$: R = *p*-tolyl, 2120 and 2145 cm^{-1} ; R = cyclohexyl, 2130 and 2160 cm^{-1}].

The role of alkoxo-ligands in copper(I) chemistry is interesting for various reasons: (i) the Cu-OR unit seems to parallel the

role of the Cu-R group in copper(I)-assisted organic syntheses;¹ (ii) activation of carbon dioxide by complexes containing the



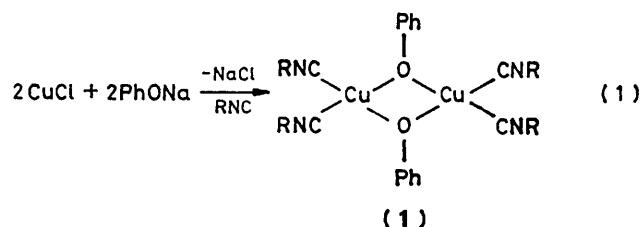
Cu-OR moiety has been achieved;² and (iii) the alkoxy-group has been recognised as a crucial bridging ligand for dinuclear copper(I) complexes capable of interacting with dioxygen in naturally occurring systems.³

In spite of these interesting features, synthetic and structural results in copper(I)-alkoxy-chemistry are rare. This has been ascribed mainly to the intrinsic instability of the Cu-OR bond.^{1,4} In a few cases homoleptic copper(I) alkoxides have been isolated and a tetranuclear structure was recognised for $[\text{Cu}_4(\text{OCMe}_3)_4]$.⁵ Dimeric structures containing either the skeleton (A) or (B) are common in copper(I) chemistry where the bridging ligand is a halogen,⁶ while no example is known when X is an alkoxy-group and very few when it contains oxygen donor atoms. Recently, a unique example of a dicopper complex has been reported to have the skeleton (B), $[\text{Cu}_2(\mu\text{-PhCO}_2)]$,⁷ with the ability to bond to a bridging carbon monoxide molecule.

We report the synthesis and the structure determination of the first dicopper(I) complexes containing the phenoxo-group as bridging ligand. Copper(I) chloride was treated with a tetrahydrofuran (THF) solution of PhONa, then NaCl was filtered off, and to the resulting light yellow solution an isocyanide (RNC: R = cyclohexyl or *p*-tolyl) was added. The crystals of complexes (1)† were recovered by addition of Et₂O (reaction 1).

The dimeric (CuOPh)₂ unit can be trapped using ancillary ligands other than isocyanides. When 1,2-bis(diphenylphosphino)ethane (dppe) was used in reaction (1) instead of RNC the complex $[\text{Cu}_2(\text{dppe})_3(\text{OPh})_2]$ † was isolated. Carbon monoxide reacts with the solution formed by reaction of CuCl with PhONa [$\nu(\text{C-O})$, 2080 cm⁻¹], though the isolation of any carbonyl-copper(I) complex is probably prevented by the lability of carbon monoxide and by the fact that an equally labile solvent molecule (THF) is probably present.

An X-ray crystal structure determination was carried out on complex (1), R = *p*-MeC₆H₄.‡ An ORTEP view of $[(p\text{-MeC}_6\text{H}_4\text{NC})_2\text{Cu}_2(\text{OPh})_2]$ is shown in Figure 1, and the caption lists the important bond distances and angles. The dinuclear complex has C_i symmetry, and the pseudo-tetrahedral geometry around each copper is provided by the bridging phenoxo-groups and two C-bonded *p*-tolyl isocyanides. The two co-ordination planes Cu, O', O and Cu, C(15), C(7) are mutually orthogonal, the dihedral angle being 92.8°. The



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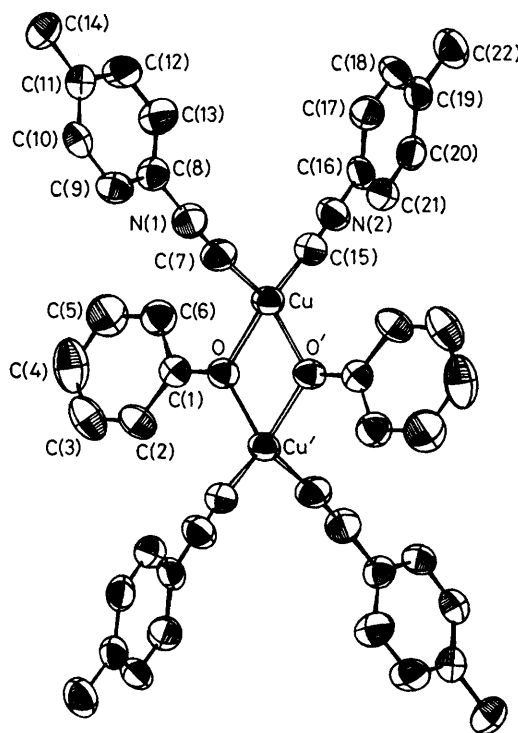


Figure 1. The structure of complex, $[(p\text{-MeC}_6\text{H}_4\text{NC})_2\text{Cu}_2(\text{OPh})_2]$. Relevant bond distances (Å) and angles (°) are: Cu . . . Cu, 3.223(1); Cu-O, 2.066(4); Cu'-O, 2.082(4); Cu-C(15), 1.907(7); Cu-C(7), 1.905(7); C(15)-N(2), 1.150(9); C(7)-N(1), 1.143(9); Cu-O-Cu', 101.9(2); O'-Cu-O, 78.1(2); O-Cu-C(7), 113.2(2); C(7)-Cu-C(15), 111.5(3); C(15)-Cu-O, 122.0(3).

Cu_2O_2 skeleton is planar. Copper-oxygen bond distances are surprisingly longer [Cu-O, 2.066(4) and Cu'-O, 2.082(4) Å] than those found in $[\text{Cu}_4(\text{OCMe}_3)_4]$, [Cu-O_{av}, 1.854(9) Å].⁵ The Cu . . . Cu separation [3.223(1) Å] is probably too long for any kind of metal-to-metal interaction. The Cu-O-Cu' angle [101.9(2)°] is close to that expected for tetrahedral geometry around oxygen atoms. Structural parameters of the Cu-C-N-R moieties are very close to those found in the first well characterized copper(I)-isocyanide complex.⁸

The structure reported is novel owing to the nature of the ligands surrounding copper(I), and the existence of a dinuclear $\text{Cu}_2(\mu\text{-OPh})_2$ unit with an unusually stable Cu-OPh bond. The role of ancillary ligands which stabilise the Cu-OR unit by forming a dimeric structure needs clarifying. The chemistry of two copper(I) centres separated by *ca.* 3.5 Å,³ and of the Cu-OR unit, should be of great interest.

† Satisfactory analytical data have been obtained for all complexes reported.

‡ *Crystal data:* C₄₄H₃₈Cu₂N₄O₂, *M* = 781.9, monoclinic, space group *P*2₁/*n*, *a* = 11.288(3), *b* = 10.374(3), *c* = 16.449(4) Å, β = 95.62(3)°, *U* = 1916.9(9) Å³, *Z* = 2, *D_c* = 1.355 g cm⁻³, *F*(000) = 808, μ(Mo-*K*_α) = 11.5 cm⁻¹. Intensities of 3378 independent reflections were measured (6° < 2θ < 50°) on a Philips PW 1100 diffractometer using Mo-*K*_α radiation. 1932 Reflections [*I* > 3σ(*I*)] were used in the refinement. The structure was solved by the heavy atom and Fourier methods and refined anisotropically to *R* = 5.19%. The atomic co-ordinates for this work 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.

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