Monomeric Alkoxo Complexes of Copper(I): Syntheses and Structures of Di(p-tolyl isocyanide)(2,6-di-t-butylphenoxo)copper(I) and a Di(2,6-dimethylphenoxo)cuprate(I)

Paolo Fiaschi,[a] Carlo Floriani,*[a] Marco Pasquali,[a] Angiola Chiesi-Villa,[b] and Carlo Guastini[b]

[a] *Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy*

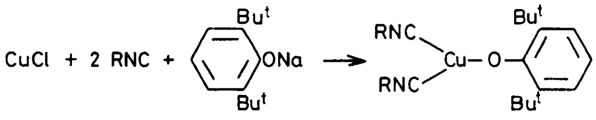
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy*

Copper(I) chloride reacts with 2,6-$Bu^t{}_2C_6H_3ONa$ in the presence of p-MeC_6H_4NC to give $[(p\text{-}MeC_6H_4NC)_2Cu(2,6\text{-}Bu^t{}_2C_6H_3O)]$ containing a tri-coordinated copper(I) atom [Cu–O, 1.917(3) Å], while the solution obtained from 'CuCOCl' and 2,6-$Me_2C_6H_3ONa$ reacts with PhCH=N–CH_2CH_2–N=CHPh, BEN, to give the diphenoxo-cuprate(I) $[Cu(BEN)_2]^+$ $[(2,6\text{-}Me_2C_6H_3O)_2Cu]^-$ [Cu–O, 1.806(6) and 1.798(8) Å].

The organometallic functionality [Cu–OR] plays an important role in metal assisted transformations of various organic substrates by copper(I).[1,2] In spite of this, knowledge of the chemistry and structure of this grouping is very restricted. There have been a few reports of syntheses of homoleptic tetranuclear copper(I) alkoxo complexes, namely $[Cu(OBu^t)]_4$,[3] (**1**), and $[Cu(OCHBu^t{}_2)]_4$,[4] (**2**), but the only structures available are that of (**1**) and its carbon monoxide adduct $[Cu(OBu^t)(CO)]_4$.[5] The structure of a few other alkoxo–copper(I) complexes, bearing an additional donor atom on the alkoxo ligand, have been reported.[6] The isolation of complexes from the reaction of copper(I) halides and sodium phenoxide is possible only in the presence of ancillary ligands such as isocyanides[7] and phosphines.[7,8] The structure of only one of these complexes, namely $[Cu_2(p\text{-}MeC_6H_4NC)_4(\mu\text{-}PhO)_2]$,[7] (**3**), has been determined. The nature of the ancillary ligand and of the substituents on the phenoxo group are crucial for the stability, the bonding mode of the OR ligand, and the nature of the [Cu-OR] functionality, as we report here.

$[Cu(OBu^t)]_4$ (**1**) $[Cu(OCHBu^t{}_2)]_4$ (**2**)

$[Cu_2(p\text{-}MeC_6H_4NC)_4(\mu\text{-}PhO)_2]$ (**3**)



(1)

(**4**)

ν(C—N) 2145 and 2170 cm^{-1}

R = p-MeC_6H_4

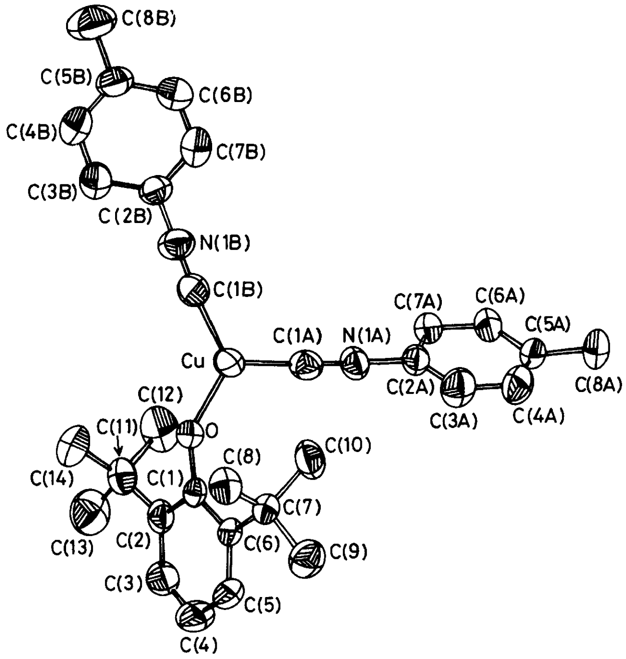
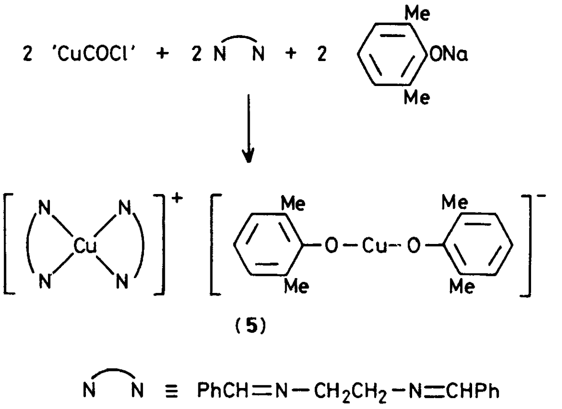


Figure 1. An ORTEP view of complex (**4**), [(*p*-$MeC_6H_4NC)_2Cu(2,6\text{-}Bu^t{}_2C_6H_3O)$]. Bond distances (Å): Cu–O 1.917(3), Cu–C(1A) 1.891(4), Cu–C(1B) 1.891(4), O–C(1) 1.320(4), C(1A)–N(1A) 1.154(5), C(1B)–N(1B) 1.160(5); bond angles (°): O–Cu–C(1A) 121.8(2), O–Cu–C(1B) 115.4(2), C(1A)–Cu–C(1B) 121.8(2), Cu–O–C(1) 134.3(2), Cu–C(1A)–N(1A) 171.2(3), Cu–C(1B)–N(1B) 174.4(4).



(2)

(**5**)

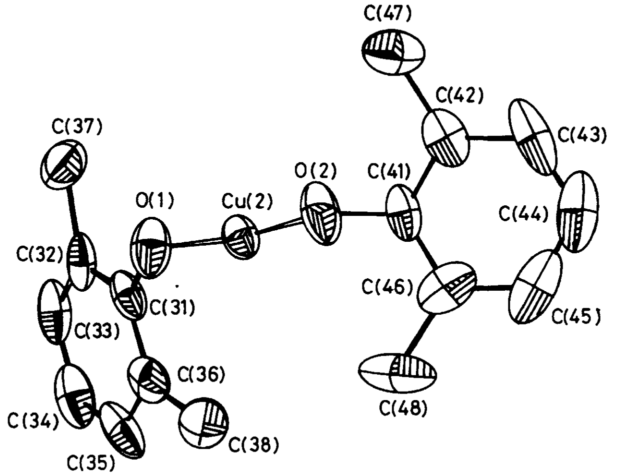


Figure 2. An ORTEP view of the anion $[(2,6\text{-}Me_2C_6H_3O)_2Cu]^-$ in complex (**5**). Bond distances (Å): Cu(2)–O(1) 1.806(6), Cu(2)–O(2) 1.798(8), C(31)–O(1) 1.319(11), C(41)–O(2) 1.323(10); bond angles (°): O(1)–Cu(2)–O(2) 169.8(3), Cu(2)–O(1)–C(31) 137.0(5), Cu(2)–O(2)–C(41) 135.2(5).

A thf (tetrahydrofuran) solution of CuCl (1 mol) and *p*-tolyl isocyanide (2 mol) reacted with a solution of $2,6\text{-}Bu^t{}_2C_6H_3ONa$ in the same solvent [equation (1)]. Sodium chloride was filtered off, and, when left, the final solution gave crystals of (**4**).†

Complex (**4**)‡ is monomeric with the copper(I) atom in a trigonal planar co-ordination geometry. An ORTEP view of the structure is shown in Figure 1. Important bond distances and bond angles are listed in the caption. Copper(I) is 0.114(1) Å out of the plane defined by the three donor atoms C(1A), C(1B), and O. Structural parameters for the isocyanide ligands are as expected.[7] The Cu–O bond distance [1.917(3) Å] has an intermediate value between those found for di-co-ordinate [1.854(9) Å][3] and tetra-co-ordinate copper(I).[5,6] Using sterically demanding phenoxo groups and appropriate ancillary ligands it seems possible to stabilize the [Cu–OR] unit with RO^- in a terminal bonding mode. The [Cu–OR] functionality does not suffer from any intrinsic instability.

When copper(I) chloride reacted with $2,6\text{-}Me_2C_6H_3ONa$ under a carbon monoxide atmosphere, a stable solution of a phenoxocopper(I) carbonyl [ν(C–O) 2080 cm^{-1}] was formed, but its isolation from the solution was unsuccessful. When this solution reacted with *N*,*N′*-ethylenebis(benzylideneimine), $PhCH{=}N{-}CH_2CH_2{-}N{=}CHPh$, BEN, carbon monoxide was lost. Simple displacement by the bidentate ligand of the ancillary ligands in the labile complex [probably with a structure similar to (**3**) or (**4**)] did not occur; instead, a ligand disproportionation, as shown in reaction (2), formed the alkoxocuprate(I) (**5**).

The nature of complex (**5**) was shown by an *X*-ray analysis.‡ An ORTEP view of the anion is shown in Figure 2 with related bond distances and bond angles in the caption. The structure of the cation is very similar to those of other cationic copper(I) complexes containing two bidentate nitrogen donor ligands.[9] The copper(I) atom has nearly linear di-co-ordination in $[(2,6\text{-}Me_2C_6H_3O)_2Cu]^-$ with an O–Cu–O angle of 169.8(3)°.

---

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

‡ *Crystal data* for (**4**): $C_{30}H_{35}CuN_2O$, $M = 503.2$, monoclinic, space group $P2_1/n$, $a = 23.179(4)$, $b = 9.456(1)$, $c = 12.509(2)$ Å, $\beta = 94.02(2)°$, $U = 2735.0(7)$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}, $F(000) = 1064$, $\mu(Cu\text{-}K_\alpha) = 12.6$ cm^{-1} ($\lambda = 1.5418$ Å). Data were measured ($6 < 2\theta < 120°$) on a Philips PW 1100 diffractometer and 2623 reflections with $I > 2\sigma(I)$ were considered as observed and used to solve the structure by standard Patterson and Fourier methods; final anisotropic refinement converged to $R = 3.9\%$.

Crystal data for (**5**): $C_{48}H_{50}Cu_2N_4O_2$, $M = 8420$, monoclinic, space group $P2_1/n$, $a = 13.643(3)$, $b = 21.528(5)$, $c = 15.538(4)$ Å, $\beta = 111.31(3)°$, $U = 4252(2)$ Å^3, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $F(000) = 1760$, $\mu(Cu\text{-}K^\alpha) = 15.2$ cm^{-1}. Intensities of 4975 independent reflections were measured in the range $6 < 2\theta < 110°$ using a Philips PW 1100 diffractometer. 2410 Reflections with $I > 2\sigma(I)$ were used in the calculations. The structure, solved using heavy atom methods, was refined with anisotropic thermal parameters to a final $R = 4.2\%$.

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.

Copper–oxygen bond distances are very short, with a significant double bond character, and close to those found in complex (**1**) which contains a di-co-ordinate copper(I) atom[3] [Cu–O, 1.854(9) Å].

The nature of the phenoxocopper(I) complexes is very dependent on the substituents on the phenoxo group and on the ancillary ligand used for the [Cu–OR] stabilization and isolation. Different [Cu–OR] functionalities have been obtained and structurally identified in complexes (**3**), (**4**), and (**5**). This is an important aspect, then, of the chemistry of alkoxocopper(I) species, which are normally prepared *in situ* in the presence of ancillary ligands and then used in organic synthesis.[1]

This work was supported by a grant from Ricerca Scientifica (Ministero della Pubblica Istruzione).

Received, 11th April 1984; Com. 525

References

1 G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, 1973, **95**, 7788; M. Kubota, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 146; G. M. Whitesides, J. S. Sadowski, and J. Lilburn, *J. Am. Chem. Soc.*, 1974, **96**, 2829; J. Cornforth, A. F. Sierakowski, and T. W. Wallace, *J. Chem. Soc., Chem. Commun.*, 1979, 294; T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Am. Chem. Soc.*, 1972, **94**, 658.

2 T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431; T. Tsuda, S. I. Sanada, and T. Saegusa, *J. Organomet. Chem.*, 1976, **116**, C10; T. Yamamoto, M. Kubota, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 680; T. Tsuda, S. I. Sanada, K. Ueda, and T. Saegusa, *Inorg. Chem.*, 1976, **15**, 2329.

3 T. Greiser and E. Weiss, *Chem. Ber.*, 1976, **109**, 3142.

4 M. Bochmann, G. Wilkinson, G. B. Young, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1863.

5 R. L. Geerts, J. C. Huffman, K. Folting, T. H. Lemmen, and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 3503.

6 M. Berry, W. Clegg, C. D. Garner, and I. H. Hillier, *Inorg. Chem.*, 1982, **21**, 1342; M. Pasquali, P. Fiaschi, C. Floriani, and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1983, 613.

7 M. Pasquali, P. Fiaschi, C. Floriani, and A. Gaetani-Manfredotti, *J. Chem. Soc., Chem. Commun.*, 1983, 197.

8 M. Kubota and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2909; W. T. Reichle, *Inorg. Chim. Acta*, 1971, **5**, 325.

9 M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti, and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 1982, **104**, 4092; P. J. Burke, D. R. McMillin, and W. R. Robinson, *Inorg. Chem.*, 1980, **19**, 1211.