Reactivity of Metallic Copper with Acidic Organic Compounds in the Presence of Molecular Oxygen. Crystal Structure of [{Cu(NCO)(py)$_2$}$_2$]·H$_2$O †

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The reactivity of metallic copper with organic compounds containing acidic hydrogen atoms such as MeOH, PhOH, PhCO$_2$H, and MeNO$_2$ in the presence of O$_2$ and pyridine has been studied. The reaction with MeNO$_2$ is particularly interesting as it gives cyanide, isocyanate, and nitrite compounds, depending on the reaction conditions. The crystal structure of a minor product, the previously unknown complex [{Cu(NCO)(py)$_2$}$_2$]·H$_2$O, has been determined by X-ray diffraction methods. It consists of a copper dimer, where each metal is in a tetrahedral arrangement determined by two N atoms from pyridine ligands and two N atoms from two isocyanate ligands acting as asymmetric bridges; angles at the bridging N atoms are very acute, 68.6(5) and 71.8(6)°, and the Cu · · · Cu distance is very short, 2.396(3) Å.

Copper complexes are important catalysts for the oxidation and oxygenation of organic compounds both in chemical and biological systems, and the role of the oxidation states Cu^I and Cu^{II} in promoting oxygen activity has been discussed.[1,2]

Less is known, however, about the interaction of metallic copper with molecular oxygen and it is only recently that the application of analytical surface techniques has allowed the detection of peroxo species and adsorbed atomic oxygen on copper.[3] In the presence of suitable ligands, a stronger interaction can occur and bulk copper reacts to give co-ordination compounds. Thus Beveridge and Walker[4] found that when air is bubbled into an aqueous suspension of the metal in the presence of a chelating ligand, such as 1,10-phenanthroline or 2,2'-bipyridine, the copper dissolves and binuclear hydroxo-bridged complexes are formed. Moreover, metallic copper, in the presence of O$_2$, reacts with α-diketones and *o*-quinones to give carboxylatocopper(II) complexes as a result of an oxidative C–C cleavage.[5] A direct synthesis of copper catecholates from copper and phenols can be performed in the presence of O$_2$ and catalytic amounts of CuCl.[6]

During our efforts to use heterogeneous copper catalysts for the oxidation of phenols instead of the homogeneous copper(II) systems[7,8] we found that Cu–Al$_2$O$_3$ and Cu–Cr$_2$O$_3$ were able to promote the oxidation of phenol to 4,5-dimethoxy-1,2-benzoquinone at room temperature. However, after reaction most copper had been removed from the oxide matrix, owing to oxidation and complexation reactions. The easy interaction of molecular O$_2$, Cu^0, and phenol prompted us to perform a detailed investigation on the reactivity of metallic copper with O$_2$ in the presence of various organic reagents. Here we report the results obtained using methanol, phenol, nitromethane, and benzoic acid.

Results and Discussion

A suspension of metallic copper in methanol is quite stable under an oxygen atmosphere up to 60 °C. However, by adding

pyridine (py) a rapid uptake of 0.7 mol of O$_2$ per mol of copper could be observed at room temperature, which was concomitant with copper consumption and the formation of an insoluble blue powder. The reaction product, Cu(OMe)$_2$, formed according to reaction (1) was identified on the basis of

$$Cu + 2\ MeOH + 0.5\ O_2 \longrightarrow Cu(OMe)_2 + H_2O \qquad (1)$$
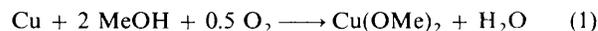
elemental analysis, i.r. spectrum, and comparison of chemical and physical properties with those of an authentic sample, obtained from anhydrous CuCl$_2$ and Li(OMe).[9,10] Moreover, the composition of the product was confirmed by reaction with dilute HCl which produced the expected amount of methanol as determined by gas–liquid chromatography (g.l.c.). The absence of peroxidic species, inferred by the I$^-$–I$_2$ test, suggests that the excess of O$_2$ (0.2 mol per mol of Cu) is consumed by methanol. However, we failed to detect either HCHO or HCO$_2$H in the reaction mixture.

The interaction of metallic Cu with phenol and O$_2$ proceeds rapidly and exothermically at room temperature and requires, as in the case of MeOH, the presence of pyridine. From the complex mixture, yellow-red polymers were found as major components. However, when the reaction was carried out in methanol–pyridine solution the crystalline 4,5-dimethoxy-1,2-benzoquinone could be separated from the resulting solution. The isolation of a substituted *o*-quinone suggests a reaction pathway similar to that observed by Capdevielle and Maumy[6] in the absence of pyridine but in the presence of MeCN and catalysed by CuCl. Although we were not able to isolate the expected copper(II)–catecholate complex, the absence of isomeric quinones and of muconic acid (hexa-2,4-dienedioic acid) derivatives in the reaction mixture seems to indicate that the oxidation of phenol proceeds through a concerted orthohydroxylation followed by facile oxidation of the catecholate complex to a substituted quinone. On the basis of the observed O$_2$ uptake, O$_2$:PhOH = 1.54, the stoicheiometry (2) can be proposed.

In conclusion, the interaction of phenol with oxygen in the presence of metallic copper is very similar to that observed in the presence of homogeneous copper-(I) and -(II) systems. The polymerization of phenol to polyphenylene ethers or diphenyl-quinones, catalysed by CuCl and pyridine in the absence of methanol, has been reported by Hay,[11] whereas the oxidation of

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† Di-μ-isocyanato-1,1,2,2-tetrakis(pyridine)dicopper(I) hydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.,* 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: 1 mmHg ≈ 133 Pa.

$$2 \ \text{PhOH} + Cu + 3O_2 + 2\,MeOH$$

$$\downarrow$$

$$4\,H_2O + \text{MeO-quinone} + Cu(\text{catecholate}) \quad (2)$$
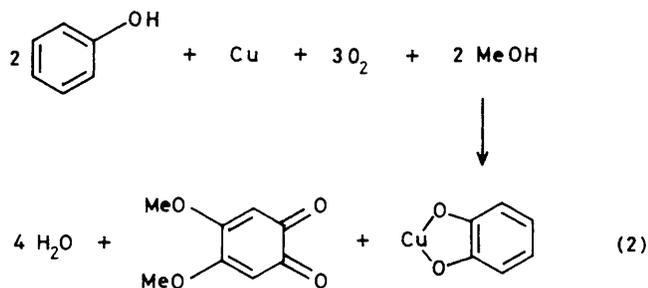
phenol to *o*-quinone derivatives was observed by Brackman and Havinga [12] by treating copper(II) salts with phenols and amines in the presence of O_2.

The observation that the more acidic phenol ($pK_a = 9.89$) reacts much more smoothly with respect to the less acidic methanol ($pK_a = 16$), and the necessity to operate in the presence of a co-ordinating base, suggests that the activation and complexation of the organic reagent requires hydrogen abstraction as a preliminary step. This hypothesis agrees with the fact that organic molecules lacking mobile hydrogens, such as substituted alkynes, alkenes, and halogenated hydrocarbons, failed to react, whereas those containing very weak acids, like ethanol and phenylacetylene, produced very slow oxygen consumption. This point of view is confirmed by the very easy interaction of Cu and O_2 with $MeNO_2$ ($pK_a = 10.21$) and with benzoic acid ($pK_a = 4.19$). The reaction with the latter occurs in a few minutes at room temperature, according to the stoicheiometry in equation (3). The known benzoate complex

$$Cu + 2\,PhCO_2H + 2\,py + 0.5O_2 \longrightarrow$$
$$[Cu(OCOPh)_2(py)_2] + H_2O \quad (3)$$
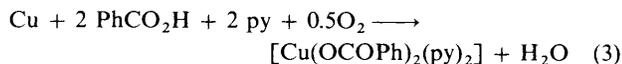
was identified through its chemical and physical properties.

The interaction of Cu, O_2, and $MeNO_2$ in pyridine at room temperature is dangerously exothermic. By working at 0 °C and by using a 1:1 $MeNO_2$–Cu ratio, we obtained crystalline $[Cu(NO_2)_2(py)_2]$, besides other amorphous material and CO_2. This rapid oxidation of nitromethane is quite surprising. In order to get more insight into the reaction pathway we attempted the isolation of possible intermediates.

Working at 0 °C and limiting the oxygen uptake to 0.5 mol per mol of copper, new and unexpected products were obtained. By careful addition of diethyl ether to the reaction mixture, we were able to isolate $[Cu(CN)(py)_2]$ and $[\{Cu(NCO)(py)_2\}_2]\cdot$ H_2O, whereas no CO_2 was detected in the gas phase. A third major component was also obtained, whose chemical properties and analytical data are close to those of the known complex $[Cu(NCO)_2(py)_2]$.[13] This third component reacts with diluted H_2SO_4 to give carbon dioxide; neither hydroxylamine nor formic acid could be detected after this treatment, excluding the presence of fulminate groups. However the product appears dark green instead of blue[13] and its i.r. spectrum exhibits splitting of the pyridine bands with respect to the known complex. We were not able to obtain crystals suitable for an X-ray determination.

The known compounds $[Cu(CN)(py)_2]$[14] and $[Cu(NO_2)_2(py)_2]$[15] are obtainable from copper salts and the corresponding ligands. The copper(I) isocyanate complex $[\{Cu(NCO)(py)_2\}_2]\cdot H_2O$, however, is new and its structure has been fully elucidated by X-ray diffraction methods. The bonding of the isocyanate ligands through the nitrogen atoms was also confirmed by the chemical reactivity of the complex.

Crystal Structure of $[\{Cu(NCO)(py)_2\}_2]\cdot H_2O$.—The crystal structure of $[\{Cu(NCO)(py)_2\}_2]\cdot H_2O$ consists of dimeric copper

Table 1. Selected bond distances (Å) and angles (°) for $[\{Cu(NCO)_2(py)_2\}_2]\cdot H_2O$

Cu(1)–Cu(2)	2.396(3)	Cu(2)–N(5)	2.08(2)
Cu(1)–N(1)	2.04(1)	Cu(2)–N(6)	1.97(2)
Cu(1)–N(2)	2.03(1)	N(5)–C(21)	1.16(2)
Cu(1)–N(5)	2.00(2)	N(6)–C(22)	1.16(2)
Cu(1)–N(6)	2.26(2)	C(21)–O(1)	1.23(2)
Cu(2)–N(3)	2.07(1)	C(22)–O(2)	1.22(2)
Cu(2)–N(4)	2.09(2)		
N(1)–Cu(1)–N(2)	107.4(5)	N(4)–Cu(2)–N(6)	110.6(6)
N(1)–Cu(1)–N(5)	112.0(6)	N(5)–Cu(2)–N(6)	114.0(7)
N(1)–Cu(1)–N(6)	107.2(5)	Cu(1)–N(5)–Cu(2)	71.8(6)
N(2)–Cu(1)–N(5)	117.6(6)	Cu(1)–N(6)–Cu(2)	68.6(5)
N(2)–Cu(1)–N(6)	106.4(5)	Cu(1)–N(5)–C(21)	146(1)
N(5)–Cu(1)–N(6)	105.6(6)	Cu(2)–N(5)–C(21)	141(1)
N(3)–Cu(2)–N(4)	102.4(5)	Cu(1)–N(6)–C(22)	135(1)
N(3)–Cu(2)–N(5)	107.7(6)	Cu(2)–N(6)–C(22)	156(1)
N(3)–Cu(2)–N(6)	113.4(6)	N(5)–C(21)–O(1)	177(2)
N(4)–Cu(2)–N(5)	108.1(6)	N(6)–C(22)–O(2)	179(1)
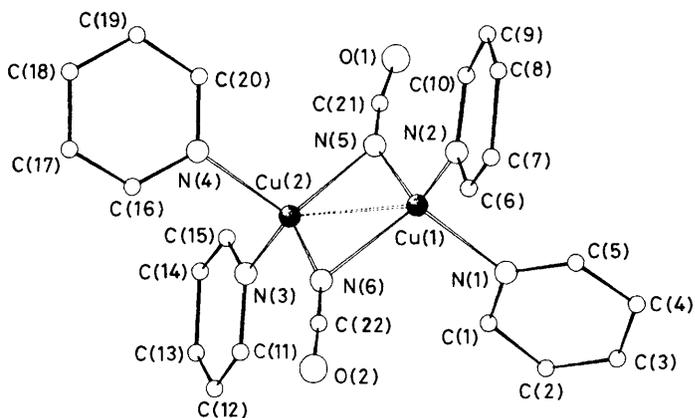
Figure 1. View of the $[\{Cu(NCO)(py)_2\}_2]$ complex with the atomic numbering scheme

complexes and water molecules linked by hydrogen bonds. The structure of the copper complex is represented in Figure 1, together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. The two copper atoms are doubly bridged by isocyanato ligands bonded through the nitrogen atoms. Both bridges are asymmetric [Cu(1)–N(5) 2.00(2) and Cu(2)–N(5) 2.08(2); Cu(1)–N(6) 2.26(2) and Cu(2)–N(6) 1.97(2) Å] and the Cu_2N_2 array is perfectly planar. The co-ordination around each copper atom is completed by two nitrogen atoms from pyridine ligands with Cu–N bond distances ranging from 2.03(1) to 2.09(2) Å. The N–Cu–N bond angles are very close to those required for tetrahedral co-ordination of the copper atoms, ranging from 102.4(5) to 117.6(6)°, so that the six nitrogen atoms can be considered as the vertices of two tetrahedra with a shared edge.

It is interesting that the separation between the two copper atoms is very short, 2.396(3) Å, and one may question if this is indicative of a weak attractive Cu^I–Cu^I interaction. It has already been pointed out by Mehrotra and Hoffmann[16] that a short metal–metal separation alone is not a sign of metal–metal bonding, especially when bridging atoms are present. Moreover in the 'tetrahedral' metal dimeric complexes of the M_2L_6 type,[17] the perturbation of a metal–metal interaction should be manifest as a distortion from the simple edge-sharing geometry
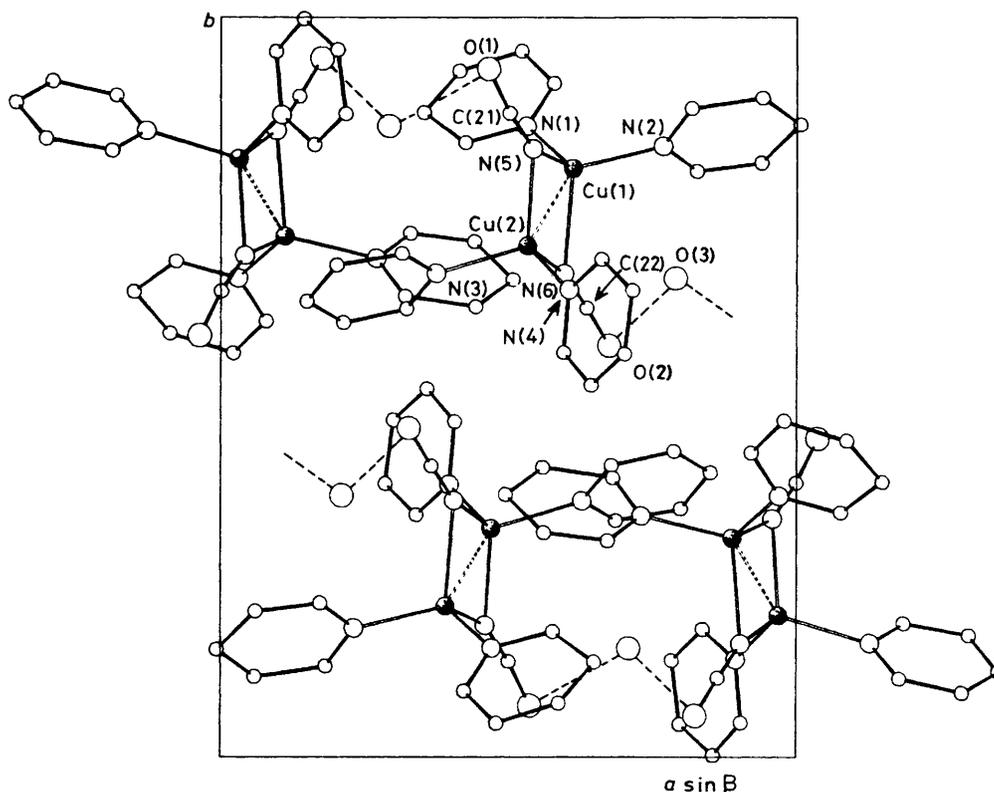
Figure 2. Projection along the c axis of the crystal structure of [{Cu(NCO)(py)$_2$}$_2$]·H$_2$O showing the network of hydrogen bonds involving the copper dimeric complex and the water molecules

which requires an angle of 109.5° at the metals and an angle of 70.5° at the bridging atoms. In the present case the N(5)–Cu–N(6) angles are 105.6(6) and 114.0(7)°, and the Cu–N–Cu angles are very acute, 71.8(6) and 68.6(5)°, so that the distortion from the tetrahedral edge-sharing geometry is negligible. In conclusion, even if the Cu–Cu separation is very short, a metal–metal interaction, if it exists, would be very weak.

The flexibility of the isocyanate group when acting as a bridge is shown if the structural results of the [Cu^{II}(NCO)$_2$L] (L = 2,4-dimethylpyridine) complex are examined.[18] Also, in this case, the isocyanate ligands act as bridges, one very asymmetric, Cu–N 2.458(18) and 1.975(18) Å, the second almost symmetric, Cu–N 2.056(20) and 2.100(19) Å, but they determine polymeric chains with rather long Cu–Cu separations, 3.22 and 3.44 Å. Correspondingly the Cu–N–Cu angles are much larger, 99.8 and 101.6°, than in the present copper(I) dimer. The NCO groups always act as bridges in the [Cu^{II}(NCO)$_2$(py)$_2$] complex,[19] but in a different way, as they are bonded to two copper atoms, through the nitrogen and oxygen atoms.

In the present dimer the N–C and C–O bonds, and the Cu–N–O bond angles involving the isocyanate ligands [1.16(2) and 1.16(2), 1.23(2) and 1.22(2) Å, 177(2) and 179(1)°] fall in the normal ranges found for metal isocyanates.[20]

The packing in the crystal is determined by a network of hydrogen bonds. The hydrogen atoms of the water molecules form hydrogen bonds with the oxygen atoms of the isocyanate ligands. A view of the packing of the copper dimers and the water molecules is represented in Figure 2. Even if the hydrogen atoms of the water molecules could not be localized from the X-ray analysis, the two O···O contacts, O(3)···O(2) 2.79(2) and O(3)···O(1) ($x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z - \frac{1}{2}$) 2.87(2) Å, can be considered as hydrogen bonds on the basis of the short distances and their orientation.

Conclusions

The knowledge of molecular interactions on copper surfaces and the results obtained in the present study can be used to rationalize the reaction mechanism of organic molecules with Cu in the presence of dioxygen.

As reported by Rao and co-workers,[3] different surface analytical techniques (electron energy loss spectroscopy, u.v., and X-ray photoelectron spectroscopy) indicate that the interaction of molecular oxygen with the copper (110) surface, and also with polycrystalline copper surfaces, involves the formation of an initial layer of atomic oxygen.

The oxygen-covered surface can interact with proton donor molecules (HCl, MeOH, H$_2$S, and NMe$_2$H) to give an hydroxylation reaction.[21] Therefore, the following general Scheme 1 can be drawn. Our work indicates that the evolution

$$Cu \ + \ \tfrac{1}{2} O_2 \ \longrightarrow \ Cu\!\sim\!\!\sim\!\!O \ \text{(surface)}$$

$$Cu\!\sim\!\!\sim\!\!O \ + \ HX \ \longrightarrow \ Cu\!\!<^{OH}_{\ X}$$

$$(A)$$
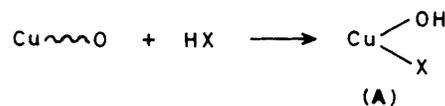
Scheme 1.

of the surface species (**A**), responsible for the bulk reaction of copper, requires the presence of a base, B [equation (4),

$$Cu\!<^{OH}_{\ X} + HX \xrightarrow{\ B\ } CuX_2 + H_2O \qquad (4)$$
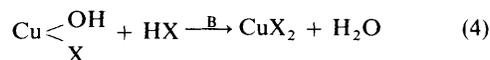
X = OMe or OCOPh]. The role of the base seems to be the ability to produce the co-ordinating X$^-$ anion which competes

with OH⁻, thus allowing the formation of the observed complexes, through elimination of H_2O.

Therefore, it is not surprising that already deprotonated anions, such as those present in amino acids, react easily with Cu and O_2 in the absence of an added base, whereas basic ligands like 1,10-phenanthroline and 2,2'-bipyridine, in the absence of external hydrogen abstractors, stabilize hydroxo species (A).[4]

The reaction of Cu with O_2 and nitromethane requires further comment. The oxidation of $MeNO_2$ to nitrite and carbon dioxide could be due to instability of organometallic intermediates towards oxygen e.g. Scheme 2. This point of view

$$Cu\text{---}O + 2\ MeNO_2 + 2\ L \longrightarrow L_2Cu\begin{smallmatrix}CH_2NO_2\\CH_2NO_2\end{smallmatrix}$$
$$+$$
$$H_2O$$

$$L_2Cu\begin{smallmatrix}CH_2NO_2\\CH_2NO_2\end{smallmatrix} + 3O_2 \longrightarrow Cu(NO_2)_2L_2 + 2CO_2 + 2H_2O$$
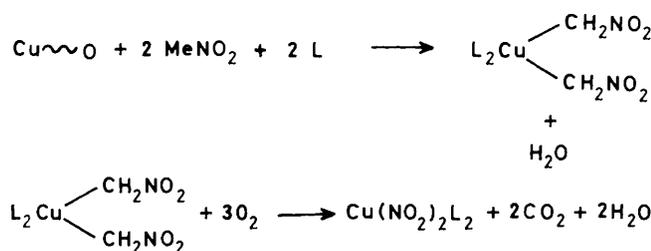
Scheme 2.

is supported by the previous work of Marsich and Camus.[22] They observed the easy oxidation of nitrophenylmethane to nitrite anion promoted by copper, whereas organometallic derivatives were stabilized only in the presence of bidentate nitrogen ligands. Nitrite anions were also detected in nitromethane solution during the oxygenation of copper(I) complexes.[23] In our case the use of a limited amount of oxygen led to cyanide and isocyanate derivatives instead of the expected organometallic intermediates.

The formation of cyanide and cyanate complexes from $MeNO_2$ is not new; low-valent complexes of Pt, Pd, and Rh undergo oxidative addition of nitromethane to produce unstable intermediates.[24]

Internal redox reactions, involving the nitromethanide anion $(CH_2NO_2^-)$ and easily oxygenated ligands, and the isomerization of the fulminate group have been postulated to explain formation of the derived species in the absence of molecular oxygen. In the case of copper compounds, redox reactions involving Cu^0 should also be taken into account to justify the presence of the cyanide ligand and the formation of copper(I) complexes (Scheme 3).

$$L_2Cu\begin{smallmatrix}CH_2NO_2\\CH_2NO_2\end{smallmatrix} \xrightarrow{-2H_2O} L_2Cu\begin{smallmatrix}CNO\\CNO\end{smallmatrix} \longrightarrow L_2Cu\begin{smallmatrix}NCO\\NCO\end{smallmatrix}$$

$$Cu(NCO)_2L_2 + Cu + 2L \longrightarrow 2Cu(NCO)L_2$$
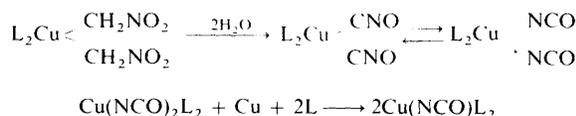
Scheme 3.

Experimental

Metallic copper powder (C. Erba, 99.99%) was washed with 2 mol dm⁻³ HCl, then with water. Organic substrates (C. Erba, R.P. grade) were used without further purification. Solvents were purified with standard procedures. I.r. spectra were recorded on a Perkin-Elmer 577 instrument, ¹H n.m.r. spectra on a Varian XL200 spectrometer. G.l.c. determination of MeOH from $Cu(OMe)_2$ and HCl was performed on a Hewlett-Packard 5880 instrument equipped with a methyl silicone fluid capillary column. Gas analyses were performed by means of a C. Erba gas chromatograph equipped with a Carbosieve column. The copper content was determined by atomic absorption spectrometry at $\lambda = 3\ 247$ Å.

Reactions of Copper.—With methanol and oxygen. Copper powder (620 mg, 9.8 mmol), methanol (15 cm³), and pyridine (5 cm³) were placed in a reaction vessel connected to a mercury sealed gas burette containing dioxygen at atmospheric pressure. The suspension was magnetically stirred at 20 °C until O_2 consumption ceased (7.2 mmol in ca. 8 h). The resulting blue product $[Cu(OMe)_2]$ was filtered off under an inert atmosphere (N_2), washed with methanol, and dried under reduced pressure (0.1 mmHg). Yield 1.02 g (83%) (Found: Cu, 50.9. Calc. for $C_2H_6CuO_2$: Cu 50.6%). I.r.: $v_{max.}$(KBr) 2 920s, 2 890s, 2 810s, 1 460s, 1 435s, and 1 057br cm⁻¹. A sample of the product (155 mg) was treated with an excess of 1 mol dm⁻³ HCl to give a clear solution. After neutralization, methanol was quantitatively determined by g.l.c. (ethanol as an internal standard) (Found MeOH/Cu = 1.9).

With phenol and oxygen. Copper powder (107 mg, 1.7 mmol), phenol (322 mg, 3.4 mmol), methanol (10 cm³), and pyridine (5 cm³) were stirred under O_2 at 20 °C. The gas uptake (5.2 mmol) stopped after a few hours. Low-boiling components were evaporated under reduced pressure and the dark red residue was dissolved in boiling ethyl acetate. Upon cooling, long needles (140 mg) of 4,5-dimethoxy-1,2-benzoquinone were obtained. N.m.r.: δ_H(CDCl₃) 3.9 (6 H, OMe) and 5.8 (2 H, C_6H_2). Efforts to separate crystalline copper derivatives from the ethyl acetate residue were unsuccessful.

With nitromethane and oxygen. (a) Copper powder (1.06 g, 16.7 mmol), nitromethane (1.14 g, 16.7 mmol), and pyridine (9 cm³) were stirred under O_2 at 0 °C for 2 d. After reaction a sample of the gaseous phase above the solution revealed the presence of CO_2, which was not quantitatively determined owing to its solubility in the reaction medium. The resultant dark brown solution was treated, under N_2, with diethyl ether (5 cm³). The first amorphous precipitate (ca. 0.3 g) was filtered off and the solution cooled at −30 °C. Long, greenish black needles (2 g, 37%) of $[Cu(NO_2)_2(py)_2]$ crystallized out in a few days (Found: C, 37.9; H, 3.2; Cu, 20.2; N, 17.5. Calc. for $C_{10}H_{10}CuN_4O_4$: C, 38.3; H, 3.2; Cu, 20.3; N, 17.9%).

(b) Copper powder (275 mg, 4.3 mmol), nitromethane (525 mg, 8.6 mmol), and pyridine (5 cm³) were stirred as above under O_2 until a gas consumption of 2.2 mmol was measured. At this point no CO_2 was detected in the gas phase by g.l.c. The resultant solution was filtered to remove a small residue and then carefully treated with diethyl ether (5 cm³) under N_2. Three different fractions were collected. The first consisted of a few crops, ca. 100 mg, of yellow-brown needles identified as $[Cu(CN)(py)_2]$ (Found: C, 52.1; H, 4.2; Cu, 24.9; N, 16.7. Calc. for $C_{11}H_{10}CuN_3$: C, 53.3; H, 4.1; Cu, 25.7; N, 17.0%). I.r.: $v_{max.}$(CN) (Nujol) 2 110s cm⁻¹.

The second fraction consisted of pale yellow plates, ca. 60 mg, unstable to oxygen, characterized as $[\{Cu(NCO)(py)_2\}_2]\cdot H_2O$ by the X-ray analysis (Found: C, 49.7; H, 3.7; Cu, 23.1; N, 14.3. Calc. for $C_{22}H_{22}Cu_2N_6O_3$: C, 48.5; H, 4.0; Cu, 23.3; N, 15.4%). I.r.: $v_{max.}$(NCO) (Nujol) 2 215vs,br and 1 335s cm⁻¹.

The third fraction consisted of a dark green powder (0.92 g), apparently stable to oxygen, whose nature has not been fully elucidated. Its chemical composition is similar to that of $[Cu(NCO)_2(py)_2]$ (Found: C, 45.0; H, 3.2; Cu, 19.9; N, 18.2. Calc. for $C_{12}H_{10}CuN_4O_2$: C, 47.1; H, 3.3; Cu, 20.8; N, 18.3%). I.r.: $v_{max.}$(NCO) (Nujol) 2 220vs,br and 1 345s cm⁻¹. On reaction with diluted H_2SO_4 this product develops 0.13 cm³ mg⁻¹ of CO_2 {calculated for $[Cu(NCO)_2(py)_2]$ 0.15 cm³ mg⁻¹}.

With benzoic acid and oxygen. Copper powder (1 g, 15.7 mmol), benzoic acid (3.85 g, 31.5 mmol), methanol (15 cm³), and pyridine (7.5 cm³) were stirred under O_2 at room temperature. The solution rapidly turned deep blue and long blue needles of $[Cu(PhCO_2)_2(py)_2]\cdot H_2O$ began to form (7.3 g, 97%) (Found: C, 59.2; H, 4.6; Cu, 13.1; N, 5.5. Calc. for $C_{24}H_{22}CuN_2O_5$: C, 59.9; H, 4.6; Cu, 13.2; N, 5.8%).

Table 2. Fractional atomic co-ordinates ($\times 10^4$), with e.s.d.s in parentheses, for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c
Cu(1)	6 107(1)	7 961(1)	6 634(2)
Cu(2)	5 313(1)	6 908(1)	7 528(1)
O(1)	4 682(10)	9 321(8)	8 706(11)
O(2)	6 744(9)	5 538(7)	5 385(9)
O(3)	7 934(13)	6 472(8)	4 274(13)
N(1)	5 293(8)	8 500(7)	5 077(9)
N(2)	7 707(9)	8 264(7)	7 025(10)
N(3)	3 697(9)	6 543(7)	7 117(10)
N(4)	6 045(9)	6 303(7)	9 111(9)
N(5)	5 390(12)	8 218(10)	7 814(15)
N(6)	5 992(11)	6 534(10)	6 390(14)
C(1)	4 244(11)	8 291(10)	4 516(15)
C(2)	3 612(14)	8 714(13)	3 483(15)
C(3)	4 112(15)	9 309(13)	3 029(14)
C(4)	5 199(17)	9 549(10)	3 618(15)
C(5)	5 730(12)	9 120(10)	4 635(14)
C(6)	8 304(11)	7 894(9)	6 461(13)
C(7)	9 472(16)	8 031(13)	6 795(21)
C(8)	9 975(14)	8 569(13)	7 749(19)
C(9)	9 361(12)	8 926(11)	8 301(14)
C(10)	8 249(13)	8 765(10)	7 939(13)
C(11)	3 195(13)	6 059(9)	6 199(14)
C(12)	2 107(14)	5 851(9)	5 883(15)
C(13)	1 531(12)	6 144(10)	6 498(17)
C(14)	2 011(13)	6 654(10)	7 522(15)
C(15)	3 126(12)	6 818(8)	7 774(13)
C(16)	5 980(13)	5 482(9)	9 164(14)
C(17)	6 457(15)	5 035(10)	10 147(15)
C(18)	7 050(13)	5 453(11)	11 176(13)
C(19)	7 142(16)	6 316(12)	11 114(14)
C(20)	6 584(13)	6 730(10)	10 034(14)
C(21)	5 025(10)	8 742(7)	8 240(11)
C(22)	6 361(10)	6 044(7)	5 908(11)

X-*Ray Data Collection, Structure Solution, and Refinement.*— The few crystals of [{Cu(NCO)(py)$_2$}$_2$]·H$_2$O were of very poor quality; one of them (of approximate dimensions $0.10 \times 0.45 \times 0.50$ mm) was selected, sealed in a glass capillary under N$_2$ and used for data collection. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centred reflections (with θ in the range 10—15°).

Crystal data. C$_{22}$H$_{22}$Cu$_2$N$_6$O$_3$, $M = 545.55$, monoclinic, $a = 12.961(6)$, $b = 15.709(8)$, $c = 12.276(6)$ Å, $\beta = 109.15(2)°$, $U = 2\ 361(2)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.535\ \mathrm{g\ cm^{-3}}$, $F(000) = 1\ 112$, $\mu(\mathrm{Mo}\text{-}K_\alpha) = 18.40\ \mathrm{cm^{-1}}$.

Data were collected at room temperature on a Siemens AED diffractometer using niobium-filtered radiation ($\lambda = 0.710\ 73$ Å) and the θ—2θ scan technique, the individual profiles having been analyzed according to Lehmann and Larsen.[25] All reflections in the range 3—25° were measured. Of 4 199 independent reflections, 2 016, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A correction for the absorption effects was applied[26] using the program ABSORB.[27]

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms.[28] The hydrogen atoms, except those of the water molecule, were placed at their geometrically calculated positions and introduced in the final structure-factor calculation. The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.6700$ and $g = 0.0285$. The final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. Final R and R' values were 0.0996 and 0.1071 respectively. Atomic scattering factors, corrected for the anomalous dispersion of Cu, were taken from ref. 29. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates (except those of the water molecule), thermal parameters and remaining bond distances and angles.

Acknowledgements

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