Unsubstituted Phenoxo-derivatives of Copper(II) and *p*-Benzoquinone Adducts of Copper(I) Chloride and Bromide

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The reaction of [$CuCl_2L$] [L = 2,2′-bipyridyl (bipy) or ethylenediamine (en)] with sodium phenoxide in tetrahydrofuran yields the extremely moisture-sensitive diphenoxo-derivatives [$Cu(OPh)_2$(bipy)] (1) and [$Cu(OPh)_2$(en)]·PhOH (2). The reaction of CuX (X = Cl or Br) with *p*-benzoquinone in pyridine gives the diamagnetic adducts [CuX(py)]$_2$.$C_6H_4O_2$ (3); i.r. data suggest that (3) are olefin complexes.

SUBSTITUTED phenols were reported to undergo polymerisation[1] *via* oxidative coupling in the presence of O_2 and CuX, only copper(II) derivatives containing polyhalogenated phenoxide groups could be isolated,[1,2] and attempts to prepare monohalogenated phenoxo-complexes (4-chloro- and 4-bromo-2,5-dimethylphenoxo) of Cu^{II} failed;[1] more recently, *ortho*-substituted phenoxo-complexes have been isolated.[3] Preliminary *X*-ray data on (tetramethylenediamine)bis(2,4,6-trichlorophenoxo)copper(II)[4] have shown a distorted square-planar co-ordination around the copper.

No copper(II) complexes containing unsubstituted phenoxide groups have yet been reported, the implicit explanation for the non-existence of these complexes being that they would be unstable towards reductive elimination to phenoxy-radicals, which would then couple to give diphenoquinone or 1,4-phenylene-ethers[5] with the assistance of the metal. We now report the isolation of the first unsubstituted diphenoxo-complexes of Cu^{II} stabilised by co-ordination with 2,2′-bipyridyl (bipy) and ethylenediamine (en), namely [$Cu(OPh)_2$(bipy)] (1) and [$Cu(OPh)_2$(en)]·PhOH (2). The *p*-benzoquinone adducts of CuX (X = Cl or Br) obtained in pyridine–tetrahydrofuran are also described.

EXPERIMENTAL

Infrared spectra were recorded with Perkin-Elmer model 337 and 283 spectrophotometers.

Anhydrous copper(I) chloride, copper(I) bromide, and copper(II) chloride were prepared according to literature methods.[6] Green [$CuCl_2$(bipy)] was prepared from anhydrous $CuCl_2$ and the stoicheiometric amount of bipy in anhydrous tetrahydrofuran (thf). The ethylenediamine complex [$CuCl_2$(en)] was obtained from anhydrous $CuCl_2$ and the stoicheiometric amount of the diamine in thf. The resulting blue solid gave satisfactory elemental analysis for [$CuCl_2$(en)]·0.1 thf (Found: C, 13.85; H, 4.45; Cu, 32.05; N, 13.15%). A solid of composition $CuCl_2$(en) had been prepared earlier from the components in dry ethanol[7a] or in aqueous solution.[7b] The compound Na[OPh]·PhOH was obtained from the reaction of an excess of PhOH with sodium sand in n-pentane. The reaction of PhOH with a slight (*ca.* 20%) molar excess of sodium in thf yielded a solid of composition Na(OPh).

The diphenoxo-derivatives were prepared and handled with the most rigorous exclusion of air and especially moisture.

Preparations.—(2,2′-*Bipyridyl*)*diphenoxocopper*(II), (1). The bipyridyl complex [$CuCl_2$(bipy)] (2.335 g, 8.03 mmol) was suspended in thf (650 cm^3) and Na[OPh]·PhOH (16 mmol) was added to the resulting suspension. After stirring for 1.5 h the brown solution was filtered and then concentrated under reduced pressure to a volume of *ca.* 70 cm^3. The resulting brown precipitate was filtered off and dried *in vacuo* (75% yield) (Found: C, 64.4; H, 4.55; N, 6.45. $C_{22}H_{18}CuN_2O_2$ requires C, 65.1; H, 4.45; N, 6.90%). The molecular weight in nitrobenzene for a 0.021 mol kg^{-1} solution was found to be 404.5 (required 405.9). The complex is extremely sensitive to moisture in solution. The i.r. spectrum [combined Nujol and $(C_2ClF_3)_n$ mulls and KBr pellets] has bands at 3 120w, 3 060m, 3 020w, 1 600 (sh), 1 580s, 1 470s, 1 440s, 1 290s, 1 270s, 1 160m, 1 100w, 1 060m, 1 025m, 1 020m–w, 985m–s, 865w, 840m–w, 820m–s, 750s, 730m–s, 690m–s, 655w, 650w, 630w, 540w–m, and 510w cm^{-1}. The room-temperature e.s.r. spectrum of a *ca.* 10^{-2} mol dm^{-3} solution in thf has a resonance characterized by $g_{iso.} = 2.13$ and $A_{iso.} = 73$ G.† The magnetic susceptibility at room temperature is $\chi_M^{corr} = 1\,209 \times 10^{-6}$ c.g.s. units, corresponding to $\mu_{eff.} = 1.69$ B.M. (diamagnetic correction = -232×10^{-6} c.g.s. units).

[$Cu(OPh)_2$(en)]·PhOH, (2). The ethylenediamine complex [$CuCl_2$(en)] (2.05 mmol) was suspended in thf (180 cm^3) and treated with Na[OPh]·PhOH (4.1 mmol). After *ca.* 1.5 h, sodium chloride was filtered off and the resulting green solution was then evaporated under reduced pressure to about one third its original volume. The green microcrystalline solid obtained after keeping the solution in a refrigerator was filtered off and dried *in vacuo* (62% yield) (Found: C, 59.65; H, 5.95; N, 6.80. $C_{20}H_{24}CuN_2O_3$ requires C, 59.45; H, 6.00; N, 6.95%). Similar to (1), the complex in solution is extremely sensitive to moisture. The i.r. spectrum [combined Nujol and $(C_2ClF_3)_n$ mulls] has bands at 3 360w, 3 350w, 3 330w, 3 260w, 1 580m–s, 1 565m, 1 480s, 1 410m, 1 270m, 1 235m, 1 160w–m, 1 085w, 1 070w, 1 030m, 990w, 890w–m, 825m, 770m, 758m, 700w, 695m, 650w, 615w, 560w, 515w, and 470w cm^{-1}. The room-temperature e.s.r. spectrum of a *ca.* 10^{-2} mol dm^{-3} solution in thf has a resonance characterised by $g_{iso.} = 2.10$ and $A_{iso.} = 74$ G. The magnetic susceptibility at room temperature is $\chi_M^{corr} = 1\,358 \times 10^{-6}$ c.g.s. units, corresponding to $\mu_{eff.} = 1.78$ B.M. (diamagnetic correction = -234×10^{-6} c.g.s. units).

The p-*benzoquinone adduct* [CuCl(py)]$_2$·$C_6H_4O_2$. Copper(I) chloride (0.713 g, 7.2 mmol), pyridine (2.47 g, 31.2 mmol), and *p*-benzoquinone (0.387 g, 3.58 mmol) were stirred in thf (150 cm^3). After several hours the reaction mixture was heated under reflux for some minutes to improve the crystallisation of the red solid product. The latter was

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† Throughout this paper: 1 G = 10^{-4} T; 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 mmHg ≈ 13.6 × 9.8 Pa.

filtered off at room temperature and dried *in vacuo* (1.45 g, 86.7% yield) (Found: C, 41.9; H, 3.20; N, 6.30. $C_{16}H_{14}Cl_2Cu_2N_2O_2$ requires C, 41.4; H, 3.05; N, 6.05%). The i.r. spectrum (KBr pellet) has bands at 3 040w, 1 740w, 1 660m–s, 1 645s, 1 605m–s, 1 485w–m, 1 470m, 1 445m–s, 1 355w, 1 335w, 1 280s, 1 240w, 1 220w, 1 150w, 1 145w, 1 070m–w, 1 040m–s, 1 015w, 1 000w, 895w, 860w, 750m, 695m–s, 635w, 425w, and 405m–w cm^{-1}. The magnetic susceptibility at room temperature is $\chi_M^{corr} = 33 \times 10^{-6}$ c.g.s. units (diamagnetic correction = -234×10^{-6} c.g.s. units). A sample was heated at *ca.* 100 °C (5×10^{-2} mmHg) in a sublimation apparatus. Pyridine was found in the cold-trap (*ca.* −75 °C), while *p*-benzoquinone was collected on the cold-finger maintained at room temperature. The involatile residue was CuCl.

The p-*benzoquinone adduct* $[CuBr(py)]_2 \cdot C_6H_4O_2$. The bromo-derivative was prepared in approximately quantitative yields as a deep red microcrystalline substance, slightly soluble in thf, by a procedure similar to that described above for the chloro-analogue (Found: C, 34.5; H, 2.75; N, 5.00. $C_{16}H_{14}Br_2Cu_2N_2O_2$ requires C, 34.75; H, 2.55; N, 5.05%). The i.r. spectrum [Nujol and $(C_2ClF_3)_n$ mulls] was generally similar to that of the corresponding chloro-derivative, as reported above. The magnetic susceptibility at room temperature is $\chi_M^{corr} = 0.7 \times 10^{-6}$ c.g.s. units (diamagnetic correction = -244×10^{-6} c.g.s. units).

RESULTS AND DISCUSSION

The reaction of $[CuCl_2(bipy)]$ with the stoicheiometric amount of $Na[OPh] \cdot PhOH$ in thf yielded the diphenoxo-derivative (1) [equation (i)]. The brown complex is

$$[CuCl_2(bipy)] + 2Na[OPh] \xrightarrow{thf} 2NaCl + \underset{(1)}{[Cu(OPh)_2(bipy)]} \quad (i)$$

moderately soluble in thf, monomeric in nitrobenzene, and the e.s.r. parameters suggest a distorted-tetrahedral arrangement around copper. Similarly, the reaction of the ethylenediamine complex $[CuCl_2(en)]$ with $Na[OPh] \cdot PhOH$ gave the green derivative (2) [equation (ii)].

$$[CuCl_2(en)] + 2Na[OPh] \cdot PhOH \xrightarrow{thf} 2NaCl + PhOH + \underset{(2)}{[Cu(OPh)_2(en)] \cdot PhOH} \quad (ii)$$

Treatment of (2) with PhOH did not modify its composition and attempts to isolate the solid complex free from PhOH failed. Although molecular-weight determinations could not be carried out because of the low solubility of the complex, the spectroscopic (i.r. and e.s.r.) properties suggest that (1) and (2) should have similar structures.

In the case of complex (2) the extra phenol present is probably hydrogen-bonded either to the phenoxide oxygen or to the amine groups of the en ligand. The observation that no phenol-containing complex could be obtained for the bipy derivative suggests that the latter assumption is more reasonable. The presence of the hydrogen-bonded phenol in (2) is evidenced by the bands between 3 250 and 3 400 cm^{-1} which are much more numerous than in the starting $[CuCl_2(en)]$ complex. The experimental observations are consistent with a monomeric formulation for the two complexes, the co-ordination sphere around copper probably being of the N_2O_2 type. This is substantiated by the observation that the i.r. spectra of the two complexes show absorptions around 1 250 cm^{-1} which should be attributed to the C–O stretching vibration of the oxygen-bonded co-ordinated phenoxide group. However, attention should also be paid to the fact that both complexes exhibit a strong i.r. absorption at *ca.* 1 580 cm^{-1}, which is particularly significant for the bipy derivative. In the latter case, comparison with the starting $[CuCl_2(bipy)]$ complex reveals the presence of relatively weak absorptions in this region due to the C–C and C–N stretching vibrations of co-ordinated bipy. In view of the fact that a strong absorption around 1 580 cm^{-1} has been attributed [8] to π-bonded phenoxide groups in some ruthenium(II) complexes, the possibility should not be disregarded *a priori* that at least one of the phenoxide groups in our complexes is π-bonded. A definite answer to this question can only come from an *X*-ray investigation.

Considerable attention has been given in the literature to reactions between dioxygen and copper(I) complexes, especially in attempts to mimic the behaviour of copper in oxidative biological systems.[9] Reversible oxygen uptake was reported [10] for a copper–polyamine system. The rates of oxygen uptake by bis(phenanthroline)-copper(I) systems have been studied [11] and, more recently, a polydentate ligand in a binuclear copper(I) complex was reported to absorb dioxygen reversibly in the solid state.[12] The CuX–O_2–amine system, which is responsible for several catalytic oxidations, for example the dehydrogenation of alcohols to aldehydes [13] and the previously mentioned coupling of phenols, has been the subject of several studies [14–16] aimed at clarifying the nature of the metallic species involved in the catalytic cycle.

In an attempt to contribute to the understanding of the phenomena involved in these electron-transfer processes, we decided to study the behaviour of *p*-benzoquinone with CuX (X = Cl or Br). Earlier work from these Laboratories [17] had in fact shown that cobalt(II) and iron(II) complexes of a quadridentate Schiff base undergo adduct formation with *p*-benzoquinone yielding binuclear compounds better regarded as cobalt(III) and iron(III) complexes of the $[C_6H_4O_2]^{2-}$ ligand. Moreover, an electron transfer between CuX and *p*-benzoquinone would have resulted in the formation of compounds resembling the phenoxo-complexes described above.

We have found that CuX reacts with *p*-benzoquinone in the presence of pyridine yielding complexes (3) [equation (iii)]. However, contrary to our expectations,

$$2CuX + 2py + C_6H_4O_2 \xrightarrow{thf} \underset{(3;\ X = Cl\ or\ Br)}{[CuX(py)]_2 \cdot C_6H_4O_2} \quad (iii)$$

these complexes should probably be regarded as *olefin* complexes of copper(I), rather than as copper(II) derivatives of the $[C_6H_4O_2]^{2-}$ ligand. The intensely coloured complexes are diamagnetic, poorly soluble in thf. The ligands are loosely bonded and both pyridine and *p*-benzoquinone are lost *in vacuo* at *ca.* 100 °C. Although molecular-weight determinations could not be carried out, the low solubility in the common organic solvents suggests a rather high molecular complexity. Further information about the structure of these complexes comes from the i.r. spectra. The spectrum of the chloro-derivative from 3 500 to *ca.* 250 cm^{-1} is generally identical to that of the corresponding bromo-analogue. Furthermore, two strong absorptions are present at 1 660 and 1 640 cm^{-1}, attributed to the C–O stretching vibration of the co-ordinated quinone, to be compared with the 1 674 and 1 662 cm^{-1} bands for the free ligand (in $CHCl_3$).[18] This almost insignificant decrease of the C–O stretching vibration upon complexation suggests that no electron transfer to the quinone has taken place and that the C–O groups are not directly involved in the co-ordination to copper.

That the *p*-benzoquinone adducts reported in this paper should be regarded as olefin complexes is supported by the observation that a labile adduct has also been obtained between CuCl and dimethyl fumarate, in the presence of pyridine. The latter complex, whose isolation in an analytically pure state was not possible because of ready loss of co-ordinated dimethyl fumarate and/or pyridine, is characterised by an i.r. band at 1 740 cm^{-1} attributed to the C–O stretching vibration of the ester group, to be compared with the value of 1 720 cm^{-1} for the free ligand under the same experimental conditions (Nujol). This strongly suggests that the fumarate derivative is an olefin complex and that the ester group is not involved in the co-ordination. Similar results have also been obtained in the course of the preparation of a dimethyl fumarate complex of (diethylenetriamine)copper(I).[19]

It is noteworthy that a diamagnetic complex of formula $[CuCl(py)]_2 \cdot C_6H_4O_2$ was obtained [20] by the reaction of an alkoxo-derivative of copper(II), $[CuCl(OMe)(py)]_n$, with hydroquinone. This reaction may formally be regarded as a protonic attack on co-ordinated methoxide, followed by MeOH elimination. Since the reported [20] properties are very similar to those found for the *p*-benzoquinone adduct in this study, (**3**; X = Cl), we conclude that we are dealing with the same substance and that reaction (iii) is a more straightforward method of preparing the quinone adducts.

Finally, the virtual identity of the i.r. spectra of complexes (**3**; X = Cl or Br) from 3 500 to *ca.* 250 cm^{-1} suggests that no change of structure takes place on going from the chloro- to the bromo-derivatives. Furthermore, the lack of observation of bands attributable to the Cu–X stretching vibration suggests that these vibrations are at <250 cm^{-1} (bands around 300 cm^{-1} have been reported [21] for some amine derivatives of copper) or, alternatively, that complexes (**3**) are ionic with X outside the co-ordination sphere of the metal.

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