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Copper(II) Complexes Resulting from the Oxygenation of (2,9-Dimethyl-1,10-phenanthroline)copper(I) Chloride in the Presence of Dimethylformamide

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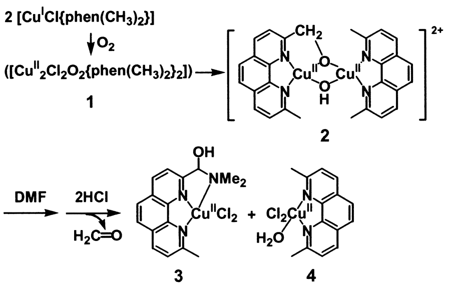
The oxygenation of (2,9-dimethyl-1,10-phenanthroline)copper(I) chloride in THF, followed by a treatment with DMF and acidification with HCl, afforded dichloro[2-(dimethylamino)(hydroxy)methyl-9-methyl-1,10-phenanthroline]copper(II) and (aqua)dichloro(2,9-dimethyl-1,10-phenanthroline)copper(II) quantitatively.

When metal complexes [M] react with O_2 in an overall $[M]:O_2 = 2:1$ stoichiometry, the resulting dinuclear complexes with an M_2O_2 core show two complementary types of reactivities.[1] On one hand, the M_2O_2 complexes can release a coordinated O_2 molecule, depending on the O_2 concentration, thus allowing transport of the O_2 molecule.[2] On the other hand, they can foster a breaking of the O–O bond, thus providing a high-valent species with a strong oxidizing ability.[3] A peculiar example of the latter is the synthesis of poly(thio-1,4-phenylene) by the vanadium-catalyzed polymerization of diphenyl disulfide,[4] which proceeds at the expense of O_2 that is predominantly reduced to H_2O.[5] It has been established that splitting of the O–O bond in O_2 is fostered by the homolytic character of the μ-peroxo-κ^2 O,O′-divanadium(IV) which forms during the reaction of O_2 with an oxophilic vanadium(III).[6] Recently, a growing number of relevant studies have shown that M_2O_2 complexes, particularly those of copper,[7] manganese,[8] cobalt,[9] ruthenium[10] and iridium,[11] can display C–H bond activation to provide a variety of hydroxylated and/or oxidatively coupled products. In particular, a number of examples have been found for oxygen-atom insertion into an aliphatic C–H bond proximal to the Cu/O_2 core.[12] However, copper(I) complexes tend to react with O_2 in an overall 4:1 stoichiometry,[13] possibly via disproportionation of the M_2O_2 complexes. The prevalent formation of Cu_2O_2 complexes has thus been limited to those with multidentate ligands bearing imidazolyl,[12a] pyrazolyl,[14] pyridinyl[15] and peralkylated amino[16] groups. Although the Cu_2O_2 moiety is also frequently invoked with 1,10-phenanthroline ligands,[17] there has been no unequivocal evidence for the involvement of such species. The reaction of (1,10-phenanthroline)copper(I) with O_2 has been extensively investigated with the view to allow a catalytic reduction of O_2 by the complex adsorbed on graphite electrodes.[18] In this report, we describe that oxygen-atom insertion can take place at the 2-methyl group of the 2,9-dimethyl-1,10-phenanthroline ligand when its copper(I) complex is reacted with O_2. The reaction stoichiometry and analogy to previous studies provide indications that the corresponding Cu_2O_2 complex is likely to intervene.



Scheme 1.

In attempts to synthesize a dicopper-O_2 complex bearing $phen(CH_3)_2$ ligands ($phen(CH_3)_2$ = 2,9-dimethyl-1,10-phenanthroline), a copper(I) complex $[CuCl\{phen(CH_3)_2\}]$ was reacted with O_2 in THF. Stirring a solution of $[CuCl\{phen(CH_3)_2\}]$ under an O_2 atmosphere at room temperature, followed by a treatment with DMF, however, did not afford the desired product, but instead gave a mixture of the copper(II) complexes dichloro[2-(dimethylamino)(hydroxy)methyl-9-methyl-1,10-phenanthroline]copper(II) (**3**) and (aqua)dichloro(2,9-dimethyl-1,10-phenanthroline)copper(II) (**4**) (Scheme 1), which were almost quantitatively obtained in a 1:1 yield. The striking structural feature of **3** (Fig. 1a) is the formation of a (dimethylamino)(hydroxy)methyl group resulting from the oxygenation of a methyl group in the $phen(CH_3)_2$ ligand in the presence of DMF, and coordination of the amino nitrogen to the copper atom, thus allowing a five-coordination geometry. Well-refined X-ray data allowed the positioning of all hydrogen atoms, which corroborated the sp^3 arrangement around the substituted methyl carbon. The other counterpart **4** is a five-coodinate copper(II) hydrate (Fig. 1b).

The present C–N bond formation should consist of several reactions, such as O–O bond splitting and a rearrangement of the dimethylamino group. Preliminary labeling experiments using $^{18}O_2$ (vide infra) have revealed that the origin of the oxygen atom in the hydroxy group of **3** is O_2. Although a further study is needed to clarify the mechanism, complex **2** from its precursor **1** can be proposed as a likely intermediate by analogy to previous studies[7–12,14–16] and based on the following consideration: i) The treatment of $[CuCl\{phen(CH_3)_2\}]$ with O_2 in THF in the absence of DMF afforded a hygroscopic green powder having a composition of $C_{28}H_{30}Cl_2Cu_2N_4O_5$ (**2**·$3H_2O$). The product was ESR silent, and showed an O–H stretching band near 3276 cm^{-1}, which is typically observed for μ-hydroxo-dicopper(II) complexes.[19] ii) The treatment of the product with DMF, followed by HCl under argon, quantitatively af-

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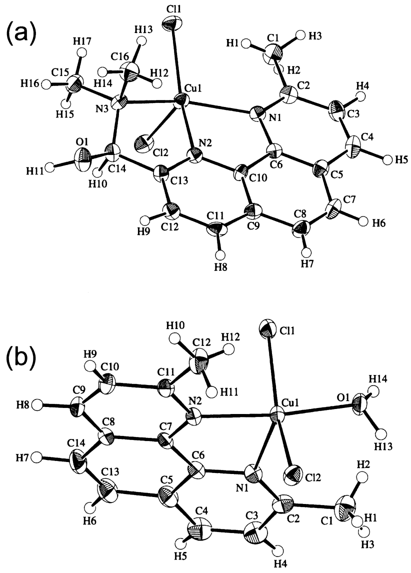

Fig. 1. ORTEP view (30% probability ellipsoids) of (a) **3**. and (b) **4**. Selected bond lengths (Å) angles (deg) for **3**: Cu(1)–N(1), 2.210(4); Cu(1)–N(2), 1.956(5); Cu(1)–N(3), 2.148(4); N(1)–Cu(1)–N(3), 154.2(2); N(2)–Cu(1)–N(3), 78.4(2); Selected bond lengths (Å) angles (deg) for **4**: Cu(1)–N(1), 2.249(3); Cu(1)–N(2), 1.994(3); Cu(1)–O(1), 1.962(3); N(1)–Cu(1)–N(2), 79.5(1); N(1)–Cu(1)–O(1), 107.4(1); N(2)–Cu(1)–O(1), 172.7(2).

forded **3** and **4**. A reasonable amount of formaldehyde was detected in the reaction mixture. iii) The stoichiometric ratio Cu : O_2 for the overall reaction of [CuCl{phen(CH_3)$_2$}] with O_2 in THF was determined to be 2 : 1 by manometry. While the crystal structure determination of **2** has been unsuccessful, the 1 : 1 formation of **3** and **4** also indicates the intervention of **2**.

Experimental

Preparation. The copper(I) complex [{phen(CH_3)$_2$}CuCl] was prepared from copper(I) chloride and phen(CH_3)$_2$ (0.21 g) in THF (30 mL) under argon. The resulting complex (0.15 g, 5×10^{-4} mol) was dissolved in THF (30 mL) under argon. After stirring for 30 min, the atmosphere was replaced with O_2 and the mixture was constantly stirred for 14 h. The amount of O_2 uptake (5.5 mL, 2.3×10^{-4} mol) was determined by manometry using an air-tight vessel equipped with a manometer. The resulting green precipitate was collected by filtration, washed with THF, and dried under a vacuum to give a dicopper(II) complex as a hygroscopic powder, which was provisionally identified to be **2** (0.16 g, 2.3×10^{-4} mol). Anal. Calcd for $C_{28}H_{30}Cl_2Cu_2N_4O_5$ (**2**·$3H_2O$): C, 48.0; H, 4.32; N, 8.00%. Found: C, 47.8; H, 4.30; N, 7.60%. IR (KBr): 3272, 1624, 1563, 1503, 1447, 1374, 1148, 861, 775, 731, 654 cm^{-1}. MS (FAB, *m*-nitrobenzyl alcohol matrix, *m*/*z*): calcd for $C_{28}H_{24}Cl_2Cu_2N_4O_2$: 646.5 [$M^+$]. Found: 646, 575 ([$M^+ - 2Cl$]). The green powder was next dissolved in DMF. Crystallization of the product was performed by layering the solution with diethyl ether. Crystalline products were obtained only when the mother solution was slightly acidified with HCl. X-ray crystallographic measurements revealed that the product consisted of dark-green cubic crystals of **3** (0.084 g, 2.1×10^{-4} mol) and light-green prismatic crystals of **4** (0.072 g, 2.0×10^{-4} mol). A GC analysis of the acidified solution revealed the formation of formaldehyde in 95 mol% with respect to **3**.

Labeling experiments were performed using $^{18}O_2$. The products of the oxygenation of [CuCl{phen(CH_3)$_2$}] with $^{18}O_2$ were also dark-green cubic crystals (**3′**) and light-green prismatic crystals (**4′**). **3′**: MS (FAB, *m*-nitrobenzyl alcohol matrix, *m*/*z*): calcd for $C_{16}H_{17}N_3Cl_2Cu^{18}O$: 403.8 [$M^+$]. Found: 404, 333 ([$M^+ -$ 2Cl]), 402, 331. The identification of **4′** failed due to a rapid exchange of hydrated $H_2{}^{18}O$ in **4′** with external molecules.

X-ray Crystallography. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 160934 and 160935.

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