Effects of a Side Chain Aromatic Ring on the Reactivity of Copper(I) Complexes with Dioxygen**

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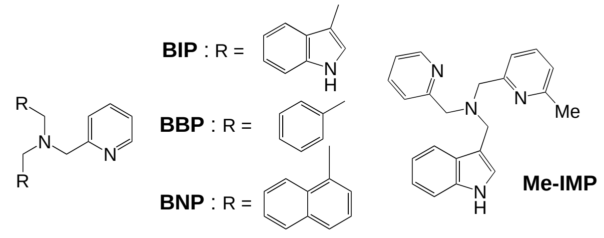
Close contact between a metal ion and an aromatic ring has been observed for planar metal complexes with an aromatic ring in the side chain, such as the tryptophan indole and the tyrosine phenol ring,[1] and for complexes where intramolecular aromatic-ring stacking occurs.[2] We reported previously that the Cu^I complex of a tripodal N3 ligand with a pendent indole ring has a unique Cu^I–indole η^2-type bond through the C2–C3 moiety.[3] A pendent naphthyl group of a Cu^I complex of a NS2 macrocyclic ligand has been reported to form a similar bond.[4]

These observations suggest that the proximity of indole or other aromatic rings to the metal center may affect the reactivity of the complex, such as in the formation of a metal–dioxygen adduct in the course of dioxygen activation—which is of current interest for its importance in biological as well as chemical systems.[5] Significant progress has been made in the chemistry of the intermediate complexes formed in the course of the reaction of Cu^I species with dioxygen.[6] *trans*-μ-Peroxodicopper(II),[7] (μ-η^2:η^2-peroxo)dicopper(II),[8] and bis(μ-oxo)dicopper(III)[9–14] complexes have drawn particular attention as a consequence of their known or potential relevance to intermediates in biological oxygenation. The bis(μ-oxo)dicopper(III) species was characterized by X-ray crystallography and shown to have a unique diamond-shaped structure formed by two Cu^{III} and two bridging oxo ions, $Cu_2(\mu\text{-}O)_2$,[9–12] and the reactivities of this and other species have been explored in connection with the oxidative activation of C–H bonds.[9–15] These intermediates often reacted with aliphatic C–H bonds[15] and in a few cases activated the aromatic ring.[14]

Here we report that the Cu^I complexes of N-donor ligands with one or two pendent indole rings (Scheme 1) form a dioxygen adduct as an intermediate which decomposes to give a product formed by a unique radical-coupling reaction between the indole rings.



Scheme 1. Structures of N-donor ligands with pendent aromatic rings.

The bidentate ligand *N*,*N*-bis[(3-indolyl)methyl]-*N*-[(2′-pyridyl)methyl]amine (BIP) reacted with CuI ions to give a dimeric complex $[Cu(bip)I]_2 \cdot 2CH_3COCH_3$ (**1**), the X-ray crystal structure analysis[16] of which has shown that each Cu^I site has a distorted tetrahedral geometry formed by two bridging iodine atoms, a tertiary amine nitrogen atom, and a pyridine nitrogen atom (Figure 1). The two side-chain indole rings are uncoordinated, and neither the stacking nor the Cu^I–indole η^2-type bond[3] were detected in the solid state or in solution. The reaction of a similar ligand, Me-IMP (*N*-(3-indolylmethyl)-*N*-(6-methyl-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine),[3] and CO with $[Cu(CH_3CN)_4]ClO_4$ gave $[Cu(Me\text{-}imp)(CO)]BPh_4$ (**2**), which was revealed to have a tetrahedral geometry (Figure 2).

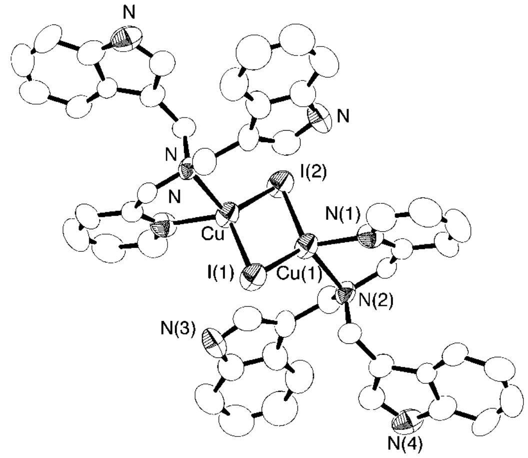


Figure 1. ORTEP view of $[Cu(bip)I]_2 \cdot 2CH_3COCH_3$ (**1**) drawn with the thermal elliposids at the 50% probability level and atomic numbering scheme (CH_3COCH_3 molecules omitted for clarity). The hydrogen atoms and solvents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)-N(1) 2.075(6), Cu(1)-N(2) 2.223(5), Cu(1)-I(1) 2.585(1), Cu(1)-I(2) 2.625(1); N(1)-Cu(1)-N(2) 79.5(3), N(1)-Cu(1)-I(1) 112.7(2), N(1)-Cu(1)-I(2) 105.9(2), I(1)-Cu(1)-I(2) 120.51(3).

A colorless solution of **1** in THF reacted with O_2 at −90 °C to give a brown solution with an intense absorption band centered at 374 nm and a shoulder peak at 516 nm. The resulting solution was ESR inactive at 77 K. Complex **2** also reacted with O_2 in THF to give a brown solution exhibiting an absorption spectrum with similar peaks at 379 and 510 nm.[17] The resonance Raman spectrum of this solution gave a Raman peak at 595 cm^{-1} with $^{16}O_2$ which shifted to 568 cm^{-1} upon substitution with $^{18}O_2$ (406.7-nm Kr^+ laser excitation; Figure 3). No peaks were observed in the 700–800 cm^{-1} region, where the band resulting from the μ-peroxo dimer is

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

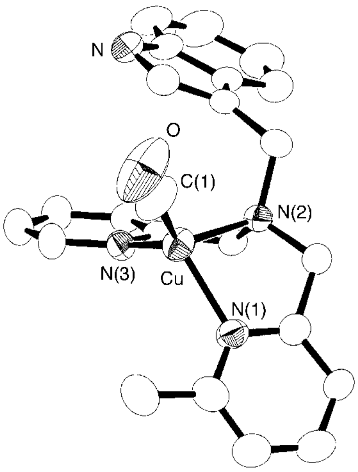


Figure 2. ORTEP view of the $[Cu(Me\text{-}imp)(CO)]^+$ ion in **2** drawn with the thermal ellipsoids at the 50% probability level and atomic numbering scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)-N(1) 2.048(4), Cu(1)-N(2) 2.134(4), Cu(1)-N(3) 2.021(4), Cu(1)-C(1) 1.790(9); N(1)-Cu(1)-N(2) 81.6, N(1)-Cu(1)-N(3) 108.1(2), N(2)-Cu(1)-N(3) 83.4(2), N(1)-Cu(1)-C(1) 122.0(3), N(2)-Cu(1)-C(1) 125.5(3), N(3)-Cu(1)-C(1) 123.6(2).

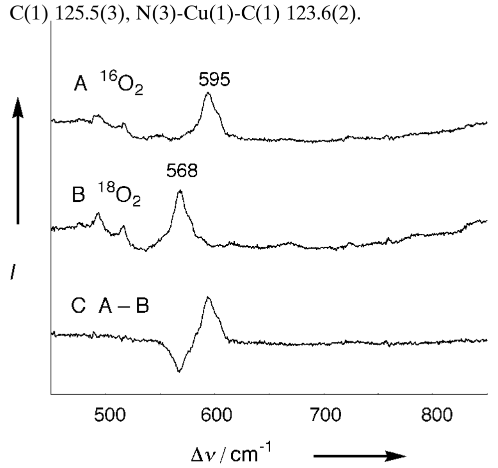
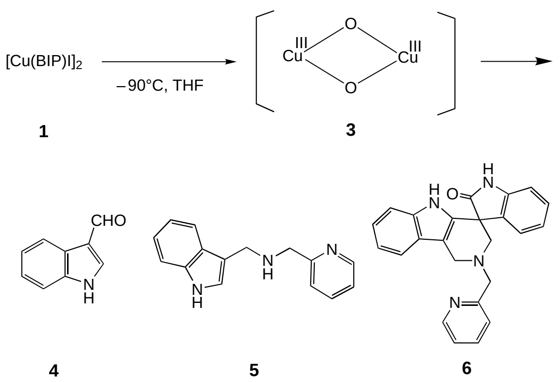


Figure 3. Resonance Raman spectra of **2** after oxygenation with $^{16}O_2$ and $^{18}O_2$ in THF at −90 °C (406.7-nm Kr^+ laser excitation).

expected. We measured the resonance Raman spectrum with 514.5-nm laser excitation in order to detect the possible existence of the peroxo species. The spectrum showed a weak band at 590 cm^{-1}, but no peroxo band at about 750 cm^{-1}. The absorption and resonance Raman spectra of **3** agreed well with the values of 378 and 494 nm, and 590 cm^{-1}, respectively, reported for $[Cu_2(O)_2(Me_2\text{-tpa})_2]^{2+}$ (Me_2-tpa = bis(6-methyl-2-pyridylmethyl)-2-(pyridylmethyl)amine) which was isolated and structurally established by Suzuki and co-workers.[12] In this latter complex each Cu^{III} ion has two weakly bound 6-methyl-2-pyridylmethyl side arms in the axial positions. Our spectra also corresponded with other previous observations[9b, 10, 11, 13b, 18, 19] and are typical of the $Cu_2(\mu\text{-}O)_2$ core, and gives support to the assumption that the brown solution contained an intermediate species (**3**) having the same bis(μ-oxo) dimer structure (Scheme 2). However, we should mention that while the above resonance Raman data suggest the presence of the bis(μ-O) core, they do not rule out the formation of the peroxo species during the course of the reaction.



Scheme 2. Reactions of Cu^I-BIP complexes with dioxygen.

The formation and decay of the oxygenated species **3** followed the first-order rate law, which indicates that the peroxo species was not formed or was too unstable to be detected during the reactions. On the other hand, BBP and BNP (BBP = *N,N*-bis(benzyl)-*N*-[(2′-pyridyl)methyl]amine; BNP = *N,N*-bis[(1-naphthyl)methyl]-*N*-[(2′-pyridyl)methyl]amine (Scheme 1)) reacted with CuI to give [Cu(bbp)I] and [Cu(bnp)I],[20] respectively, and both reacted with O_2 in THF at −90 °C to give a green color almost instantaneously. In order to examine the difference in reactivity in detail we measured the difference spectra for the reaction of [Cu(bnp)I] with O_2 under the same conditions by the rapid-scan technique. This study revealed a transient shoulder peak at approximately 380 nm during the first 5–20 s and finally peaks at around 360 and 600 nm.[17] This observation indicates that an oxygenated intermediate similar to **3** is also formed with BNP, but it may be much less stable than that formed from **1** or **2**. This fact suggests there is a stabilizing effect of the $Cu_2(\mu\text{-}O)_2$ core in the complexes by the pendent indole rings.

Intermediate **3** was short-lived compared with some of the reported $Cu_2(\mu\text{-}O)_2$ species and changed to a green species below −80 °C. The first-order decay constant k_{obs} of the brown species in THF was estimated to be $1.5 \times 10^{-2}\,s^{-1}$ (half-life $t_{1/2} < 1$ min) at −90 °C, as determined by UV/Vis spectroscopy. Indole-3-carboxaldehyde (**4**; 10%) and *N*-(3-indolyl)-methyl-*N*-[(2′-pyridyl)methyl]amine (**5**; 10%) were detected among the decomposition products formed by N-dealkylation (Scheme 2), which has been reported to occur with other $Cu_2(\mu\text{-}O)_2$ species.[9c, 12] In addition to these products, an interesting decay product **6** was isolated as crystals (15%). The X-ray structure analysis[16] of the product disclosed that it has a bis(indolyl) moiety which is considered to have resulted from a radical-coupling reaction (Scheme 2).[17] This structure supports the theory that the indole ring was located sufficiently close to the metal center to undergo an indole C–H bond scission, to form an indolyl radical in the course of the oxidative decomposition. [Cu(bbp)I] and [Cu(bnp)I] were observed to undergo N-dealkylation to give the corresponding aldehydes and secondary amines in low yields (< 5%), but no radical-coupling product was detected.

In conclusion, the Cu^I complexes of ligands with pendent aromatic rings exhibited different reactivities with O_2 which depended on the nature of the aromatic rings. The present finding indicates that the vicinal noncoordinating indole ring containing the NH moiety, as compared with the phenyl and naphthyl rings without it, may stabilize the bis(μ-oxo)dicopper(III) intermediate and affect subsequent reactions. Further studies along this line are under way.

Experimental Section

Synthesis of BIP: Indole (2.34 g, 20 mmol), formalin (37 %, 1.62 g, 20 mmol), and a few drops of acetic acid were added to a solution of 2-pyridylmethylamine (1.08 g, 10 mmol) in methanol (100 mL). The reaction mixture was stirred overnight at room temperature and then concentrated almost to dryness in vacuo. The residue was dissolved in a saturated aqueous solution of $NaHCO_3$ (50 mL) and extracted with $CHCl_3$. The white powder obtained from the extract was recrystallized from ethyl acetate. Yield: 1.89 g (52 %); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, 2H), 3.88 (s, 4H), 7.08 (dd, 1H), 7.09 (dt, 2H), 7.17 – 7.19 (m, 4H), 7.34 (d, 2H), 7.54 – 7.60 (m, 2H), 7.69 (d, 2H), 8.07 (brs, 2H), 8.48 (d, 1H).

Synthesis of BBP and BNP: BBP was prepared by the reaction of dibenzylamine (1.97 g, 10 mmol) with 2-pyridinecarboxaldehyde (0.63 g, 10 mmol) in methanol and subsequent reduction by sodium cyanotrihydroborate (0.63 g, 10 mmol). Yield: 1.28 g (35 %); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.62$ (s, 4H), 3.74 (s, 2H), 7.12 (m, 1H), 7.23 (m, 2H), 7.31 (t, 2H), 7.32 (t, 2H), 7.41 (d, 4H), 7.64 (t, 2H), 7.66 (dt, 1H), 8.49 (d, 1H). BNP was prepared in a similar way from 2-pyridylmethylamine (1.07 g, 10 mmol), 1-naphthaldehyde (3.12 g, 20 mmol), and sodium cyanotrihydroborate (1.26 g, 20 mmol). Yield: 3.32 g (87 %); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.82$ (s, 2H), 4.08 (s, 4H), 7.10 (m, 1H), 7.20 (m, 2H), 7.38 (t, 2H), 7.42 (t, 2H), 7.51 (t, 2H), 7.56 (d, 2H), 7.77 (d, 2H), 7.80 (d, 2H), 7.86 (d, 2H), 8.47 (d, 1H).

Synthesis of complexes: Complex **1** was prepared as pale yellow crystals from BIP (0.366 g, 1.0 mmol) and CuI (0.190 g, 1.0 mmol) in acetone/CH_3CN (4/1) under a nitrogen atmosphere. Yield: 0.372 g (74 %); elemental analysis (%) calcd for **1** $\cdot 2\,CH_3COCH_3$ ($C_{54}H_{56}N_8O_2Cu_2I_2$): C 52.73, H 4.59, N 9.11; found: C 52,68, H 4.47, N 8.95. [Cu(bbp)I] and [Cu(bnp)I] were prepared in THF in a similar way. Elemental analysis (%) calcd for [Cu(bbp)I] ($C_{20}H_{20}N_2CuI$): C 50.17, H 4.21, N 5.85; found: C 50.11, H 4.24, N 5.85. Elemental analysis (%) calcd for [Cu(bnp)I] ($C_{28}H_{24}N_2CuI$): C 58.09, H 4.18, N 4.84; found: C58.13, H 4.20, N 4.87. Complex **2** was prepared as colorless crystals from Me-IMP[3] (0.205 g, 0.6 mmol), $[Cu(CH_3CN)]ClO_4$ (0.164 g, 0.6 mmol), and sodium tetraphenylborate (0.205 g, 0.6 mmol) in CH_3OH under a CO atmosphere. Elemental analysis (%) calcd for **2** ($C_{47}H_{42}N_4OBCu$): C 74.95, H 5.62, N 7.44; found: C 75.59, H 5.60, N 7.41.

Ligand recovery:[14, 21] In a typical experiment, **1** (1.23 g, 1.0 mmol) was dissolved in THF (20 mL) under a nitrogen atmosphere, and O_2 was passed through the solution for 10 min at $-80\,^{\circ}C$. The solution was kept standing for one day at room temperature, and the resulting green solution was evaporated to dryness in vacuo. The residue was dissolved in concentrated NH_3 (10 mL) and extracted with $CHCl_3$ (3×10 mL). The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated in vacuo to leave a brown oil. The decomposition products **4** – **6** were separated by column chromatography on silica gel, and their structures and relative amounts were determined by ^{1}H NMR spectroscopy. Crystals of **6** suitable for X-ray structure determination were prepared by recrystallization from $CHCl_3$. Elemental analysis (%) calcd for **6** $\cdot 1.5\,CHCl_3$ ($C_{25.5}H_{21.5}N_4OCl_{4.5}$): C 54.74, H 3.87, N 10.01; found: C 54.44, H 3.99, N 9.70; ^{1}H NMR (300 MHz, CD_3OD): $\delta = 3.02$ (dd, 2H), 3.96 (dd, 2H), 3.98 (q, 2H), 4.12 (d, 1H), 6.97 (t, 3H), 7.03 (t, 1H), 7.19 (t, 2H), 7.27 (t, 1H), 7.35 (d, 1H), 7.39 (d, 1H), 7.67 – 7.78 (m, 2H), 8.43 (d, 1H).

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[16] The X-ray experiments for complexes **1** and **3** were carried out on a Rigaku RAXIS imaging plate area detector with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). The crystals were mounted on a glass capillary tube. In order to determine the cell constant and orientation matrix, three oscillation photographs were taken with an oscillation angle of 2° and the exposure time of 8 min for each frame. Intensity data were collected by taking oscillation photographs. Refraction data were corrected for both Lorentz and polarization effects. The unit-cell parameters used for the refinement were determined by least-squares calculations on the setting angles for 25 reflections that were collected on a Rigaku AFC-5R four-circle automated diffractometer. The measurement for **6** was carried out on

a Rigaku AFC-5R four-circle automated diffractometer using a rotating anode generator with graphite monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The crystals were mounted on a glass capillary tube. The reflection intensities for **6** were monitored by three standard reflections at every 2 h and 150 measurements, and the decay of intensities for the crystals was within 2%. Refraction data were corrected for both Lorentz and polarization effects. **1**: $C_{54}H_{56}N_8O_2Cu_2I_2$, pale yellow crystals, monoclinic, space group $P2_1/n$, $a = 13.704(9)$, $b = 8.349(2)$, $c = 23.318(4)$ Å, $\beta = 89.88(3)^\circ$, $V = 2667(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.531$ g cm^{-3}, $R = 0.081$, $R_w = 0.141$ for all 6345 reflections ($I > 2.0\sigma(I)$) and 308 parameters. **2**: $C_{47}H_{42}N_4OBCu$, colorless crystals, monoclinic, space group $P2_1/n$, $a = 11.5365(3)$, $b = 22.5800(5)$, $c = 15.8994(5)$ Å, $\beta = 107.8117(6)^\circ$, $V = 3934.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.269$ g cm^{-3}, $R = 0.061$, $R_w = 0.100$ for all 7975 reflections ($I > 2.0\sigma(I)$) and 488 parameters. **6**: $C_{26}H_{22}N_4OCl_6$, colorless crystals, monoclinic, space group $P2_1/c$, $a = 10.743(3)$, $b = 17.820(4)$, $c = 15.673(3)$ Å, $\beta = 105.72(2)^\circ$, $V = 2887(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.424$ g cm^{-3}, $R = 0.085$, $R_w = 0.088$ for all 4287 reflections ($I > 2.0\sigma(I)$) and 335 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159430–159432, for **1**, **2**, and **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] Spectral changes observed on oxygenation of **2** and [Cu(bnp)I] as well as an ORTEP view of **6** can be found in the Supporting Information.

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[20] [Cu(bbp)I] was revealed to have the same dimeric structure as that of **1** by X-ray analysis (unpublished result), while the structure of [Cu(bnp)I] is not established yet. Therefore, these complexes are tentatively expressed as monomers.

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Immobilization of π-Assembled Metallo-Supramolecular Arrays in Thin Films: From Crystal-Engineered Structures to Processable Materials[**]

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Material and device performance is critically dependent on the spatial arrangement of the functional constituents. The ability to control the short- and long-range correlation of position and orientation of components is crucial for full exploitation of a material's potential and the encoding of new properties.[1] Supramolecular synthetic methodologies enable the systematic design and construction of tailored architectures through a sequence of directed assembly processes.[2] Metallo-units are particularly attractive functional components because of their inherent magneto-,[3] electro-,[4] and/or photochemical[5] properties.

By means of crystal engineering, solid-state multimetal arrays can be constructed by using interactions of metal ions with multitopic ligands[6] or other intermolecular forces to organize metallo-units.[7–9] However, processing a crystalline solid into a device remains a challenge. Moreover, in a single crystal, it is difficult to achieve attractive features such as gradients, often necessary for vectorial functions. Thin films play an important role in applications[10] such as storage, display, and sensing, yet to date there are no generic methodologies for incorporating and ordering discrete cationic metal complexes into thin films.[11] To address this challenge and to attempt to bridge the gap between fundamental supramolecular crystal engineering and layered materials, we investigated whether π-aggregated metallo-arrays can be incorporated into ordered two-dimensional thin films.

A particularly attractive method to assemble thin films is the layer-by-layer (LbL) method, which rests primarily on

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