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Synthesis and Characterization of a Coupled Binuclear Cu^I/Cu^{III} Complex

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Abstract: The synthesis through reaction of a C_α,C_{ortho} dilithiated phosphazene with CuBr and structural characterization of the first example of a binuclear mixed valence $[Cu^I(N_2)/Cu^{III}(C_4)]$ complex showing a metal−metal bond, as well as its applications in cyclopropanation and oxidation reactions, are described.

Copper-mediated carbon−carbon and carbon−heteroatom bond-forming reactions are of fundamental importance in organic synthesis.[1] Although experimental[2] and mechanistic[3] studies support the participation of Cu(III) species in a number of these transformations, very few Cu(III) complexes containing Cu−C bonds have been structurally characterized and only five examples show the Cu(III) tetracoordinated to carbon[4] based on carborane[4a,b,e] or fluorine-containing[4c,d] ligands (Chart S1).[5] Binuclear mixed-valence M^I/M^{III} group 11 complexes have been characterized for silver and gold. Based on electron counting and geometric parameters, it has been suggested that Cu^I and Cu^{III} centers coexist in a heteronuclear Co_4Cu_3 cluster[6] and in the product formed by electrochemical reduction of the coordination polymer $[Cu^{III}(\text{pyrazine-2,3-diselenyl})_2]Na\cdot 2H_2O$ during 1 month.[7] However, no charge transfer has been detected between the metal centers. Here, we describe the first synthesis of a mixed valence Cu^I/Cu^{III} complex **2** obtained by reaction of a dilithiated phosphazene with Cu(I) salts. We demonstrate unambiguously via spectroscopic studies and theoretical calculations the structure of the complex, the oxidation state of the metal centers, and the existence of d^8-d^{10} metal−metal interaction. Preliminary applications in catalysis are also reported.

The reaction of dianion **1**[8] with 2.2 equiv of CuBr at −90 °C in THF for 8 h gave after aqueous workup a mixture of the diastereomeric copper bimetallic complexes **2** and **3** in 53% yield and a ratio of 4.4:1 together with small amounts (<7%) of phosphine oxides **4** and **5** (dr of 1.3:1) (Figure 1). The air and moisture stable complex **2** was isolated (37% yield) through column chromatography (ethyl acetate/hexane 1:3) and recrystallized from dichloromethane. The X-ray structure of **2** consists of two ligands connected through two copper bridges, which define a C_2 symmetry axis (Figure 1). Cu(1) is coordinated to the four carbanionic centers and adopts a slightly distorted square planar geometry. The C−Cu bond lengths are quite similar (1.976−1.989 Å) and significantly longer than those found in the only two examples known of Cu^I complexes of monolithiated phosphazenes[9] (1.905(5)[9b]−1.954(2)[9a] Å). Compound **2** is the first example of a Cu(III) complex with the metal coordinated to four nonfluorinated carbons and showing two different hybridizations. The second metal center, Cu(2), is near linearly coordinated to two nitrogen atoms (bond angle N(1A)−Cu(2)−N(1B) = 178.99(12)°) with equal distances (N(1A)/(1B)−Cu(2) = 1.898(3) Å).

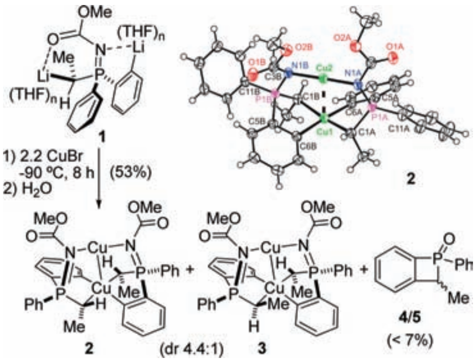

Figure 1. Formation of Cu^I/Cu^{III} complex **2** and X-ray structure.

The Cu(1) and Cu(2) coordination modes are typical of copper oxidation states +3 and +1, respectively.[10] Complex **2** is neutral and can be viewed as a d^8-d^{10} diamagnetic ate complex containing a $Cu^{III}C_4$ anion and a Cu^IN_2 cation. The Cu(1)···Cu(2) distance of 2.7448(6) Å is shorter than the sum of van der Waals radii (2.8 Å). The topological analysis of the X-ray experimental Fourier map[11] of **2** confirmed the existence of a Cu−Cu bond critical point (BCP) characterized by the values of the electron density $\rho = 0.0189\ e^-/\text{Bohr}^3$ and Laplacian $\nabla\rho = 0.0493\ e^-/\text{Bohr}^5$. Interestingly, weak metal−metal bonding has been described for d^8-d^{10} complexes of Pt(II)−Cu(I) with heterometallic distances of 2.74−3.02 Å (sum of van der Waals radii of 3.15 Å).[12] The NMR spectroscopic data of complex **2** are in agreement with the retention in solution of the structure characterized in the solid state (Supporting Information).

The EXAFS spectrum of **2** is consistent with the X-ray structure (Figure 2a). The XANES spectrum provides unequivocal evidence of the oxidation state of the Cu ions of **2** (Figure 2b). Edge position was taken as the maximum of the negative second derivative of the spectra. Complex **2** showed its maximum at 8982.3 eV (4*p* band) shifted +2.8 eV with respect to the Cu foil. This shift agrees with an average oxidation state of Cu^{II} in the complex. Also, the large

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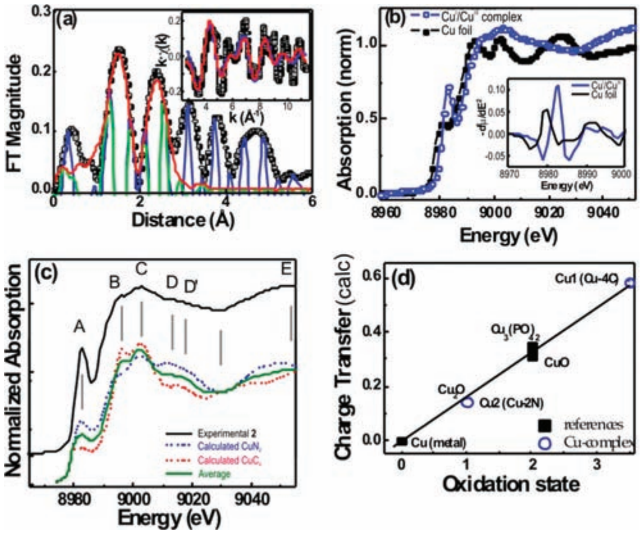


Figure 2. (a) Fourier transform of the EXAFS signal of **2**; inset: EXAFS signal (line + symbol), filtered EXAFS signal (red line), and best fit (blue line) of **2**. (b) XANES spectrum of **2** with inset showing the second derivative. A Cu foil XANES spectrum was added as a reference. (c) Best XANES calculated spectra reproducing the features of the experimental one. (d) Estimated oxidation state of copper ions of **2** based on the charge transfer obtained from XANES calculations.

amplitude pre-edge peak maximum at 8982.8 eV is characteristic of a 1*s* to 4*p* transition in linear two-coordinated Cu^I complexes.[13] These results suggest a double oxidation state Cu^I-Cu^{III} for the metallic centers in **2**. However, the broad Cu^I peak at 8982.8 eV (amplitude ca. 0.7, width of 4 eV) prevented the observation of the very weak pre-edge feature at 8981 ± 0.5 eV (1s to 3d transition, amplitude ca. 0.02) characteristic of Cu^{III} centers (Figure S1).[14] Additional support about the electronic structure of the two copper ions of **2** was obtained from XANES computations giving the best fit of the experimental features (Figure 2c, Supporting Information).

Calculations have been extended to well-known references such as Cu^0 metal, $Cu^I{}_2O$, $Cu^{II}O$, and $Cu^{II}{}_3(PO_4)_2$ for establishing the correlation between charge transfer and oxidation (Table S1). Computations showed that a fraction of an electron is transferred and is usually 1/5 to 1/10 the net charge transfer. From here, estimated oxidation states of +1 and +3.5 for the copper coordinated to two nitrogens and four carbons have been obtained, respectively (Figure 2d). These results support the description of **2** as a Cu^I/Cu^{III} complex. To the best of our knowledge, this is the first time that a mixed-valence complex showing two coupled Cu^I-Cu^{III} metals has been synthesized and unambiguously characterized.

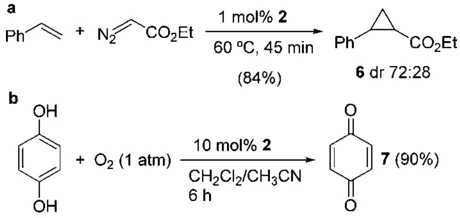
The UV−vis absorption spectrum of **2** in $CHCl_3$ solution shows two intense bands at $\lambda_{max} = 295$ ($\epsilon = 6243$ M^{-1} cm^{-1}) and 343 ($\epsilon = 8377$ M^{-1} cm^{-1}) nm, together with a weak shoulder at $\lambda_{max} = 392$ nm (Figure S2). These bands represent a large bathochromic and hyperchromic shift with respect to the UV−vis spectrum of the neutral ligand. The high energy absorption is proposed to originate from metal to ligand charge transfer (MLCT). Most importantly, the absorption band at 343 nm can be assigned to a $^1[d\sigma^* \rightarrow p\sigma]$ transition mixed with some MLCT character, which is diagnostic of an interatomic metal−metal interaction.

DFT geometry optimization (B3LYP/6-311G**) supports the experimental structural features of **2** (Supporting Information). The calculated Cu···Cu distance of 2.86 Å is in good agreement with the experimental value of 2.7448(6) Å. Calculations predicted that complex **2** is 0.32 kcal·mol⁻¹ more stable than the diastereoisomer **3** and that the triplet state of **2** is 31.5 kcal·mol⁻¹ less stable than the singlet state. The Atoms in Molecules analysis of the electron density found a bond critical point between the Cu atoms. The values for ρ and the Laplacian at this BCP are 0.0163 e/Bohr³ and 0.0564 e/Bohr⁵, respectively, which match very well those experimentally obtained. These values are characteristic for a metallic bond.[15] The existence of the latter BCP leads to the formation of two five-rings in compound **2** (Figure S16).

The Electron Localization Function (ELF) analysis[16] shows that the sum of the basins population corresponding to the core basin, C(Cu), of the tetracoordinated Cu atom and the four disynaptic valence basins $V(Cu,C_i)$ between these atoms, equals 34.23 electrons. Considering the traditional electron count, where 18 electrons correspond to the copper core, then we have a 16 electron square planar compound. This agrees with the picture of a d^8 complex, Cu^{III}, coordinated to four 2 electron donor ligands. The energy, composition, and nature of the orbitals of **2** contributing to the Cu(1)···Cu(2) interaction are given in the Supporting Information. The TD-DFT calculated excitation energies, with the largest oscillator strength within the range of 280−400 nm, including solvent (chloroform) effects using a Polarizable Continuum Model are 339, 330, and 286 nm. The first two are responsible for the main signal of the UV spectra observed at 343 nm. These transitions are from orbitals with a high contribution of d orbitals of the Cu(2) atom to the LUMO.

The reactivity of complex **2** as catalyst was investigated in two benchmark reactions where Cu(I) and Cu(III) species play a significant role: cyclopropanation[17] and oxidation.[18] Heating a mixture of styrene and ethyl diazoacetate in the presence of 1 mol % of **2** at 60 °C for 45 min afforded the cyclopropyl derivative **6** in a yield of 84% and a diastereomeric ratio of 72:28 (Scheme 1). On the other hand, stirring a solution of hydroquinone in dichloromethane/acetonitrile (ratio of 5/3) under a dioxygen atmosphere in the presence of **2** (10 mol %) at room temperature afforded after 6 h 90% of *p*-benzoquinone **7**. Significantly, the ³¹P NMR spectra of the crude reaction mixtures of both types of reactions showed the characteristic signal of the catalyst, which indicates that it remains unaffected during the transformations.

Scheme 1. (a) Cyclopropanation of Styrene and (b) Oxidation of Hydroquinone Catalyzed by Complex **2**



In conclusion, we have synthesized and structurally characterized an unprecedented binuclear $Cu^IN_2/Cu^{III}C_4$ complex **2** showing interatomic metal−metal interactions using a simple and reproducible procedure. Preliminary reactivity studies indicate that complex **2** catalyzed prototypal reactions involving Cu(I) and/or Cu(III) species in the reaction mechanism. Further work in this field is in progress.

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Supporting Information Available: Experimental procedures, characterization data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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