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In Situ Reduction of Copper(II) Forming an Unusually Air Stable Linear Complex of Copper(I) with a Fluorescent Tag

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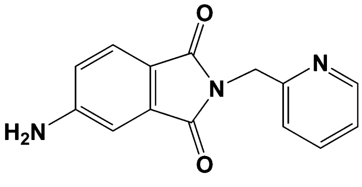
A new fluorescent ligand ($\phi_f = 0.8$ in dioxane), 2-(4′-aminophthalimidomethyl)pyridine (**L**), has been synthesized. A one-pot synthesis of its copper(I) complex upon reduction of copper(II) is achieved at room temperature. This complex, which has been characterized by X-ray crystallography, shows a linear N–Cu–N geometry with Cu–N bond lengths of 1.89 Å. X-ray structure reveals weak Cu···O interactions between copper and one of the imide oxygen atoms of the ligand framework. Additional weak Cu···O interactions between copper and oxygen atoms of the ClO_4^- counteranion are detected that lead to a zigzag polymeric chain with alternate ClO_4^- and copper ions. A 2-D intermolecular hydrogen bonding network is also observed. This complex is found to be highly inert toward oxidation both in the solid state and in solution.

Copper is an important metal ion in biological systems, and it plays diverse roles in living organisms.[1,2] The knowledge of the chemistry of well defined, coordinatively unsaturated copper(I) complexes is necessary for the understanding of the metal reactivity in various biological processes. Two-coordinate copper(I) complexes with nitrogen ligands are represented scarcely in the literature and structurally characterized ones are even rarer.[3−6] Sorrell et al. observed that two-coordinate copper(I) complexes having sterically hindered heterocyclic ligands or having increased orbital overlap between the ligating atom and copper(I) are inert toward reaction with CO and less reactive with O_2 in aprotic solvents.[3] However, in protic solvents, these complexes react rapidly and irreversibly with dioxygen to form Cu^{2+}. On the other hand, Le Clainche et al. reported that the preorganization provided by the calix[4]arene platform together with an increased orbital overlap between the imidazol-nitrogen atom and copper(I) stabilizes the two-coordinate linear complex of copper(I) that was inert toward dioxygen in the solid state as well as in coordinating or protic solvents.[5] However, the analogous pyridine-based complex is extremely sensitive to air and undergoes auto-oxidation within seconds.[5]

Chart 1



L

As a part of our ongoing research toward the design and development of selective fluorescent sensors based on a photoinduced intramolecular electron transfer (PIET)[7] mechanism for various transition metal ions,[8] we have synthesized a 2-methylpyridine appended 4-aminophthalimide as a new fluorescent probe (**L**). It was shown previously that the electron-deficient nature of 4-aminophthalimide (**AP**) nullifies the quenching influence of transition metal ions and thus enables the development of simple and effective fluorescent sensors that give chelation enhanced fluorescence (CHEF) in the presence of transition metal ions, which are otherwise very efficient fluorescent quenchers.[9] However, the coordination properties of the metal ions with these fluorophores are still unexplored primarily because of the lack of definite structural information on these systems. Even though **L** turns out to be not an effective fluorescent sensor for transition metal ions due to inefficient PIET, the change in the absorption spectrum of **L** upon subsequent addition

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Table 1. Absorption and Fluorescence[a] Properties of 4-Aminophthalimide (AP) and **L** in Dioxane, Tetrahydrofuran (THF), and Acetonitrile (AN)

	dioxane			THF			AN		
compd	λ_{max}^{abs} [b]	λ_{max}^{flu} [b]	ϕ_f[c]	λ_{max}^{abs} [b]	λ_{max}^{flu} [b]	ϕ_f[c]	λ_{max}^{abs} [b]	λ_{max}^{flu} [b]	ϕ_f[c]
AP[d]	352	435	0.73	357	445	0.7	357	458	0.63
L	361	440	0.80	365	453	0.75	366	472	0.78

[a] λ_{exc} = 360 nm; all λ_{max} values reported in nanometers. [b] ±2 nm. [c] ±10%. [d] These data have been collected from ref 11.

of metal ions indicates that it does form a complex with most of the transition metal ions in solution (Figure S1). Herein we present the synthesis and characterization of the ligand **L** and of a two-coordinated linear complex of copper(I) with **L**, which is characterized by X-ray crystallography. This complex appears to be totally inert toward oxidation in the solid state and stable in air even in potentially coordinating or protic solvents. To the best of our knowledge, no two-coordinate linear complex of copper(I) with monodentate ligands, that is exceptionally inert to aerial oxidation, is known. Moreover, the spectroscopic properties associated with the ligand system might further extend the utility of bioinorganic modeling studies.

The new ligand **L** was prepared in a single step reaction, where 4-aminophthalimide (1 mmol) was heated with 2-aminomethylpyridine (1.2 mmol) at 65 °C for 6 h to obtain a sticky material, which was purified by column chromatography.[10] The absorption and fluorescence spectra of **L** in THF are shown in Figure S2. Broad bands typical of the transition to the intramolecular charge-transfer state of the fluorophore moiety[11] characterize the low-energy absorption as well as the fluorescence spectra. The photophysical data of **L** in various solvents are listed in Table 1.

The reaction of **L** with $Cu(ClO_4)_2 \cdot 6H_2O$[12] in methanol at room temperature in 2:1 molar ratio for 2 days and subsequent storage for slow evaporation yielded brown, tiny crystals, suitable for X-ray diffraction, of $[CuL_2]ClO_4$ in 25% yield.[13] Conductivity measurements of this complex in acetonitrile reveal the 1:1 cation/anion ratio. The complex is EPR silent.

The relative stability of copper(I) and copper(II) in solution is known to depend very strongly on the nature of the anions and other ligands present and vary considerably with solvent or nature of neighboring atoms in the crystal. For example, with acetonitrile as a ligand, $Cu^{II}(ClO_4)_2$ is a strong oxidizing agent, and $Cu^{I}ClO_4$ is highly stable.[14] In a similar fashion, complexation of the ligand **L** makes the copper(II) ion easier to reduce and, therefore, stabilizes the +1 oxidation state of the metal. The electron-deficient 4-aminophthalimide of the ligand framework reduces the electron density over the metal ions, thus stabilizing the lower oxidation state. Therefore, in this synthesis procedure, **L** acts as the reducing agent for Cu^{2+}. Although methanol can also serve as the reducing agent, the very fact that the reaction also occurs in acetonitrile suggests that the ligand is indeed the reducing agent. This is also corroborated by the low yield of the reaction. The important role of the ClO_4^- anion has to be noted here, as when the corresponding NO_3^- salt was used, neither the Cu^{2+} nor the Cu^+ complex could be isolated. In recent years, hydrothermal/solvothermal reactions under pressure have been used as a synthetic strategy to reduce various metal ions, including copper.[15] The simultaneous reduction of Cu^{2+} to Cu^+ and the formation of a stable linear complex of copper(I) at ambient temperature is thus emphasized.

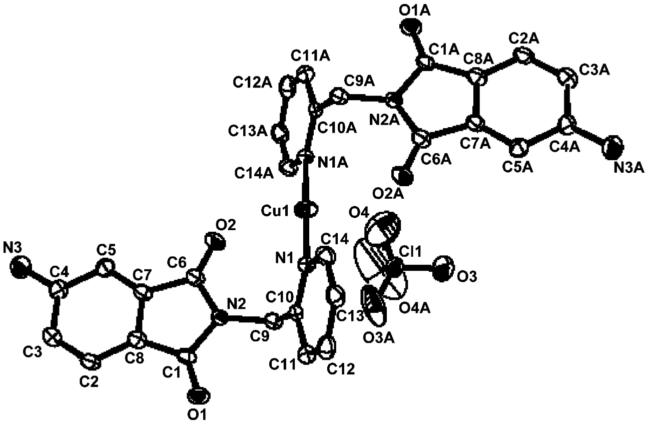

Figure 1. ORTEP diagram of $[CuL_2]ClO_4$ with atoms represented by thermal ellipsoid at the 30% probability level. Selected atom distances (Å) and bond angles (deg): Cu1−N1 = Cu1−N1A = 1.889(5), C1−O1 = 1.196(8), C6−O2 = 1.196(8), C4−N3 = 1.352(9), ∠N1−Cu1−N1A = 180.0(5). Hydrogen atoms are not shown for clarity.

The crystal structure of $[CuL_2]ClO_4$ showed a mononuclear complex in which copper is coordinated to the pyridyl nitrogen atom of each ligand unit.[16] The molecular structure is shown in Figure 1. The copper atom and the chlorine atom of the ClO_4^- anion are on a crystallographic inversion center. The geometry of the cationic portion is a linear $L-Cu^{I}-L$ moiety with Cu1−N1 = Cu1−N1A = 1.89 Å and ∠N1−Cu1−N1A = 180° (centrosymmetric, *C*2/*c*). The Cu−N bond length is quite similar to that previously reported for two-coordinate copper(I) complexes with nitrogen donor ligands.[3−5]

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(10) Yield 90%. CHN analysis calculated for $C_{14}H_{11}N_3O_2$: C, 66.4; H, 4.35; N, 16.6. Found: C, 65.8; H, 4.24; N, 16.4. ^1H NMR ($CDCl_3$): δ 4.45 (s, 2H), 4.96 (s, 2H), 6.79 (dd, 1H), 6.99 (d, 1H), 7.14 (m, 2H), 7.56−7.60 (m, 2H), 8.51 (d, 1H).

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(12) Caution! Care should be taken while treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

(13) ^1H NMR (CD_3CN): δ 4.43 (s, 2H), 5.12 (s, 2H), 6.84 (dd, 1H), 6.94 (d, 1H), 7.35−7.82 (m, 4H), 8.48 (b, 1H).

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(16) Crystallographic data: $C_{28}H_{22}ClCuN_6O_8$, $M = 669.52$; monoclinic, space group *C*2/*c*; cell dimensions $a = 21.536(8)$ Å, $b = 8.172(3)$ Å, $c = 15.408(3)$ Å, $\beta = 99.02(2)°$, $V = 2678.3(14)$ Å^3, $Z = 4$, $\rho_{calc} = 1.66$ g cm^{-3}, μ(Mo Kα radiation) = 0.981 mm^{-1}, $\lambda = 0.71073$ Å, $T = 293$ K. Reflections collected: 2418 (Enraf-Nonius Mach3 four circle CAD-4 diffractometer), 2361 unique, 207 parameters refined using 1407 reflections with $I > 2\sigma I$ to final *R* indices, R1 = 0.0744, wR2 = 0.1626, GOF = 1.033. Hydrogen atom attached to amine nitrogen atom was introduced as found on the Fourier difference maps and refined with restraint N−H = 0.87 Å and displacement parameter equal to 1.5 times that of the parent atom. All other hydrogen atoms were introduced geometrically and refined using a riding model. All non-hydrogen atoms were refined anisotropically.

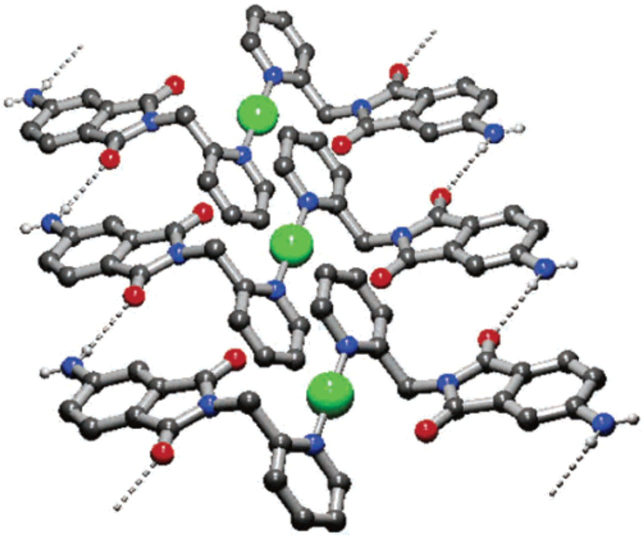

Figure 2. View of the 2-D network illustrating the intermolecular hydrogen bonding, shown as dashed lines: $d(\text{N3}-\text{H3B}\cdots\text{O1}[x, y-1, z]) = 3.133$ Å and $\angle\text{N3}-\text{H3B}\cdots\text{O1}[x, y-1, z] = 159.96°$. The anionic portion and the hydrogen atoms, except those that are involved in H-bonding, are omitted for clarity.

The plane of pyridyl ring is bent relative to phthalimido ring (dihedral angle between the pyridyl and phthalimido ring is 61.80(16)°), thus bringing O2 and O2A in close contact with copper ion (Cu1····O2 = Cu1····O2A = 3.03 Å and ∠O2····Cu1····O2A = 180°) reflecting a weak electronic interaction between Cu^I and one of the imide oxygen atoms of the ligand unit. The other imide oxygen atom is involved in intermolecular hydrogen bonding with the amino nitrogen atom of the neighboring molecule forming a 2-D network (Figure 2). Upon careful inspection, a weak $Cu^I\cdots O$ interaction between Cu^+ and oxygen atoms of the ClO_4^- anion was also observed (Cu1···O4 = Cu1···O4B = 3.116 Å and ∠O4···Cu1···O4B = 180°, by symmetry) that extends to form a zigzagged, weakly bound coordination polymer (Figure 3). Weak Cu···O interactions of about 3 Å are found in copper-containing enzymes.[17] Although such additional or multiple weak interactions[18] with an oxygen atom of the ClO_4^- anion are known for linear L−M−L complexes,[19] the resulting zigzag polymeric chain illustrates the novelty of the structure.

The stability of $[CuL_2]ClO_4$ toward oxidation is remarkable and quite interesting. Although the linear geometry is known to disfavor O_2 and CO interaction under certain conditions,[3−5] the two-coordinate copper(I) complexes with sterically unhindered monodentate ligands undergo rapid auto-oxidation in air, especially in protic solvents. However, our complex exhibits indefinite stability in the solid state.

Oxidation of Cu^+ to Cu^{2+} in polar or coordinating solvents such as acetonitrile or protic solvents such as methanol was not observed even if the samples were kept in an open air for months. Cyclic voltammetry of $[CuL_2]ClO_4$ shows an irreversible oxidation ($E_{pa} = 1.48$ V versus $FeCp_2^{+/0}$ in CH_3CN/0.1 M $[Bu_4N]ClO_4$) with very high current. However, **L** also shows a similar irreversible oxidation ($E_{pa} = 1.58$ V). The oxidation wave for the complex observable at ~1.15 V can be due to metal oxidation. Both **L** and the complex show a reduction response with very low cathodic current compared to the anodic current. The close contact with imide and perchlorate oxygen atoms, leading to the weak interactions, puts the Cu^+ ion in an octahedral hole. Therefore, this exceptional inertness is neither due to the steric hindrance nor due to the preorganization of the metal binding site, but it is solely attributable to the highly favorable electronic factors provided by the 4-aminophthalimide and the perchlorate moieties.

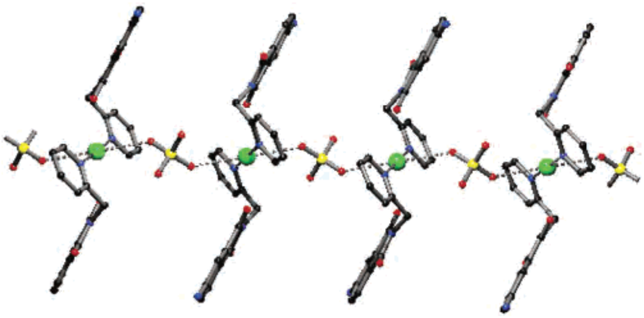

Figure 3. View along *y*-axis showing the close contact of copper with oxygen atoms of the ClO_4^- counteranion leading to a linear polymeric chain: Cu1···O4 = Cu1···O4B = 3.116(17) Å and ∠O4···Cu1···O4B = 180.0°, by symmetry.

In conclusion, we have shown that a stable two-coordinate linear complex of copper(I) with monodentate ligands can be synthesized easily if both the ligand system and the counteranion are chosen judiciously. This complex is a first example of its kind that is inert toward oxidation even in a protic aerated medium. The influence of the electronic environment surrounding the metal center for the control of Cu^I oxidation reactivity has been emphasized.

Work is in progress to improve the yield of the reaction and to develop more systems based on this strategy to generalize the concept.

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Supporting Information Available: Crystallographic data in CIF format, absorption and fluorescence spectra, cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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