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Preparation of a coordinatively saturated μ-η^2:η^2-peroxodicopper(II) compound

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ABSTRACT

The synthesis and solution characterization of the mononuclear copper(I) complex $[Cu^I(PyNMe_3)(CH_3CN)]^+$ (**1**) is described. This compound presents a C_s symmetric architecture as ascertained by NMR spectroscopy and corroborated by DFT calculations. The reactivity of **1** towards O_2 in a CH_3CN:THF 1:19 mixture at −100 °C was monitored by UV–vis spectroscopy, which evidenced the formation of a new species (**2**) with a highly intense absorption at 353 nm ($\varepsilon > 17200\ M^{-1}\ cm^{-1}$) that was not stable even at this low temperature ($t_{1/2}$ = 6 min at −100 °C). This spectroscopic signature is characteristic of μ-η^2:η^2-peroxodicopper(II) complexes, which typically exhibit one single intense absorption between 340 and 380 nm. Despite the fact that such species are involved in the catalytic cycle of tyrosinase, a copper-based enzyme that *ortho*-hydroxylates phenols, attempts to hydroxylate phenolates by **2** turned out to be unsuccessful. Most probably, the rigid macrocyclic tetradentate architecture of the $PyNMe_3$ ligand hinders simultaneous peroxide and phenolate coordination in the same copper center, a necessary step prior to the *ortho*-hydroxylation of this substrate.

1. Introduction

Copper-containing proteins are one of the most relevant subgroups of O_2-activating enzymes [1,2]. Their reaction mechanism usually entails the reductive activation of O_2 by a copper(I) center to form copper-dioxygen adducts (Cu_n:O_2) in which the oxidation state of the metal center is +2 or +3 and the O_2 moiety has been reduced to superoxide, peroxide or oxide moieties. These Cu_n:O_2 adducts are key intermediates in the catalytic cycle of the enzymes and they are directly involved in the oxidation/oxygenation of organic substrates [3,4]. However, their intrinsic reactivity turns them into elusive species which are difficult to trap and characterize. In this context, a particularly valuable strategy to get information about such compounds involves the synthesis, characterization, and detailed evaluation of the reactivity of discrete molecules that contain copper−oxygen moieties [5–7]. Such small molecular bioinspired models serve as platforms to unravel key aspects about the structure and electronic properties of these biologically relevant Cu_n:O_2 adducts.

These studies have enabled the characterization of a myriad of copper-dioxygen adducts, ranging from mononuclear centers to multinuclear or heterometallic configurations. In most cases, neutral N-based ligands combining tertiary amines, imines or heterocyclic amines (pyridines, pyrazoles, imidazoles) constitute the coordination environment around the copper center. In the present work, we use a tetradentate nitrogen-based marocyclic ligand ($PyNMe_3$), which coordinates the metal center through three aliphatic nitrogens and one pyridine (Fig. 1). We will study the ability of $PyNMe_3$ to coordinate to copper(I) and the binding and activation of O_2 by the resulting copper(I) complex. Noteworthy, $PyNMe_3$ has been previously used in our laboratory for the synthesis of high-valent iron-oxygen species [8,9], and later Cho et al. reported its use for the synthesis of mononuclear (hydro)peroxidocobalt(III) species [10].

2. Experimental section

2.1. Materials and methods

Anhydrous solvents were purchased from Scharlau or Sigma-Aldrich and used as received. Reagents were of commercially available reagent quality. Ligand $PyNMe_3$ was synthesized following previously reported procedures [8,9].

NMR spectra were recorded on Bruker Ultrashield Avance III400 and Ultrashield DPX300 spectrometers. Mass spectra were

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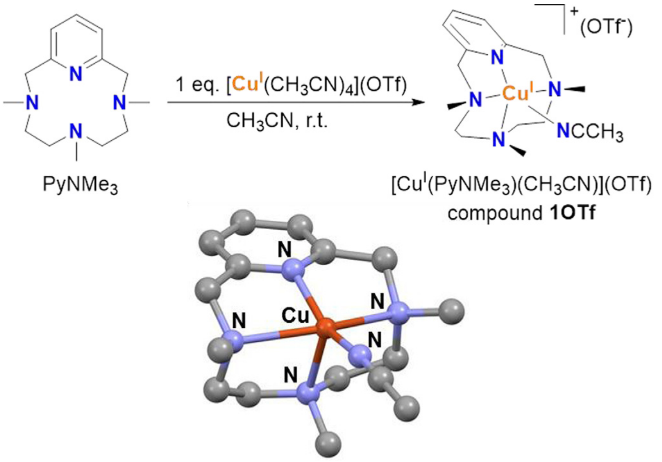

Fig. 1. Synthesis of $[Cu^I(PyNMe_3)(CH_3CN)](OTf)$ (**1OTf**) by reaction of $PyNMe_3$ with 1 equiv $[Cu^I(CH_3CN)_4](OTf)$ along with the DFT computed structure for **1**.

performed by electrospray ionization in a high-resolution mass spectrometer Bruker micrOTOF QII (Q-TOF) with a quadrupole analyzer with positive and negative ionization modes. UV–vis spectroscopy was performed on an Agilent 8453 UV–vis spectrophotometer with 1 cm quartz cells and low temperature control was achieved with a cryostat from Unisoku Scientific Instruments (Japan).

*2.2. Synthesis of $[Cu^I(PyNMe_3)(CH_3CN)](OTf)$ (**1OTf**)*

In the glovebox, $PyNMe_3$ (4.6 mg, 0.02 mmols) was dissolved in anhydrous CH_3CN (1 mL) and $[Cu^I(CH_3CN)_4](OTf)$ (OTf = trifluoromethanesulfonate) (7.0 mg, 0.02 mmols) was added directly as a solid. The resulting yellow mixture was stirred for 5 min. Spectroscopic and mass spectrometry analyses of the resulting solution indicated the formation of the title compound. CD_3CN was used as solvent for the NMR characterization of **1OTf**. ^{1}H-NMR (CD_3CN, 400 MHz, 298 K) δ, ppm: 7.76 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 3.95 (d, J = 15.2 Hz, 2H), 3.59 (d, J = 15.2 Hz, 2H), 2.68 (s, 6H), 2.58 (m, 2H), 2.47 (s, 3H), 2.32 (m, 2H), 2.23 (m, 2H), 1.83 (m, 2H); ^{13}C-NMR (CD_3CN, 400 MHz, 298 K) δ, ppm: 156.72, 137.81, 122.37, 63.34, 56.10, 53.93, 45.94, 44.28. HR-MS (m/z): Calc. for $[Cu^I(PyNMe_3)]^+$ 311.1291, found 311.1319; calc. for $[Cu^I(PyNMe_3)(CH_3CN)]^+$ 352.1557, found 352.1535.

*2.3. Reaction of $[Cu^I(PyNMe_3)(CH_3CN)](OTf)$ (**1OTf**) with O_2*

Samples of **1OTf** to monitor its reaction with O_2 by UV–vis spectroscopy were prepared under an inert atmosphere in the glovebox. A freshly prepared 20 mM solution of **1OTf** in CH_3CN (see above) was diluted 10 times to afford a 2 mM stock solution of the copper(I) complex in CH_3CN. A UV–Vis cuvette with a cell path length of 1 cm was charged with 100 μL of the 2 mM stock solution of **1OTf** and 1.9 mL of dry THF were added. Thus, the final concentration of **1OTf** in the sample was 0.1 mM in a CH_3CN:THF 1:19 mixture. The UV–vis cuvette was capped with a septum, taken out of the glovebox and placed in a Unisoku thermostated cell holder designed for low-temperature experiments at 173 K. After reaching thermal equilibrium a UV–vis spectrum of the starting complex was recorded. Dioxygen was injected into the cell with a balloon and a needle through the septum causing immediate reaction.

2.4. DFT calculations

All calculations were performed with the *Gaussian 09* package [11]. The B3LYP level of theory [12–15] and the 6-311G(d) basis set [16–20] were used to optimize the geometries and calculate the frequencies of each structure. Empirical dispersion was included with the Grimme's GD3BJ model [21] and solvation effects in acetonitrile were taken into account with the PCM-SMD model [22]. Also, under the same conditions, Single Point Energy (SPE) computations were performed with the cc-pVTZ basis set [23,24], a more flexible basis set, to obtain more accurate energy values. Additionally, a correcting factor in the Gibbs energy was included to compensate the change from gas-phase standard concentration of 1 atm to 1 M gas-phase standard concentration (+1.89 kcal mol^{-1} for the species and +3.64 kcal mol^{-1} for the acetonitrile, which is defined as the solvent).

3. Results and discussion

*3.1. Synthesis and characterization of $[Cu^I(PyNMe_3)(CH_3CN)](OTf)$ (**1OTf**)*

1OTf was synthesized by mixing equimolar amounts of $[Cu^I(CH_3CN)_4](OTf)$ and $PyNMe_3$ in the glovebox at room temperature. THF, CH_2Cl_2, acetone and CH_3CN were tested as solvents. Unfortunately, the synthesis of **1OTf** in THF, CH_2Cl_2 or acetone caused the immediate disproportionation of copper(I) as evidenced by the formation of copper mirror and a deep-blue colored solution attributable to copper(II) species. Such disproportionation reactions are not uncommon in the chemistry of copper(I) and they depend on the stability of Cu^I relative to Cu^{II}, which is affected by both the solvent and the ligand geometry [25–29]. In contrast, CH_3CN prevented the decomposition of copper(I), and an intense yellow solution was obtained. ESI-MS analysis of this solution by high-resolution mass spectrometry afforded a clean spectrum dominated by a peak at m/z 311.1319 with a mass value and isotopic pattern fully consistent with the desired copper(I) ion $[Cu^I(PyNMe_3)]^+$ (Fig. S1). Attempts to crystallize or isolate this complex were unsuccessful because disproportionation of the metal complex occurred during the crystallization or isolation process even in CH_3CN.

Although an X-ray structure of this compound could not be obtained, most likely $PyNMe_3$ behaves as a tetradentate ligand as previously observed for the corresponding iron(II) and cobalt(II) compounds [9,10]. DFT calculations were performed in order to get a picture of the possible structure of the copper(I) complex (see SI). From all the calculated structures, the most stable geometry corresponded to a C_s symmetric distorted square pyramidal compound with the copper(I) center coordinated to the four nitrogens of the $PyNMe_3$ ligand and to one CH_3CN ligand (*trans* to the pyridine ring), yielding $[Cu^I(PyNMe_3)(CH_3CN)](OTf)$ as the general formula for the copper(I) complex of the $PyNMe_3$ ligand (**1OTf**, Fig. 1). Optimization of the structures where the CH_3CN ligand is bound *trans* to the N-methyl group always led to the formation of the isomer with the CH_3CN *trans* to the pyridine. The optimized geometry with no coordinated CH_3CN was less stable by 9.3 kcal mol^{-1} (Gibbs free energy difference, ΔG°) and no structure could be optimized with the copper(I) center ligated to two acetonitrile molecules. The optimized geometry for $[Cu^I(PyNMe_3)(CH_3CN)]^+$ (**1**) is in agreement with the structures reported for copper(I) complexes with other tetradentate ligands, in which a CH_3CN molecule fullfills a square-pyramidal pentadentate coordination environment [30,31]. Indeed, the high-resolution ESI-MS spectrum of **1OTf** (Fig. S1) also showed the presence of a small peak corresponding to the coordination of one CH_3CN mole-

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