Research paper

Experimental and spin-orbit coupled TDDFT predictions of photophysical properties of three-coordinate mononuclear and four-coordinate binuclear copper(I) complexes with thioamidines and bulky triarylphosphanes

Fani Karasmani [a], Athanasios Tsipis [b,*], Panagiotis Angaridis [a], Antonios G. Hatzidimitriou [a], Paraskevas Aslanidis [a]

[a] *Laboratory of Inorganic Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*
[b] *Section of Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece*

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ABSTRACT

The reactions of copper halides CuX with the N-heterocyclic thioamidine 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH) in the presence of the sterically demanding tri(o-tolyl)phosphane (totp), depending on the halide, affords either the mononuclear compound [CuX(totp)(mtdztH)] (**1**), when X = I, with the thione acting as a terminal S-bound ligand or the symmetrical, thione-S-bridged binuclear compound [CuX(totp)(μ-S-mtdzt)]$_2$ (**2**), when X = Cl. The steric effects of the large cone-angle phosphane ligand are further demonstrated by the distorted coordination environments of the copper centers in the solid-state structures of the two complexes. The two compounds are photoluminescent in the solid state at ambient temperature, with their emission maxima located in the blue region of the electromagnetic spectrum and influenced by the type of halide present in each case. Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations were employed in order to elucidate the mechanism of the photoluminescence of the two Cu(I) complexes. The emissive T$_1$ state exhibits a ^{3}MLCT character and minor structural distortions compared to the S$_0$ state. Employing self-consistent spin-orbit coupling TDDFT (SOC-TDDFT) calculations the radiative lifetimes and the zero-field splitting (ZFS) were estimated to be in the ranges 21–375 μs and 1–4 cm^{-1} respectively. The highest values for the Spin - Orbit matrix elements, calculated with the SOC-TDDFT method, are the $< S_2|H_{SO}|T_1>$ and $<S_4|H_{SO}|T_1>$ for **1** and the mononuclear counterpart of **2** (**2′**) indicating a thermal singlet–singlet deactivation path followed by ISC from S$_1$ to T$_1$. In contrast, the highest value SOC matrix element for 2 is the $< S_1|H_{SO}|T_1>$ and therefore this complex should exhibit a direct ISC from S$_1$ to T$_1$ without a preceding thermal deactivation. The very small values of the energy difference between S$_1$ and T$_1$ states ($\Delta E(S_1\text{-}T_1)$) calculated to be in the range 1–9 kcal/mol for these complexes, should also favor the ISC process between these excited states.

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1. Introduction

Photoluminescence coordination compounds have received much attention during the past decades because of their numerous commercialized technological applications as sensitizers in solar-energy conversion systems [1,2], as components for luminescent-based chemical sensors [3,4], as emitting materials in OLEDs [5–7], and display devices [8,9], or as photoactive components in photocatalytic systems [10–12]. While complexes based on third-row transition metal ions are predominantly used so far,

luminescent copper(I) complexes have also gained high attractiveness as alternative resource- and cost-efficient emitting materials in recent years. Many of these complexes are based on N-donor polypyridine and/or phosphane ligands, and are found to possess particularly useful luminescence characteristics such as high emission efficiency and color tunability by variations of the ligand's electronic and steric properties [13–17], while for some of them the usefulness with regard to the above mentioned applications has already been established [18].

Experimental and theoretical data reveal a dominant MLCT character in the emissive excited state of Cu(I) complexes, which is often reflected in a flattening distortion of the molecular geometry, leading to emission quenching via non-radiative relaxation

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* Corresponding author.
  E-mail address: attsipis@uoi.gr (A. Tsipis).

mechanisms. In this case, introduction of sterically demanding ligands proved to be an efficient way to prevent such a re-organization during the excitation process [19].

Heteroleptic copper(I) complexes incorporating S-donor, N-heterocyclic thione/thiolate ligands, in combination with other types of ligands, such as P-donor arylphosphanes, or halides, have been reported to exhibit a reach variety of molecular architectures [20–23]. and interesting photophysical properties [24–28]. In an effort to get a deeper insight into the factors that determine the overall geometrical characteristics of these compounds, we were involved in the synthesis of mixed-ligand copper(I) halide complexes containing ligands with large steric requirements. Taking into account that steric effects are at least as important as electronic effects in determining the coordinative behavior of a ligand, we primarily focused on the steric bulk of the thione ligands, whereby we recognized that this parameter only marginally affects the metal-site geometry, causing moderate angular distortions away from the ideal tetrahedral geometry [29–32]. Consequently, attention has been then drawn to the possibility of tuning the geometry through the steric demands of the phosphane ligand, having in mind that the steric requirements of a symmetrical phosphane can be accurately calculated and well expressed by it's Tolman cone angle [33,34]. Indeed, a few examples of three-coordination have been realized on substituting the medium sized triphenylphosphane or tri(m-tolyl)phosphane with the bulkier tri (o-tolyl)phosphane, a fact that may reasonably be attributed to steric effects on the part of the phosphane ligand, in particular because of the peculiar positioning of the methyl groups surrounding copper [35,36].

In this paper we report on two new copper(I) halide compounds containing tri(o-tolyl)phosphane (totp) and the rather small-sized 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH shown in Scheme 1.

Although the two complexes were prepared according to the same experimental procedures, and despite their common stoichiometry, their solid state structures exhibit different nuclearities and coordination numbers. In particular, a mononuclear trigonal planar complex is obtained in the case of CuI, while CuCl leads to the formation of a thione-S-bridged binuclear compound with each metal featuring a distorted tetrahedral environment consisting of a PS$_2$Cl donor set. Regarding the coordination chemistry of mtdztH, work reported so far involves N-coordinated mononuclear complexes of Ni(II) [37], Zn(II) [38], Pd(II) [39], as well as mononuclear S-coordinated complexes of Ni Cu(II), Cd(II) and Hg(I) [40], while the first two examples of dinuclear Cu(I) complexes bearing this heterocyclic thioamide in a S-bridging coordination mode were reported recently [41].

2. Experimental

2.1. General procedures and chemicals

All manipulations were carried out under atmospheric conditions, unless otherwise mentioned. Solvents were purified according to established methods and allowed to stand over molecular sieves for 24 h. Copper(I) chloride, copper(I) iodide, tri(o-tolyl) phosphane (totp) and 5-methyl-1,3,4-thiadiazole-2(3H)-thione (mtdztH) were obtained from commercial sources and used without any further purification.

2.2. Instrumentation

Elemental analyses were obtained on a PerkinElmer 240B elemental microanalyzer. Infrared spectra were recorded on a Nicolet FT-IR 6700 spectrophotometer as KBr discs in the region of 4000–400 cm^{-1}. UV–Vis electronic absorption spectra were obtained on a Shimadzu 160A spectrophotometer as solutions 1.0×10^{-4} M in CH$_2$Cl$_2$. Solid-state emission/excitation spectra were obtained on a Hitachi F-7000 fluorescence spectrometer.

2.3. X-ray crystal structure determinations

Single-crystals of compounds **1** and **2**, suitable for X-ray crystallographic analysis, were mounted on thin glass fibers with the aid of an epoxy resin. X-ray diffraction data were collected on a Bruker Apex II CCD area-detector diffractometer, equipped with a Mo Ka (λ = 0.71,070 Å) sealed tube source, at 295 K, using the φ and ω scans technique. The program Apex2 (Bruker AXS, 2006) was used in data collection, cell refinement, and data reduction [42]. Structures were solved and refined with full-matrix least-squares using the program Crystals [43]. Anisotropic displacement parameters were applied to all non-hydrogen atoms, while hydrogen atoms were generated geometrically and refined using a riding model. Molecular plots were obtained by using the program Mercury [44].

2.4. Computational details

Full geometry optimization without symmetry constrains were carried out in the gas phase, for both the singlet ground state (S$_0$) and the lowest triplet excited state (T$_1$) of compounds **1** and **2**, using the full-range PBE0 non-local hybrid GGA functional [45–48] combined with the Def2-TZVP basis set of Ahlrichs et al. [49]. for Cu metal atoms and the 6-31G(d,p) for all other non metal atoms (the computational protocol is denoted as PEB0/Def2-TZVP (Cu,I) ∪ 6-31G(d,p)(E) level of theory). The attainment of the energy minimum was verified by calculating the vibrational frequencies that result in the absence of imaginary eigenvalues (NImag = 0). The computed electronic energies were corrected to constant pressure and 298 K, for zero point energy (ZPE) differences and for the contributions of the translational, rotational and vibrational partition functions. Time dependent density functional theory (TDDFT) [50–52] calculations were performed employing the same computational protocol used for the optimization calculations. The TDDFT calculations were performed taking into account the CH$_2$Cl$_2$ solvent effects by employing the Polarizable Continuum Model (PCM) model [53] for the singlet ground state (S$_0$), using the structural parameters obtained from the geometry optimization calculations, including the lowest 30 singlet–sin-
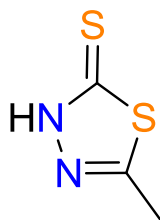
Scheme 1. Molecular structure of 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH).