Polyhedron 30 (2011) 614–623

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, structure, photochromism and DFT calculations of copper(I)-triphenylphosphine halide complexes of thioalkylazoimidazoles

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ARTICLE INFO

Article history:
Received 30 September 2010
Accepted 25 November 2010
Available online 7 December 2010

Keywords:
Copper(I)-thioalkylazoimidazole-halide
X-ray structure
Photochromism
Electrochemistry
DFT computation

ABSTRACT

[Cu(SRaaiNR′)(PPh$_3$)X] complexes are synthesized by the reaction of CuX (X = Cl, Br, I), triphenylphosphine and 1-alkyl-2-[(*o*-thioalkyl)phenylazo]imidazole (SRaaiNR′). The single crystal X-ray structure of [Cu(SEtaaiNH)(PPh$_3$)I] (SEtaaiNH = 2-[(*o*-thioethyl)phenylazo]imidazole) shows a distorted tetrahedral geometry of the copper center with bidentate, N(azo), N(imidazole) chelation of SEtaaiNH and coordination from PPh$_3$ and iodine. These complexes show a *trans*-to-*cis* isomerization upon irradiation with UV light. The reverse transformation, *cis*-to-*trans* isomerization, is very slow with visible light irradiation and is thermally accessible. The quantum yields ($\phi_{t\to c}$) of the *trans*-to-*cis* isomerization of [Cu(SRaaiNR′)(PPh$_3$)X] are lower than the free ligand values. This is due to the increased mass and rotor volume of the complexes compared to the free ligand data. The rate of isomerization follows the order: [Cu(SRaaiNR′)(PPh$_3$)Cl] < [Cu(SRaaiNR′)(PPh$_3$)Br] < [Cu(SRaaiNR′)(PPh$_3$)I]. The activation energy (E_a) of the *cis*-to-*trans* isomerization is calculated by a controlled temperature reaction. DFT computation of representative complexes has been used to determine the composition and energy of the molecular levels.

1. Introduction

Azobenzene displays reversible photoisomerization and the derivatives are very useful as an optical response function (trigger and switching) molecule, because the molecular shape and polarity greatly change on optical illumination [1–7]. This has inspired changing either or both aryl rings of azobenzene with heterocycles and to explore their photophysical properties as well as the influence of metal coordination or protonation. (Arylazo)heterocycles which bear pyridine, pyrimidine, imidazole or pyrazole rings have been extensively utilized in the field of coordination chemistry owing to their chelation by N(heterocycle) and N(azo) to a metal ion [8–12]. Many of them also exhibit *trans-to-cis* (Z–E) photoisomerization, and the coordination ability of the heterocyclic moiety can be changed by the photoisomerization. This activity has immense application in the design of light driven on-off switching [13,14]. Arylazoimidazoles constitute an interesting class of heterocyclic azo compounds as a potential switching group in biological applications and in coordination chemistry, since imidazole is a ubiquitous and essential group in biology, especially as a metal coordination site. This family of compounds has been extensively used as ligands to synthesize transition and non-transition metal complexes [15–22]. The photochromism of 1-alkyl-2-(arylazo)imidazole (RaaiR′) [10,11] and some complexes like Hg(II)- [23] Cd(II)- [24] and Pd(II)-azoimidazoles [25] have been reported by our group. To extend the chemistry of azoimidazoles we have synthesized 1-alkyl-2-[(*o*-thioalkyl)phenylazo]imidazoles (SRaaiNR′) (**2** and **3**) [26]. The reaction of CuX with SRaaiNR′ in the presence of PPh$_3$ has isolated [Cu(SRaaiNR′)(PPh$_3$)X] (**4–9**). The structure is confirmed by a single crystal X-ray diffraction study in one case and also by other spectroscopic studies. The photochromic property of the complexes is also examined. Quantum chemical calculations using density functional theory (DFT) have been carried out to explain the structural, electronic, spectroscopic and thermodynamic properties of the different compounds. Time-dependent density functional theory (TD-DFT) is opening new perspectives in this field [27,28], so DFT computations have been used to correlate the UV–Vis spectral and redox properties of the complexes.

2. Results and discussion

2.1. Synthesis and formulation

The 1-alkyl-2-[(*o*-thioalkyl)phenylazo]imidazoles (SRaaiNR′) (**2** and **3**) are synthesized by the reported procedure [26] (Scheme

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doi:10.1016/j.poly.2010.11.036

1). The reaction of CuX and the appropriate ligand, SRaaiNR′ in a 1:1 mole ratio in methanol, followed by the addition of one equivalent of PPh_3 has isolated [Cu(SRaaiNR′)(PPh_3)X] (**4**–**9**). The reaction was also carried out with $[Cu(PPh_3)X]_4$ and SRaaiNR′, and the same complex was isolated. However, the process is not fast and we followed the reaction *in situ*. The complexes are purified by crystallization, on slow evaporation of a solution in acetonitrile–methanol (1:1, v/v). Microanalytical data have confirmed the composition of the complexes. The complexes are sufficiently soluble in common organic solvents, *viz*. methanol, ethanol, chloroform, dichloromethane and acetonitrile, but are insoluble in hydrocarbons (hexane, benzene, and toluene). They are non-conducting in methanol/acetonitrile solution.

2.2. Spectral studies

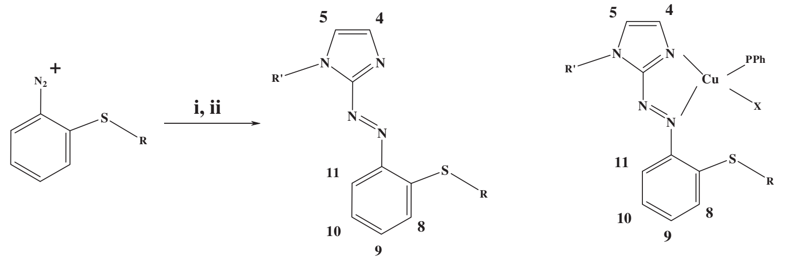
Infrared spectra of the complexes exhibit $\upsilon(\mathrm{N{=}N})$ and $\upsilon(\mathrm{C{=}N})$ at 1412–1431 and 1580–1597 cm^{-1}, respectively. These two specific frequencies, $\upsilon(\mathrm{N{=}N})$ and $\upsilon(\mathrm{C{=}N})$, are red shifted by 10–12 cm^{-1} in the complexes compared to the free ligand values. This supports coordination of azo-N and imine-N to Cu(I).

The UV–Vis spectra of the complexes exhibit three or four high intense transitions ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}) at 450–465, 400–420, 355–365 and 245–260 nm, along with a weak transition at 600–620 nm ($\varepsilon \sim 10^3$ M^{-1} cm^{-1}) (Fig. 1). The free ligand SRaaiNR′ shows intraligand charge transferences, $n-\pi^*$ and $\pi-\pi^*$, at 370–380 and 250–260 nm respectively [26]. Thus the transitions > 400 nm are assigned to $Cu(I) \rightarrow \pi^*(azo)$. The transitions are characterized based on an electronic structure calculation using an optimized geometry by the DFT computation technique (*vide infra*).

The ^1H NMR spectral data (Supplementary Material, Table S1) have been used to determine the stereochemistry of the complexes. The aryl and imidazole protons are downfield shifted on coordination of the ligand to the Cu(I) center compared to the free ligand data [26]. This implies a significant bonding interaction of the metal ion with the ligand, which effectively influences the ligand's electron density. The S–R and N(1)–R′ groups show the usual spin–spin interaction pattern in the upper field portion of the aliphatic region in the NMR spectra.

2.3. Crystal structure of [Cu(SEtaaiNH)(PPh_3)I] (*9a*)

The molecular structure of [Cu(SEtaaiNH)(PPh_3)I] (**9a**) is shown in Fig. 2. The bond parameters are listed in Table 1. The chelating ligand, SEtaaiNH, acts as a N,N′-donor (N refers to N(imidazole) and N′ refers to N(azo)), and the two other donor centers are PPh_3 and I. The –S–Et group remains uncoordinated and away from the metal center. The atomic arrangements Cu, N(4), N(3), C(3), N(1), constitute a chelate plane with a deviation < 0.02 Å. Cu(I) is at the center of a distorted tetrahedron. The pendant aryl ring makes a dihedral angle of 2.3(5)° with the chelated azoimidazole ring. The acute bite angle, Cu(N, N′), of 77.42(18)° is extended by SEtaaiNH on coordination to Cu(I) and is comparable with reported results in the series of chelated arylazoimidazole complexes of d^{10} metal complexes [29,9,30] The small chelate angle may be one of the reasons for geometrical distortion. The Cu–N(azo) bond length (2.163(5) Å), is longer than the Cu(I)–N(imidazole) bond length (2.088(5) Å), which reflects the stronger interaction of Cu(I) with N(imidazole) compared to N (azo). The N=N distance is



1 2 3

SRaaiNR′ (**2**, **3**) [Cu((SRaaiNR′)(PPh_3)X] (**4 - 9**)

i) imidazole in pH, 7; ii) NaH in THF and R′I

R = Me, R′ = H (**2a**), R = Me, R′ = Me (**2b**); Abbreviations of **a**, **b**, **c** remain the same.

R = Me, R′ = Et (**2c**), R = Et, R′ = H (**3a**); X = Cl (**4**, **5**,); Br (**6**, **7**,); I (**8**, **9**)

R = Et, R′ = Me (**3b**), R = Et, R′ = Et (**3c**)

[Cu(SMeaaiNH)(PPh_3)Cl] (**4a**), [Cu(SMeaaiNMe)(PPh_3)Cl] (**4b**), [Cu(SMeaaiNEt)(PPh_3)Cl] (**4c**),

[Cu(SEtaaiNH)(PPh_3)Cl] (**5a**), [Cu(SEtaaiNMe)(PPh_3)Cl] (**5b**), [Cu(SEtaaiNEt)(PPh_3)Cl] (**5c**)

[Cu(SMeaaiNH)(PPh_3)Br] (**6a**), [Cu(SMeaaiNMe)(PPh_3)Br] (**6b**), [Cu(SMeaaiNEt)(PPh_3)Br] (**6c**),

[Cu(SEtaaiNH)(PPh_3)Br] (**7a**), [Cu(SEtaaiNMe)(PPh_3)Br] (**7b**), [Cu(SEtaaiNEt)(PPh_3)Br] (**7c**)

[Cu(SMeaaiNH)(PPh_3)I] (**8a**), [Cu(SMeaaiNMe)(PPh_3)I] (**8b**), [Cu(SMeaaiNEt)(PPh_3)I] (**8c**),

[Cu(SEtaaiNH)(PPh_3)I] (**9a**), [Cu(SEtaaiNMe)(PPh_3)I] (**9b**), [Cu(SEtaaiNEt)(PPh_3)I] (**9c**)

Scheme 1.