C. R. Chimie 15 (2012) 255–266

Contents lists available at SciVerse ScienceDirect

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Structures and spectral properties of heteroleptic copper (I) complexes: A theoretical study based on density functional theory

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ARTICLE INFO

Article history:
Received 28 August 2011
Accepted after revision 20 October 2011
Available online 8 December 2011

Keywords:
Copper complexes
Structure
Absorption spectroscopy
Heteroleptic ligands
Density functional theory calculations
Excited states

ABSTRACT

The structures and electronic absorption spectra of newly synthesized heteroleptic copper (I) complexes $[CuL_1L_2]^+$ (L_1 = phen-imidazole and/or L_2 = dipyrido [3,2-a:2',3'-c] phenazine derivatives) are analyzed under the light of density functional theory (DFT) and time-dependent DFT (TD-DFT). The ground states geometries, characterized by π-stacking interactions, have been optimized using PBE-D functional taking into account dispersion correction. The UV-visible theoretical absorption spectra have been calculated using B3LYP functional in vacuum and taking into account solvent corrections by means of the polarized continuum model (PCM). Whereas the PBE-D functional is well adapted to the determination of the structures, it does underestimate drastically the transition energies. The spectra are characterized by high density of states, mainly metal-to-ligand-charge-transfer (MLCT) and intra-ligand (IL), between 600 nm and 250 nm. Most of the complexes show an intense band in the near-UV energy domain (~320 nm) corresponding to an IL transition. The lowest part of the absorption spectra, starting at 600 nm, corresponds to MLCT transitions leading to a shoulder observed experimentally between 400 and 500 nm. The upper part of the spectra, beyond 300 nm, puts in evidence strong mixing between ligand-to-ligand-charge-transfer (LLCT), IL and MLCT states.

Mots clés :
Complexes de cuivre
Structure
Spectroscopie d'absorption
Ligand hétéroleptriques
Calculs théorie de la fonctionnelle de la densité
États excités

RÉSUMÉ

Les structures et spectres d'absorption théoriques d'une série de complexes de Cu (I), nouvellement synthétisés, sont analysés sur la base de calculs *density functional theory* (DFT) et *time-dependent* DFT (TD-DFT). Si l'optimisation des géométries est fondée sur l'utilisation de la fonctionnelle PBE-D corrigée des effets de dispersion importants dans ces complexes à interactions de type *π-stacking*, la fonctionnelle hybride B3LYP est plus adaptée au calcul des états électroniques excités. Les effets de solvants sont pris en compte via le *polarized continuum model* (PCM). Les spectres théoriques sont caractérisés par une densité d'états, élevée entre 600 et 250 nm et présentent tous une bande large et intense, centrée autour de 300 nm et attribuée à une transition intra-ligand (IL). La présence d'états *metal-to-ligand-charge transfer* (MLCT) entre 500 et 400 nm explique l'apparition d'un épaulement dans le domaine visible. Au-delà de 300 nm, les états excités *ligand-to-ligand-charge-transfer* (LLCT), IL et MLCT interagissent fortement.

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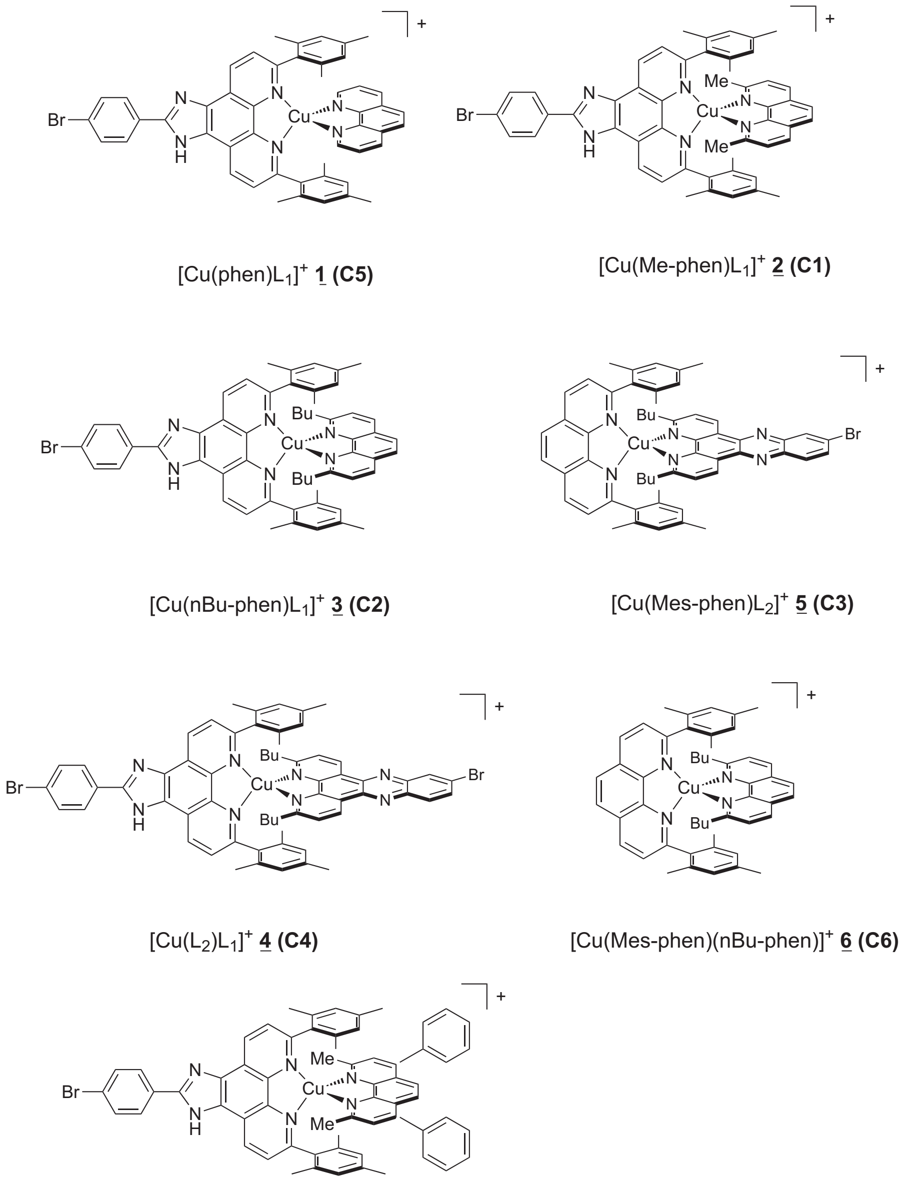
doi:10.1016/j.crci.2011.10.010

1. Introduction

Copper (II) square planar complexes are intensively investigated for their role in various domains of chemistry as versatile catalysts, in metal-organic semi-conductors, in magnetic materials or in biosystems. In contrast and because of their structural behavior at room temperature in solution, the Cu (I) tetrahedral complexes were of little use until the discovery of Sauvage and McMillin [1] who were able to stabilize the tetrahedral geometry of a copper (I)-diimine complexe using bulky ligands and to prevent a deformation to the formal copper (II) square planar arrangement, responsible for the quenching of luminescence. However, none of the many synthesized homoleptic Cu (I) complexes having a great potential as luminescent probe and electron/energy transfer carrier is able to compete with $[Ru(bpy)_3]^{2+}$ for solar conversion applications. A new generation of molecules with luminescent properties, low-lying long-lived metal-to-ligand-charge-transfer (MLCT) excited states, absorbing in the visible energy domain and rigid enough to prevent distortion of geometry and sub-sequent quenching of the excited state were synthesized [2].

As compared to the huge amount of theoretical studies devoted to Ru(II) complexes, the investigation of the structural and spectral properties of Cu(I)-diimine com-



$[Cu(phen)L_1]^+$ **1** **(C5)**

$[Cu(Me\text{-}phen)L_1]^+$ **2** **(C1)**

$[Cu(nBu\text{-}phen)L_1]^+$ **3** **(C2)**

$[Cu(Mes\text{-}phen)L_2]^+$ **5** **(C3)**

$[Cu(L_2)L_1]^+$ **4** **(C4)**

$[Cu(Mes\text{-}phen)(nBu\text{-}phen)]^+$ **6** **(C6)**

$[Cu(MePh\text{-}phen)L_1]^+$ **7**

Fig. 1. Molecular structures of the heteroleptic Cu (I) complexes **1** to **7**. The numbering corresponding to [4] and Fig. 3 is specified in parenthesis.