

Cu^I complexes with thiosemicarbazides derived from *p*-toluenesulfohydrazide: structural and luminescence studies.

Alice P. Borges¹ (PG), Sinval F. Sousa² (PG), Antônio O. T. Patrocínio (PQ)², Carolina G. Oliveira³ (PG), Victor M. Deflon³ (PQ), Pedro I. S. Maia^{1*} (PQ) *e-mail: pedro.maia@pq.cnpq.br

¹Departamento de Química, Universidade Federal do Triângulo Mineiro, 38025-440 Uberaba-MG, Brasil

²Instituto de Química, Universidade Federal de Uberlândia, Uberlândia-MG, Brasil

³Instituto de Química de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, SP, Brasil

Keywords: Thiosemicarbazides, copper(I), crystal structures, luminescence.

Abstract

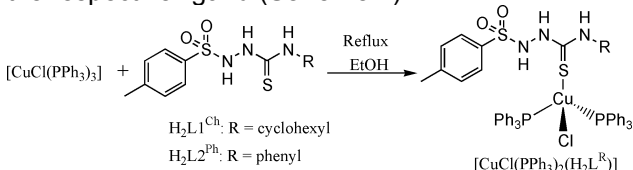
The structural and photophysical properties of Cu^I mixed-ligand complexes with thiosemicarbazides have been studied.

Introduction

Cu^I complexes with thione-containing ligands in combination with aryl-phosphines or phenanthroline have revealed interesting photophysical properties.¹ In the same context, the emission energy of such systems can be tuned through a thione-alteration related to the strength of the Cu–S bond since their emitting state is assigned as MLCT.¹ Furthermore, copper complexes containing thione-ligands and/or phosphines have also presented antimicrobial activity. In the present work, we have explored the chemistry, structural and photophysical properties of two Cu^I heteroleptic compounds containing thiosemicarbazides derived from a sulfohydrazide (**Scheme 1**) in combination with PPh₃ as co-ligands.

Results and Discussion

The ligands H₂L^{Ch} and H₂L^{Ph} (**Scheme 1**) were prepared by mixing *p*-toluenesulfohydrazide with the desired aryl-isothiocyanate. The new complexes [CuCl(PPh₃)₂(H₂L^{Ch})] and [CuCl(PPh₃)₂(H₂L^{Ph})] were synthesized by reaction of [CuCl(PPh₃)₃] with the respective ligand (**Scheme 1**).



Scheme 1. Synthesis of the complexes.

The new compounds have been characterized on the basis of FTIR, ¹H and ³¹P NMR, elemental analysis, UV-vis and fluorescence spectroscopies. The FTIR and ¹H NMR spectra of the complexes indicated no deprotonation for the H₂L^R ligands upon coordination. The presence of the phosphine ligands was confirmed in the ³¹P NMR by signals at -4.72 and -4.43 ppm for **1** and **2**, respectively. All the compounds were further studied by X-ray diffraction on single crystal, exemplarily shown in **Fig. 1** by the crystal structures of H₂L^{Ch} and of the complex **1**. As

expected from the spectroscopic data, H₂L^R binds the Cu^I center as a neutral monodentate ligand through sulfur atom with the Cu–S2 bond around 2.38 Å. A Cl⁻ and two PPh₃ ligands complete the coordination sphere, forming tetrahedral complexes.

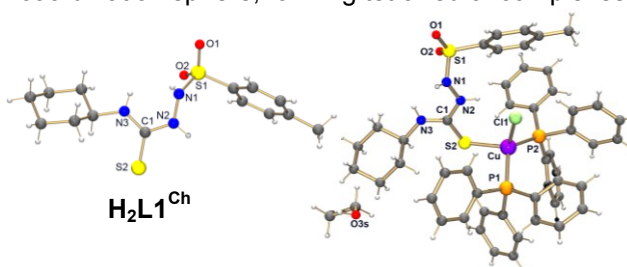


Fig. 1. Crystal structures of H₂L^{Ch} (left) and [CuCl(PPh₃)₂(H₂L^{Ch})]·EtOH (**1**·EtOH, right).

The electronic absorption spectra of the colorless compounds show a strong band in the UV region, where the λ_{max} for the complexes are found in a lower energy region than those of the respective ligands (**Fig. 2**). The fluorescence spectra of H₂L^R in MeOH show only weak emissions, while both **1** and **2** exhibit intense fluorescence bands (**Fig. 2**).

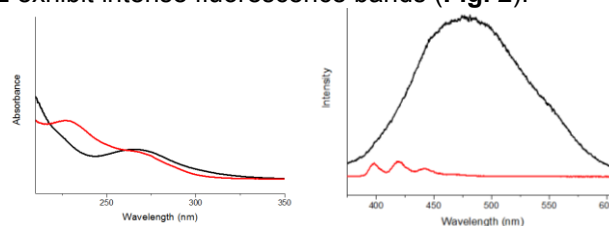


Fig. 2. Absorption (left) and emission spectra (right) of H₂L^{Ph} (red line) and of the complex **2** (black line).

Conclusions

The interaction of the ligands with Cu^I ion has significantly enhanced the fluorescence intensity and thus the origin of the fluorescence appears to be based on a MLCT excited state. Computational studies are underway in order to fully understand the photophysical properties of the present complexes.

Acknowledgements

CNPq, FAPESP, RQ-MG, GMIT and FAPEMIG

¹ Yam, V. W. W.; Lam, C. H.; Fung, W. K. M. and Cheung, K. K. *Inorg. Chem.* **2001**, *40*, 3435.