Heteroleptic zinc(II) complexes containing thiosemicarbazones and semicarbazones Ligands.

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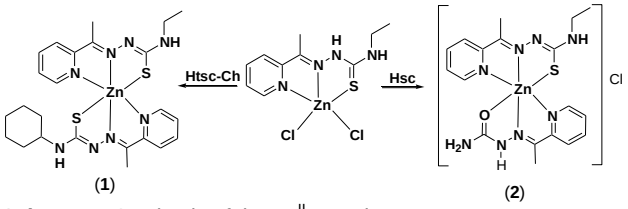
Introdução

Thiosemicarbazones (TSCs) and semicarbazones (SCs) are known as efficient metal chelators.[1] Semicarbazones differs from TSCs only by replacing the sulfur atom by oxygen. A significant feature of TSCs and SCs is their broad-spectrum biological activity.[2] Their first row transition metal coordination chemistry is well-developed. However, Zn^{II} compounds containing these two different classes of ligands haven't been reported in the literature. In this context, we focused our interest in a continuation of a previous study by developing now two new Zn^{II} compounds with mixed ligands of the type [Zn(tsc-Et)(Hsc)]Cl (**1**) and [Zn(tsc-Et)(tsc-Ch)] (**2**), where Hsc = 2-acetylpyridine-semicarbazone, Htsc-Et = 2-acetylpyridine-ethylthiosemicarbazone and Htsc-Ch = 2-acetylpyridine-cyclohexylthiosemicarbazone.

Resultados e Discussão

The heteroleptic Zn^{II} complexes were synthesized by equimolar reactions between the TSC complex $[Zn(Htsc\text{-}Et)Cl_2]$ and the corresponding SC ligand ligand (Hsc or Htsc-Ch) in the presence of base and under reflux in MeCN (**Scheme 1**).



Scheme 1. Synthesis of the Zn^{II} complexes.

The complexes were characterized by conductimetry measurements, IV, UV-Visible, 2D NMR (COSY and HMBC) and further studied by single crystal X-ray diffractometry.

The IR spectra of the free TSC ligands Hatc-R (R = Et and Ch) are characterized by two strong broad ν(NH) stretching in the range from 3349−3222 cm^{-1}. In the spectrum **1**, only one NH absorption is observed, due to the deprotonation of both ligands upon reaction, while the IR spectrum of **2** shows the ν(NH) stretches within the 3365–3175 cm^{-1} range. Besides, no significant change in the ν(C=O) wavenumbers of Hsc is detected upon coordination, which is in agreement with the fact that the Hsc ligand do not deprotonate after complexation. This is also in accord with the conductimetry measurements.

Due to the difficulty in attributing the ^1H NMR signals, both complexes were additionally studied by COSY. In the COSY spectrum of **2** the presence of a spot, which correlates the NH_2 proton and the NH proton, confirms that the Hsc ligand was not deprotonated after complexation, as predicted.

The X-ray diffraction of **2** confirmed the spectroscopic data. The crystal structure (**Figure 1**) exhibits a 6-coordinated Zn^{II} center bonded to one monoanionic atc-Et^- and one neutral Hsc ligand in *N,N,S*- and *N,N,O*-tridentate mode, respectively.

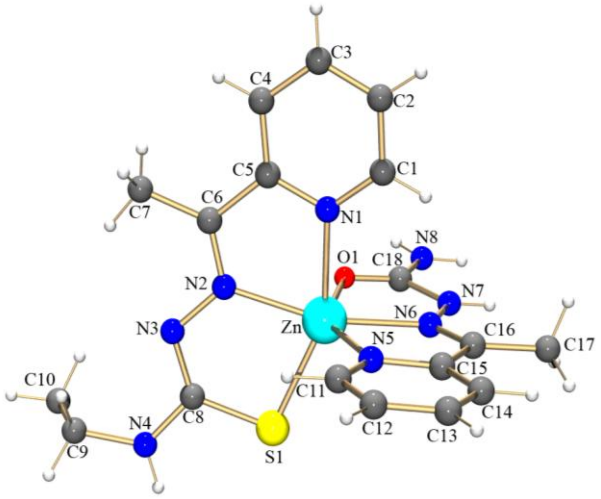


Figure 1. X-ray structure of the complex ion $[Zn(tsc\text{-}Et)(Hsc)]^+$.

Conclusões

Two new heteroleptic Zn^{II} compounds were successfully synthesized and characterized. Since those complexes possess interesting classes of ligands with rich biological properties, their biological activity will be evaluated in a near future.

Agradecimentos

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