Research paper

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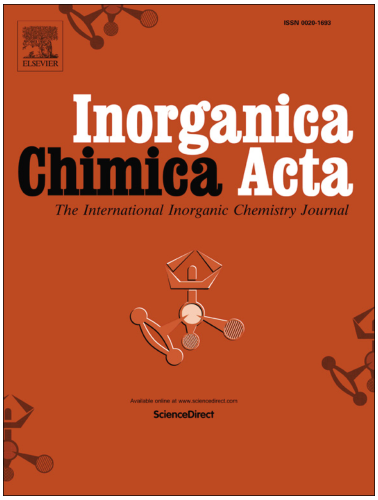

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Grid–type complexes of M^{2+} (M = Co, Ni, and Zn) with highly soluble bis(hydrazone)thiopyrimidine-based ligands: Spectroscopy and electrochemical properties

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Abstract

We present the synthesis of two types of two–site symmetric bis(hydrazone) ligands (**1** and **2**) which contain two tridentate subunits suitable for metal ion complexation, with remarkable solubility in most organic solvents, contrary to other pyrimidine-based bis(hydrazones) used for the preparation of metallogrids. As expected, compounds **1** and **2** exhibit conformational changes when coordinated metal ions (Zn^{2+}, Ni^{2+}, Co^{2+}) through the two terpyridine–like sites leading to the metal complexes **1a–c** and **2a–c**. The absorption spectra and redox properties of ligands **1** and **2** and of the metal complexes **1a–c** and **2a–c** are studied. Compounds **1** and **2** exhibit absorption spectra dominated by intense π–π* bands in the UV region, while the absorption spectra of the metal complexes **1a–c** and **2a–c** show intense bands in the UV region, due to the spin–allowed ligand–centred (LC) transitions, and in the visible, due to spin–allowed metal–to–ligand charge transfer (MLCT) transitions. Cyclic voltammetry and square wave voltammetry were carried out in order to establish the relevance of the complexation, and the grid formation in the redox potentials of the ligands **1** and **2**.

Keywords: Hydrazones; Metallogrids; Supramolecular Chemistry.