

# Novel CdCl<sub>2</sub> and HgCl<sub>2</sub> complexes with 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas: IR and Raman spectra

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## Abstract

Two series of coordination complexes of CdCl<sub>2</sub> and HgCl<sub>2</sub> with 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas were prepared and characterized. These complexes were obtained with a medium to high yield from ethanolic solutions of both ligand and salt. The formed complex results from the salt–ligand interaction with participation of both the salt anion and cation. Information on the coordination chemistry of these complexes was derived from thermal stability data, and IR, Raman and <sup>13</sup>C CPMAS NMR spectra. On coordination the electronic structure of these ligands changes as a whole, affecting practically all their vibrational pattern, however, within that complex pattern some vibrations provide valuable information on the nature of the studied complexes. These thiourea derivatives behave as neutral ligands, which coordinate the metal ion through the sulfur atom of the thiocarbonyl group. This fact is supported by the observed frequency shift, to lower values, in the ν(CS) vibration on the coordination and the appearance of a low frequency Raman line which was assigned to the metal–sulfur stretching, ν(M–S), in the formed complex. The frequency of the ν(CO) vibration always increases on complex formation, which discards the participation of the carbonyl group in the coordination process. The complexation takes place preserving the free ligand conformation, established from intra-molecular interactions, particularly in 3-monosubstituted ligands. Such features of the studied ligands and their complexes are also supported by <sup>13</sup>C CPMAS NMR spectra. This spectroscopic information correlates with the reported behavior of the ligands in ion selective electrodes.

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## 1. Introduction

The studied thiourea derivatives (3-monosubstituted and 3,3-disubstituted 1-furoylthioureas) have been successfully used as ionophores in ion selective electrodes (ISEs) for Cd(II), Hg(II) and Pb(II) [1]. This application requires a sharp modulation of the coordination strength. Formation of very stable complexes is usually related to a short electrode lifetime due to the ISEs' membrane poisoning, while a very weak metal–ligand interac-

tion does not allow appropriate ion recognition by the ligand. The best performance in that application has been observed for 3-monosubstituted 1-furoylthioureas, with a relatively high frequency of their ν(C=S) vibration [2]. It is related to an appropriated nucleophilic character of its sulfur atom and a non–chelating behavior of the ligand. Thiourea and its derivatives show versatile coordination chemistry with transition and post-transition metal ions [3–8]. In thiourea derivatives the substituents usually serve to modulate the nucleophilic character of the thioamide core, to introduce the possibility of conformational isomerism, steric effects and intra-molecular interactions and sometimes also to provide new coordination sites. From these facts, the coordination chemistry of such derivatives appears much more

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