

A Raman and infrared study of 1-furoyl-3-monosubstituted and 3,3-disubstituted thioureas

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Abstract

Raman and IR spectra of two series of 1-furoylthiourea derivatives (19 compounds) were recorded and compared in order to identify the vibrations, which involve contributions from motions within the thioureido (NCSN) core. This procedure allowed an unequivocal identification of the $\nu(\text{C}=\text{S})$ vibration in these spectra. In 3-monosubstituted furoylthioureas (Series 2) the carbonyl group and the proton on N_3 are engaged in a strong hydrogen bond interaction. This leads to an “S”-shaped conformation of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ groups where these donor sites reach a maximum separation. In this conformation, the $\nu(\text{C}=\text{O})$ vibration is not influenced by the substituent. In the absence of that hydrogen bridge, in 3,3-disubstituted thiourea derivatives (Series 1), the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ groups adopt an “U”-shaped conformation. In this conformation, the $\nu(\text{C}=\text{O})$ vibration shows a pronounced substituent dependence. These thiourea derivatives have been tested as ionophores for heavy-metal ion selective electrodes and their behavior in that sense correlates with the observed Raman and IR absorptions. The best performance in that application corresponds to compounds of Series 2, which showed the highest frequency values of the $\nu(\text{C}=\text{S})$ vibration. This fact was related to an appropriated nucleophilic character of the sulphur atom. From these data, Raman and IR spectra of these thiourea derivatives could be used as a predictor on their expected behavior in analytical applications as ionophores.

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1. Introduction

Thiourea and its derivatives are a versatile family of ligands appropriate to form complexes with ions of transition and post-transition metals [1–6]. Simple (unsubstituted) thiourea ($(\text{H}_2\text{N})_2\text{CS}$) usually behaves as a planar ligand where both, S and N atoms are donor sites able to participate in the coordination with the metal. Substituted-thioureas, however, show more diverse coordination chemistry due to their conformational isomerism, steric effects, presence of donor sites on the substituent groups and intra-molecular interactions. For instance, 1-acyl(aryl)-3-

alkylthioureas form complexes with d^8 metal ions such as Pt(II), Pd(II), Rh(III). In them only the sulphur donor atom participates [5], similar to simple thiourea. But in 1-acyl(aryl)-3,3-dialkylthioureas the oxygen atom is also involved in the coordination and the ligand behaves as bidentate [5] with the same species. With d^{10} metal ions (Zn(II), Cd(II), Hg(II), Ag(I), Cu(I)), thiourea and both derivative families show a selective metal coordination only with the S atom [3]. Many other examples could be used to illustrate the diversity of thiourea derivatives coordination chemistry.

The coordination chemistry of substituted-thioureas, even when involves a well-known class of ligands, continues attracting attention due to their applications. These compounds are used in the separation of valuable metals, particularly of platinum group metals (Pt, Pd, Ru, Os, Rh, Ir) [5],

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