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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 ν(C=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 C=O and C=S groups where these donor sites reach a maximum separation. In this conformation, the ν(C=O) vibration is not influenced by the substituent. In the absence of that hydrogen bridge, in 3,3-disubstituted thiourea derivatives (Series **1**), the C=O and C=S groups adopt an "U"-shaped conformation. In this conformation, the ν(C=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 ν(C=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.

Keywords: Infrared; Raman; Thioureas; Furoylthioureas; Thiourea derivatives; Ionophores

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 ($(H_2N)_2CS$) 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(aroyl)-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(aroyl)-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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in liquid–liquid pre-concentration processes for analytical purposes of metal ions [2,6,7] and as precursors for radiopharmaceuticals (compounds of ^{99m}Tc, ^{186}Re, ^{188}Re) [4]. Substituted-thiourea complexes also find biological applications as antibacterial [8], antiviral [9] and antifungal [10] agents. In the field of materials science, thiourea and its derivatives have been studied as non-linear optical materials [11,12]. Their complexes can be employed in the deposition of ZnS and CdS thin films from aqueous solutions [13] and in the preparation of CdS nanoparticles [14]. Thiourea derivatives have been applied to accelerate the evolution of hydrogen at the mercury electrode [15]. More recently, aroylthioureas have been successfully used in environmental control, as ionophores in ion selective electrodes (ISEs) for Cd(II), Hg(II) and Pb(II) [16]. This application requires a sharp modulation of the coordination strength and of the ligand liposolubility. Formation of very stable complexes is usually related to a short electrode lifetime due to the ISEs' membrane poisoning while a low liposolubility favors the loss of ionophore from the membrane. For this application, thiourea derivatives with non-chelating behavior and long carbon chain substituents are desirable [16].

In a previous study, the aroylthioureas were characterized using ^{1}H and ^{13}C NMR spectra in DMSO-d$_6$ [17]. Vibrational spectra (IR and Raman) regularly provide useful information on the electronic structure and conformation of a given molecule. This study was oriented to correlate the IR and Raman spectra of the studied thiourea derivatives with their ability to form complexes with ions of heavy metals. This family of compounds has been tested, with a promising performance, as ionophores in ion selective electrodes [16]. As far as we know, no similar study has been reported for an analogous family of aroylthioureas.

2. Experimental

The studied thiourea derivatives were synthesized and characterized as previously reported by Otazo-Sánchez et al. [16,17]. These compounds were synthesized following the preparative route illustrated in Fig. 1 and then re-crystallized twice (in acetone and ethanol or DMF/ethanol 20:80). Their purity was checked by TLC (glass plates of 2.6 cm × 7.5 cm, 0.25 mm thick, Silica Gel G Nach Stahl–60). Mixture of benzene–chloroform (90:10) and chloroform–water (saturated) were used as solvents.

Infrared spectra were recorded on a FT-IR spectrophotometer (Atti Mattson, Genesis Series) in the range of 4000–400 cm^{-1} using the KBr pressed disk technique. Cautions were taken to avoid influence of the milling and pressing processes in the recorded IR spectra [18]. IR spectra recorded in pressed KBr disks and of the compound dispersed on a KBr window were similar. Raman spectra were collected by a capilary sample technique on a Perkin Elmer system 2000 NIR-FT-RAMAN and a Lexel model 98 krypton ion laser ($\lambda = 647.1$ nm). The laser power at the sample surface was restricted to 40 mW. The spectral band pass of the Raman spectrometer was 4 cm^{-1} and the 90° configuration used with an incidence angle of 60° on the metal surface when taking surface-enhanced Raman scattering (SERS) spectra.

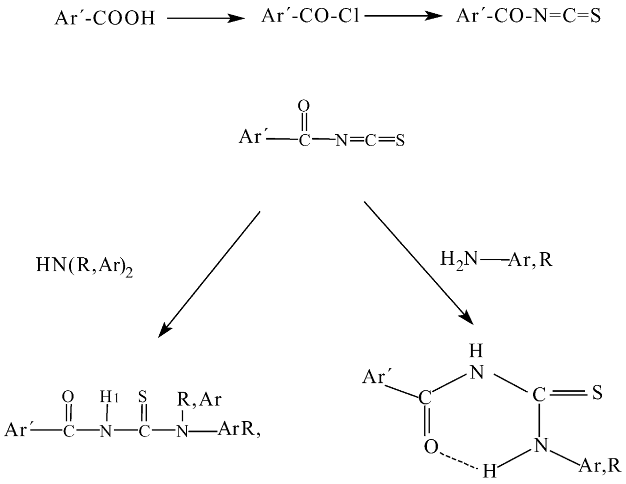


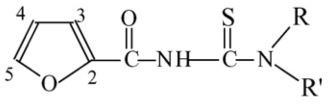
Fig. 1. Synthesis scheme of studied 1-furoylthioureas.

3. Results and discussion

According to their substituents, these compounds were labeled as Series **1** and **2** (Figs. 2 and 3). Series **1** involves 3,3-disubstituted 1-furoylthioureas while Series **2** concerns to 3-monosubstituted 1-furoylthioureas. Series **1** and **2** were previously characterized from ^{1}H and ^{13}C NMR spectra in DMSO-d$_6$ [17] and for **1e** and **2b** compositions also the crystal structure resolved from single crystal X-ray diffraction were reported [16]. Compounds of Series **2** exhibit a strong intramolecular hydrogen bond in a quasiplanar structure [19].

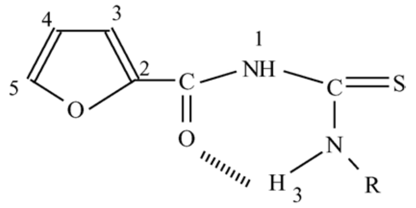
3.1. On the Raman and IR spectra of the studied thiourea derivatives

Figs. 4 and 5 show Raman and IR spectra of compounds **1b** and **2g**. In the vibrational spectra of the studied family of



No.	R	R'
1a	- CH$_2$ CH$_2$ CH$_2$ CH$_2$ CH$_2$- (piperidyl)	
1b	-CH$_2$CH$_3$	-CH$_2$CH$_3$
1c	-C$_6$H$_5$	-C$_6$H$_5$
1d	-C$_6$H$_5$	-CH$_2$C$_6$H$_5$
1e	-C$_6$H$_5$	-CH$_2$CH$_3$
1f	-C$_6$H$_5$	-CH$_3$

Fig. 2. Series **1**.



No.	R
2a	$-CH_2CH_2OH$
2b	$-C_6H_{11}$
2c	$-CH_2C_4H_3O$
2d	$-CH_2C_6H_5$
2e	$-C_{12}H_{25}$
2f	$-C_6H_5$
2g	$-(o)C_6H_5CH_3$
2h	$-(o)C_6H_5NO_2$
2i	$-C_{10}H_7$
2j	$-2-C_5H_5N$
2k	$-(m)C_6H_5CF_3$
2l	$-(p)\ C_6H_5CN$
2m	$-(p)C_6H_5C_{14}H_{29}$

Fig. 3. Series **2**.

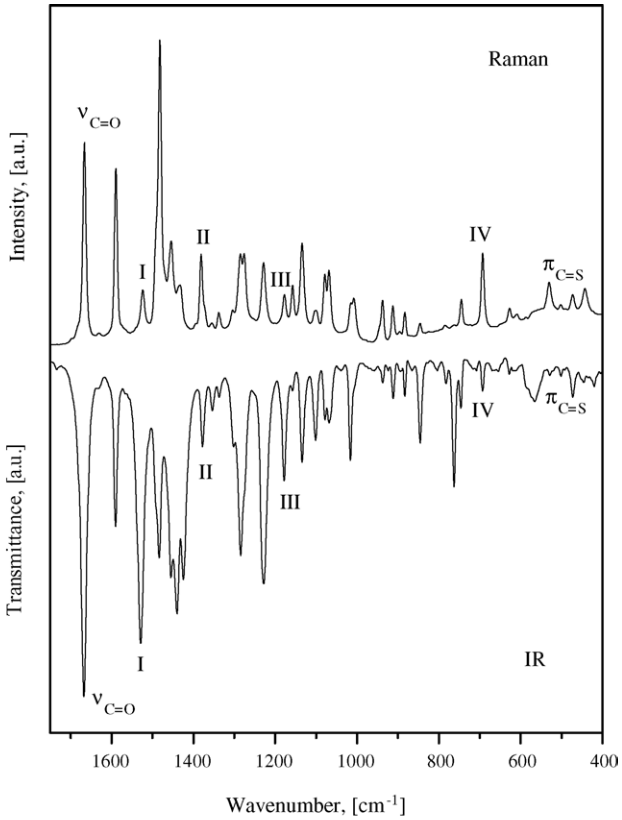


Fig. 4. FT-Raman and IR spectra of 1-furoyl-3,3-diethyllthiourea (**1b**) in the 1600–400 cm^{-1} region.

thiourea derivatives, a large number of signals are observed with pronounced overlapping. Many of these signals result from substituent groups. Concerning to the number of bands and their frequency, the Raman spectrum seems as a reflection of the corresponding IR one and vice versa. However, regarding their intensity, these spectra are quite different. In Raman, the combination bands do not occur with significant intensity, particularly those bands involving bending modes of light atoms (e.g., H) due to their relatively small polarizability gradient. On the other hand, signals from motions of heavy atoms (with a highly polarizable electronic structure) appear with relatively high intensity in the Raman spectra. In consequence, vibrations involving motions of the C=S group will be present in Raman spectra with a more prominent intensity than in IR spectra. These facts have been used to identify the C=S stretching and combination bands where it participates comparing IR and Raman spectra of each compound (Figs. 4 and 5).

The N–C and C=S bonds participate in the vibrational spectra of the studied compounds through six different motions, i.e., ν(C=S): CS stretch; ν_s(NC): N_2C symmetric stretch; ν_{as}(NC): N_2C asymmetric stretch; δ(NCN): NCN bend; δ(CS): CS bend; and π(CS): out-of-plane bend. However, in a given thiourea derivative, including unsubstituted thiourea, each of these motions appear combined (coupled) with other ones within the molecule resulting in relatively complex Raman and IR spectra [20–23]. For instance, in *N*-methylthiourea, which is one of the simplest alkyl derivatives of thiourea, the CN stretches contribute to six different fundamentals while ν(C=S) appears in three ones [21]. Due to that complexity, in the study of thiourea derivatives using Raman and IR spectroscopies, usually a set of fundamentals involving the N–C and C=S bonds are identified and could be used as indicators of the electronic structure around these bonds. In compounds containing the thioamide group (HNCS) these fundamentals are known as “thioamide” bands: I, II, III and IV [24–26]. These bands have a large contribution from ν(C–N) + δ(NH) (I), ν(C–N) + ν(C=S) (II and III) and ν(C=S) (IV) motions and are usually reported around 1470, 1250, 1080 and 750 cm^{-1}, respectively [26]. These bands emerge in a region, which is plenty of absorptions from skeletal motions within the substituent groups. It makes difficult their identification. These bands have been indicated in Figs. 4 and 5. Tables 1 and 2 show their frequencies values, so they are reported.

Raman and IR spectra of the studied family of compounds reveal fine details within a given Series and structure. These fine details follow certain regularities and differences, which are discussed below.

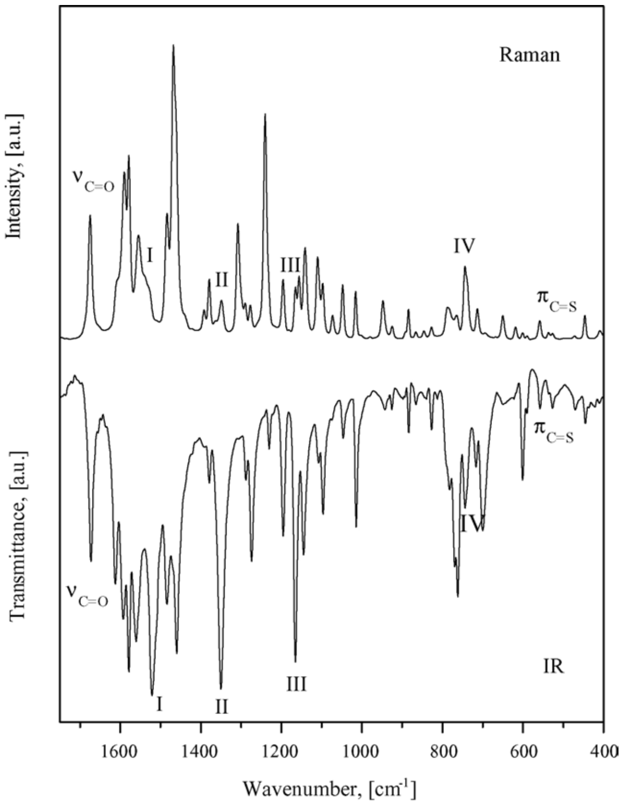


Fig. 5. FT-Raman and IR spectra of 1-furoyl-3-*o*-tolylthiourea (**2g**) in the 1600–400 cm^{-1} region.

Table 2
Series **1** and **2**: wavenumbers of IR bands in 1750–400 cm^{-1} region

No.	$\nu_{C=O}$	Thioureido bands			
		I	II	III	IV
1a	1657 (s)	1519 (s)	1374 (s)	1176 (s)	699 (m)
1b	1667 (s)	1530 (s)	1378 (s)	1177 (s)	693 (m)
1c	1699 (s)	1490 (s)	1370 (s)	1156 (m)	701 (m)
1d	1709 (s)	1534 (s)	1395 (s)	1192 (s)	712 (m)
1e	1667 (s)	1513 (s)	1372 (s)	1186 (m)	700 (m)
1f	1674 (s)	1514 (s)	1373 (s)	1187 (s)	707 (m)
2a	1668 (s)	1532 (s)	1375 (m)	1186 (s)	749 (m)
2b	1666 (s)	1515 (s)	1345 (m)	1175 (s)	756 (m)
2c	1667 (s)	1548 (s)	1324 (m)	1173 (s)	747 (m)
2d	1667 (s)	1537 (s)	1329 (s)	1177 (s)	746 (m)
2e	1673 (s)	1538 (s)	1341 (m)	1177 (s)	753 (m)
2f	1669 (m)	1525 (s)	1355 (s)	1166 (s)	741 (m)
2g	1672 (s)	1518 (s)	1349 (s)	1165 (s)	744 (m)
2h	1681 (s)	1546 (m)	1352 (s)	1165 (s)	763 (m)
2i	1662 (s)	1507 (s)	1364 (m)	1174 (s)	717 (w)
2j	1701 (s)	1555 (s)	1319 (s)	1149 (s)	797 (m)
2k	1667 (m)	1527 (s)	1336 (s)	1179 (s)	747 (m)
2l	1669 (m)	1546 (s)	1335 (s)	1161 (s)	784 (w)
2m	1666 (s)	1523 (s)	1347 (s)	1179 (s)	720 (w)

Intensity: s, strong; m, medium; w, weak.

3.2. *Raman spectra*

Figs. 4 and 5 show two typical Raman spectra representative of the studied series of thiourea derivatives. For clarity reasons, the spectral discussion will be divided in regions.

3.2.1. *The 3500–1800 cm^{-1} region*

In this region stretches of N–H groups vibrations corresponding to the thiourea core are merged with the ones of C–H groups from substituents. C–H stretching from aromatic

Table 1
Series **1** and **2**: wavenumbers of Raman bands in 1750–100 cm^{-1} region

No.	$\nu_{C=O}$	Thioureido bands				π(CS)	δ(CS)	δ(NCN)
		I	II	III	IV			
1a	1652 (m)	1516 (w)	1385 (m)	1175 (w)	699 (m)	598 (w)	369 (w)	*
1b	1666 (m)	1524 (w)	1381 (m)	1177 (w)	693 (m)	530 (w)	358 (w)	305 (w)
1c	1700 (m)	1502 (m)	1373 (m)	1175 (m)	710 (m)	565 (w)	356 (w)	310 (w)
1d	1704 (m)	1527 (w)	1395 (m)	1177 (w)	713 (w)	551 (w)	360 (w)	292 (w)
1e	1666 (m)	1518 (w)	1392 (m)	1186 (w)	701 (m)	557 (w)	351 (w)	291 (w)
1f	1673 (m)	*	1383 (w)	1166 (m)	709 (m)	548 (w)	357 (w)	291 (w)
2a	1663 (m)	1536 (w)	*	1183 (w)	752 (m)	597 (w)	374 (w)	323 (w)
2b	1659 (m)	1540 (w)	1346 (w)	1170 (w)	759 (w)	547 (w)	367 (w)	289 (w)
2c	1666 (m)	1545 (w)	1324 (w)	1181 (w)	749 (m)	595 (w)	355 (w)	295 (w)
2d	1665 (m)	1546 (w)	1331 (w)	1182 (w)	750 (m)	596 (w)	356 (w)	310 (w)
2e	1669 (m)	1542 (w)	1328 (w)	1172 (w)	743 (m)	597 (w)	*	270 (w)
2f	1675 (m)	1533 (w)	1356 (w)	1166 (w)	743 (m)	535 (w)	378 (w)	340 (w)
2g	1675 (m)	1518 (w)	1349 (w)	1165 (w)	744 (m)	558 (w)	372 (w)	310 (w)
2h	1681 (s)	1543 (w)	1385 (m)	1164 (w)	760 (m)	530 (w)	363 (w)	301 (w)
2i	1665 (m)	1502 (w)	*	*	723 (m)	563 (w)	*	302 (w)
2j	1699 (m)	1523 (w)	1340 (m)	1202 (w)	796 (m)	593 (w)	358 (w)	305 (w)
2k	1669 (m)	1532 (w)	1334 (m)	1174 (w)	748 (m)	537 (w)	375 (w)	311 (w)
2l	1667 (m)	1550 (w)	1343 (m)	1169 (w)	773 (m)	605 (w)	375 (w)	298 (w)
2m	1665 (m)	1524 (w)	*	1179 (w)	723 (m)	562 (w)	355 (w)	303 (w)

Intensity: s, strong; m, medium; w, weak.
[*] Not assigned.

groups are usually observed above 3000 cm^{-1} while those involving the aliphatic fraction fall in the 3000–2800 cm^{-1} range. These vibrations are observed in Raman spectra with a relatively low intensity, with the exception of the presence of substituents rich in aliphatic C–H groups; as **1a**, **2e** and **2m**. The 2800–1800 cm^{-1} spectral region is usually poor in absorption bands. Only **2l** shows an intense band in this spectral region, corresponding to a ν(C≡N) vibration at 2228 cm^{-1}. Very strong hydrogen bond interactions usually produce broad ν(O–H) absorption below 2800 cm^{-1} [27], which was not observed in the studied thiourea derivatives.

3.2.2. The 1800–1400 cm^{-1} region

In this region the following bands are observed: the carbonyl vibration ν(C=O), the ν(C=C) stretches from the substituent groups, the asymmetrical stretch of the NO_2 group (compound **2h**), and ν(C=N) band of pyridine ring (compound **2j**). It is also detected a combination band containing certain contribution from the ν(C–N) and δ(N–H) motion, which are related to the Thioureido Band I. Raman spectra of both Series **1** and **2** compounds show several bands in this region (Figs. 4 and 5).

The highest frequency bands correspond to the ν(C=O) vibration, which for Series **1** is observed at the 1704–1652 cm^{-1} interval while for Series **2** it falls in a relatively narrow spectral region, from 1675 to 1659 cm^{-1}, except for compounds **2h** and **2j** (Table 1). This is due to the hydrogen bond interaction in Series **2** compounds [16,17], which stabilizes the “S”-shaped conformation (Fig. 2) in the solid state. There is also a minimum energy conformation related to a maximum value of the O–S distance [28]. This intra-molecular hydrogen bond leads to a slight downshift in the frequency of the ν(C=O) band relative to the expected value in its absence. It was reported a good transmission of the electronic effects of the N_3 substituents through this bond to the furoyl group, based on the NMR study of Series **2** [17]. Series **1** compounds show a higher dispersion in the ν(C=O) values (Table 1), revealing certain conformation-substituent dependence. The higher frequency values of ν(C=O) within this series correspond to compounds with at least one aromatic substituent at N_3 (compounds **1c**, **1d**, **1e** and **1f**). A voluminous substituent could hinder the carbonyl group participation in an intermolecular hydrogen bond interaction in the solid state. Since Series **1** concerns to 3,3-disubstituted furoylthioureas no proton is available on N_3 to participate in intra-molecular hydrogen bond interaction. In this series all the interactions between the N_1 and N_3 sides of the molecule takes place only through the N–C–N bonds.

In Series **2**, the larger frequency values for the ν(C=O) stretch correspond to compounds **2h** (1681 cm^{-1}) and **2j** (1699 cm^{-1}). This suggests that the NO_2 group in **2h** has a stronger intramolecular bond interaction with the N_3H and that the C=O group is free or it has a weak hydrogen bond interaction with the N_3H. In the case of compound **2j**, the pyridyl nitrogen could be participating in another hydrogen bond interaction with the acidic N_1 proton, which inhibits the possibility of the reported hydrogen interaction between N_3 proton and the carbonyl group. The hydrogen bridge through N_1 proton leads to an “U”-shaped conformation where both, S and O atoms remain as neighbors, on the same region of the molecule. The existence of two conformers “S” and “U” in the solid state, in **2j** is excluded, because only one ν(C=O) vibration is observed in their Raman spectra. From ^1H NMR data in DMSO-d_6 solution a conformational equilibrium, between “S” and “U” conformers has been suggested for this compound [17]. The formation of a hydrogen bond interaction through N_1 proton could be particularly favored in this thiourea derivative due to the very basic character of its pyridyl nitrogen. Another explanation is the participation of NO_2 and pyridyl nitrogen in a strong inter-molecular interaction at N_1 proton of a neighboring molecule. It is interesting that compounds **2k** and **2l**, with strong electron-withdrawing groups (CF_3 and CN, respectively) in the subsituent at N_3, show their ν(C=O) values in the mean range of the Series **2**. It seems, their effect might be not significant to modify the strength of the $–C=O\cdots H–N_3–$ hydrogen bridge.

The most intense Raman band in this region corresponds to the C=C stretching vibration of the furoyl group, observed around 1470 cm^{-1} for Series **2** (Fig. 5) and in the range 1481–1464 cm^{-1} for Series **1** (Fig. 4). This band is common to all the studied thiourea derivatives. As observed for the ν(C=O) band, compounds of Series **2** show the smaller dispersion in the frequency of this ν(C=C) vibration, probably related to the stabilization of the “S”-shaped conformation, as mentioned. A similar regularity was observed in the values of ^{13}C NMR chemical shifts for the furan ring in these two series of thiourea derivatives [17]. The ν(C=C) band of the benzene ring is observed at higher frequencies, from 1594 to 1585 cm^{-1} for Series **1** (compounds **1c**, **1d**, **1e** and **1f**) and at the 1611–1565 cm^{-1} interval for Series **2** (compounds **2f**, **2g**, **2i**, **2k** and **2m**). For compound **2j** three bands at 1605, 1589 and 1580 cm^{-1} were observed and assigned to vibrations from C=C and C=N bonds within the pyridine ring. The asymmetric $-NO_2$ stretching vibration of compound **2h** was observed as a medium intensity band at 1543 cm^{-1}.

In the 1530–1500 cm^{-1} range, both, Series **1** and **2**, a medium-to-weak intensity band appears. It was assigned to a fundamental that involves the ν(C–N) and δ(N–H) motions (thioureido band I). The variation in frequency and intensity of this band for different compounds could be related to a higher or smaller δ(C–H) contribution from the substituent groups. In simple thiourea the ν(C–N) motions (symmetric and asymmetric) are reported in the interval 1412–1391 cm^{-1} [22] while in monomethylthiourea, where they appear coupled with δ(C–H) and δ(N–H) bending modes, their vibrations fall in the 1556–1489 cm^{-1} interval [21]. This absorption is more clearly assigned in Raman spectra than in IR spectra, due to the strong δ(C–H) and aromatic ν(C=C) that merge in the later.

3.2.3. The 1400–800 cm^{-1} region

This region is rich in medium intensity bands from skeletal motions and out-of-plane vibrations from the substituent groups, and also $\nu(N_3{-}C)$, ν(C–C) and ν(C–O) vibrations from some particular groups. At least two vibrations containing contributions from ν(C–N) and ν(C=S) motions in the thiourea core (NCSN) (bands II and III) are expected to appear in this region [26]. However, it seems that their contributions are relatively low to produce intense Raman bands to allow their unequivocal identification (see Figs 4 and 5). Only few bands were unequivocally assigned in this region. The furoyl group shows its ν(C–O) stretching at 1100–1050 cm^{-1} and a medium intensity absorption at 1380–1390 cm^{-1} related to a ν(C=C) motion. Compound **2h** shows intense bands at 1350 and 852 cm^{-1} due to the symmetric ν(N–O) and ν(C–N) vibrations, respectively. Vibrations related to $-CF_3$ group in compound **2k** are observed as medium intensity bands at 1340–1137 cm^{-1} [27].

3.2.4. The 800–200 cm^{-1} region

In this region, the Thioureido band IV falls. This is a spectral zone practically free from other bands and it is found to be the most interesting spectral region due to the relevance of thiourea derivatives as ligand and particularly, as ionophores for heavy metal sensors. Raman spectra of all the studied compounds in Series **1** and **2** show a medium intensity band around 700 cm^{-1} (Figs. 4 and 5). The frequency values of this band for both series of thiourea derivatives are reported in Table 1. This vibration clearly differs for both series. It is observed at 713–693 cm^{-1} for Series **1** and at 796–723 cm^{-1} for Series **2**. It has been assigned to a fundamental band with a majority contribution from ν(C=S) motion (band IV). The presence of an intra-molecular hydrogen bond interaction in compounds of Series **2** leads to a higher electronegativity of N_3 restricting the thioamidic resonance and increasing the double bond character of the C=S group. Consequently, band IV is observed at higher frequencies in this Series.

The C=S is a polarizable bond with an intense Raman dispersion. A survey of the published papers on Raman spectra of thiourea, their derivatives and complexes reveals that this fundamental is usually assigned in the 800–600 cm^{-1} frequency range [1–4,14,20–26,29–35], Few authors report its occurrence out of this interval [6,28,36,37]. As already mentioned, the ν(CS) motion is coupled with other modes within the molecule. A larger frequency value of this vibration supposes a higher contribution from these other coupled modes, which leads frequently to an inappropriate band identification. That band below 600 cm^{-1} supposes a very strong interaction at the S atom through the CN bonds. A downshift frequency of this fundamental is always reported in the complex formation via the S atom [3,4,14,31–35]. The formation of the S→M bond leads to a electron transfer from the sulphur lone pair to the metal (M). This weaks the C=S double bond and lowers the frequency of the ν(CS) mode.

The observed variations in the frequency of band IV in Series **1** and **2** (Table 1) suggests certain substituent dependence. Series **1** show the higher frequency values of that band. Compounds with aromatic substituent at N_3 (**1c**, **1d**, **1e** and **1f**) present a mean value of 703 cm^{-1} for it. The lower ones correspond to aliphatic groups at this site. Compared to aliphatic substituents, the aromatic ring interacts with the N_3 lone pair electrons and inhibits the thioamidic resonance. This leads to a smaller charge remaining in the C=S bond. This fact is favored by substituents with strong electron withdrawing groups. For instance, $-NO_2$ and -CN in compounds **2h** and **2l**, respectively, or pyridinic nitrogen in compound **2j**, where the higher frequency values of band IV are showed. In general no definite differences on the band IV frequencies are observed for compounds of Series **2**, no matter if the substituent at N_3 is aliphatic or aromatic. This fact suggests that the main cause is the planarity of the low energy "S"-shaped configuration due to the $-C{=}O\cdots H{-}N_3{-}$ hydrogen bridge. The substituent in N_3 is forced to be in the "Z" position and out of plane due to the proximity of the CS group. The bigger aromatic group (or the presence of ortho substitution in the aromatic ring), weakens the resonance effect with the N_3 electronic pair. The main effect of the aromatic substituents seem to be mainly inductive due to this "out of plane" effect. In these cases, the N_3 pair is available and thioamidic resonance is favored. This leads to a lower CS frequencies values. It can be illustrated with the lowest CS value in the naphtil substituted compound (**2i**). But, if there are electrowithdrawing groups, the negative electronic inductive effect rises the CS frequencies observed. These contradictory effects on CS stretching are not present in Series **1** as there is free rotation of the groups in N_3. Also, no direct transmission of N_3 groups electronic effects to CO group exists, as there is no hydrogen bond. In conclusion, the hydrogen bond interaction of the N_3 proton with the carbonyl group, in Series **2** compounds, is related to a smaller substituent effect on the C=S group frequencies values.

In the spectral region below 650 cm^{-1} several medium to low intensity bands were observed. Vibrations with contributions from π(CS), δ(CS) and δ(NCN) motions were assigned according to their relative intensity in Raman and IR spectra (see Figs. 4 and 5 and Table 1). In these assignments also reported results for these fundamentals in other thiourea derivatives have been considered. For thiourea and *N,N′*-diphenylthiourea the vibration corresponding to the δ(NCN) motion has been assigned at 479 and 395 cm^{-1}, respectively [32]. From calculations of potential–energy distributions and Raman and IR spectra, in monomethylthiourea the π(CS) and δ(CS) motions have been located in vibrations at 636 and 403 cm^{-1}, respectively, while δ(NCN) mode appears distributed in bands at 1297, 772, 491, 404 and 287 cm^{-1} (main contribution) [21]. An analogous study in thiourea assigns the π(CS) motion in vibrations at 735 (main contribution), 624 and 507 cm^{-1}; δ(NCN) at 1406, 737 and 456 (main contribution) cm^{-1}; and δ(CS) at 381 cm^{-1} [22]. In this region also vibrations from substituent groups appear, particularly due to rings deformation [29].

3.2.5. *IR spectra*

IR spectra absorption bands correspond to stretching and bending (in-plane and out-of-plane) motions of polar groups. The ones of light atoms are particularly intense. For instance, compounds with aromatic substituents produce intense ν(C–H) bands above 3000 cm^{-1} while, for derivatives with aliphatic groups, these bands are observed around 2800 cm^{-1}. In this region also the ν(N–H) bands fall in 3396–3204 cm^{-1} range for free NH and at 3190–3110 cm^{-1} for associated NH (as $–N_3H\cdots O{=}C–$ in Series **2**). The ν(C=O) vibration in both, Series **1** and **2**, follows the same regularities discussed above from Raman spectra. The 1600–800 cm^{-1} region is rich in intense absorption bands from substituent groups which, once identified [29], facilitates the assignment of the thioureido core absorptions (bands I, II and III; see Figs. 4 and 5 and Table 2). These bands are relatively intense in IR spectra due to contribution from polar groups. Even below 800 cm^{-1}, the studied compounds show relatively intense absorption bands, compared with those observed in the corresponding Raman spectra. These bands result from out-of-plane bending and deformation ring motions. The thioureido band IV is a moderated-weak absorption and particularly difficult to assign. The previous Raman identification of this band allowed us to report this band in the IR spectra.

3.2.6. *Raman and IR spectra and behavior of 1-furoyl-3-monosubstituted and 3,3-disubstituted-thioureas as ionophores*

The studied thiourea derivatives have been tested as ionophores in ion selective electrodes for Cd(II), Hg(II) and Pb(II) [16]. The best performance is reported for 3-monosubstituted furoylthioureas (Series **2**), according to their selectivity and sensibility. With exception of compound **2j**, the members of this series show a linear (Nernstian) response towards these ions in a wide range of concentrations with the appropriate reversibility and no membrane poisoning after several weeks. This behavior has been related to the existence of the strong intra-molecular hydrogen bridge $-C{=}O\cdots H–N_3–$ which stabilizes the S-shaped conformer and restricts the metal–ligand interaction only to the S atom. Due to this hydrogen bond, the carbonyl bands ν(C=O) show lower frequencies than the typical acylthioureas [24] (Tables 1 and 2). These compounds show the corresponding ν(CS) vibration (band IV) in the 773–723 cm^{-1} range. The relatively high frequency values of the ν(CS) indicate a large double bond character of this group and the lower nucleophilic character of the sulphur atom in comparison with alkylthioureas. The relatively high value of ν(C=O) vibration at 1699 cm^{-1} for compound **2j**, agrees with the already discussed hydrogen bond between the pyridyl nitrogen and the very acid N_1 proton. This compound presents an "U"-shaped conformation for C=O and C=S groups, providing two coordination sites for the metal (a chelate complex could be formed). An analogous behavior could be present in compound **2h**.

Compounds of Series **1** have a poor performance in heavy-metal ions selective electrodes, particularly due to its low selectivity and time of life of the sensors. In these 3,3-disubstituted thioureas, the C=O and the C=S groups adopt an "U"-shaped conformation leading to a chelate coordination to many metal ions [5]. A chelate ligand is usually related to a high stability of the resulting complex. This could explain the low reversibility and short lifetime of the obtained electrodes when these compounds are used as ionophores. DFT calculations demonstrate the higher nucleophilic character of the sulphur atom in these compounds [38]. In agreement to this report, we found the ν(C=S) at lower frequency values than in Series **2**. This means that the C=S bond have less double bond character than in Series **2**. Experimentally, the IR and Raman ν(C=S) values indicates that sulphur atom in Series **1** are more nucleophylic than in Series **2**.

The observed regularities in the ν(C=O) and ν(C=S) Raman and IR vibrations of Series **1** and **2** are in correspondence with their ionophore behavior in heavy-metal selective electrodes. In this sense, these techniques could be useful to predict the convenience of new thiourea derivatives for this analytical application.

4. Conclusions

Comparison of Raman and IR spectra provides an appropriate procedure to assign the ν(C=S) stretch in the complex vibrational spectra of thiourea derivatives. The ν(C=O) vibration appears as a good sensor on the conformation adopted by a given compound related to intra-molecular hydrogen bond interactions with participation of the carbonyl group. According to Raman and IR data, compounds of Series **2**, with exception of **2j**, adopt a "S"-shaped conformation of their donor sites, C=O and C=S, which explains their good performance as ionophores for heavy metal in ion selective electrodes. In this conformation the C=O group is unable to participate in the coordination to the metal. On the other hand, in compounds of Series **1**, without proton at N_3 to form a hydrogen bridge with the carbonyl group, the donor sites (C=O and C=S) adopt an "U"-shaped conformation. This fact could explain their bad behavior in that application. A chelate ligand is usually related to a high stability of the formed complex, which means a short lifetime when it is used in a reversible electrode. Raman and IR spectra, which serve to obtain information on the electronic structure of these potential donor sites, result appropriate techniques to shed light on the suitability of the studied thiourea derivatives in the mentioned application.

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