Available online at www.sciencedirect.com

SCIENCE DIRECT®

Spectrochimica Acta Part A 64 (2006) 961–971

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Novel $CdCl_2$ and $HgCl_2$ complexes with 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas: IR and Raman spectra

O. Estévez-Hernández [a], E. Otazo-Sánchez [b], J.L. Hidalgo-Hidalgo de Cisneros [c], I. Naranjo-Rodríguez [c], E. Reguera [a,*]

[a] *Instituto de Materiales y Reactivos (IMRE), Universidad de la Habana, San Lázaro s/n, Vedado, 10400 La Habana, Cuba*

[b] *Centro de Investigaciones Químicas (CIQ), Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo km 4.5, Colonia Ciudad Universitaria, 42074 Pachuca, México*

[c] *Departamento de Química Analítica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, España*

Received 22 June 2005; accepted 6 September 2005

Abstract

Two series of coordination complexes of $CdCl_2$ and $HgCl_2$ 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 ^{13}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 $\nu(CS)$ vibration on the coordination and the appearance of a low frequency Raman line which was assigned to the metal–sulfur stretching, $\nu(M–S)$, in the formed complex. The frequency of the $\nu(CO)$ 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 ^{13}C CPMAS NMR spectra. This spectroscopic information correlates with the reported behavior of the ligands in ion selective electrodes.

Keywords: IR; Raman; Furoylthioureas; $CdCl_2$ and $HgCl_2$ complexes; Thiourea derivative complexes

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 interaction 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 $\nu(C{=}S)$ 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

---

[*] Corresponding author. Tel.: +537 8781004; fax: +537 8783741.
E-mail addresses: edilso@fisica.uh.cu, ereguera@yahoo.com (E. Reguera).

1386-1425/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2005.09.005

varied than that of simple thiourea favoring certain practical applications in analytical and extractive chemistry, particularly for precious metals [7].

Coordination compounds formed by thiourea and its derivatives with d^{10} metal(II) ions (Zn(II), Cd(II), Hg(II)) have recently received renewed attention due to the following reasons: (a) their non-linear optical properties [9,10] supported in the large dipole moment of thiourea and the existence of polarizable electronic structures; (b) the convenient preparation of nano-structured semiconducting materials based on CdS from thermal decomposition of those complexes [11,12]; (c) their potentiality in analytical applications [2,7]. With these metals ions certain regularity concerning the coordination through the S atom has been observed [5]. An analogous behavior is expected for the coordination chemistry of 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas with $CdCl_2$ and $HgCl_2$ complexes, which have not been previously studied. This study is oriented to shed light in this sense using Raman and IR spectroscopies and ^{13}C CPMAS NMR spectrometry, as the main sensing techniques. At the same time, the results obtained serve as an appropriate complement for the application of these ligands in ion selective electrodes to sense these heavy metals in environmental control and protection [1]. Since the coordination at a given site involves charge redistribution within the ligand as a whole, its entire vibrational pattern must be affected and this fact must be considered during the evaluation of the resulting changes in Raman and IR spectra.

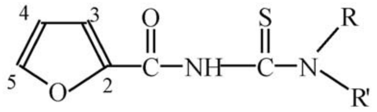
2. Experimental

2.1. Ligands, salts and preparation of their complexes

Cadmium(II) chloride dehydrated and mercury(II) chloride (both from Merck) were used without further purifications. The 1-furoylthioureas were synthesised as previously reported by Otazo-Sánchez et al. [1,13]. According to their substituents, these ligands were labelled as Series **1** and **2** (Figs. 1 and 2). Series 1 (compounds **1a**–**f**) involves 1-furoylthioureas 3-monosubstituted while Series **2** (compounds **2b**–**d** and **2f**–**k**) concerns to 3,3-disubstituted. In order to provide certain continuity with previous studies on these families of thiourea derivatives [1,13], the same numerals there used are preserved.

The complexes are formed when isoconcentrated ethanolic solutions of the involved thiourea derivative and metal chloride are mixed at room temperature in 1:1 molar ratio. The reactive mixture was left to evaporate until complex precipitated. The cadmium chloride mixtures with **1c**–**e** ligands did not form precipitate, although the solution turned turbid. The formed precipitates were collected by filtration, then washed with ethanol and finally dried in air. The peer $CdCl_2$ and $HgCl_2$ complexes obtained from both series are labelled as **$CdCl_2$–** and **$HgCl_2$–Ligand**, respectively.

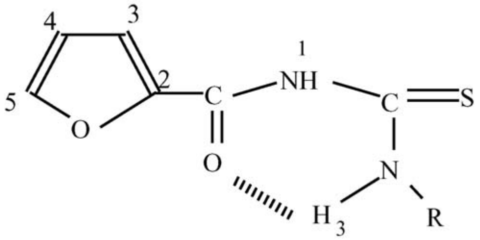
The chemical composition of the obtained solid complexes was determined from elemental chemical analysis and X-ray energy-dispersed spectroscopy (EDS) for the metal to S atomic ratio (M:S). In terms of the obtained yield (%), and the proposed formula unit, the results are the following:



No.	R	R'
1a	- CH_2 CH_2 CH_2 CH_2 CH_2- (piperidyl)	
1b	-CH_2CH_3	-CH_2CH_3
1c	-C_6H_5	-C_6H_5
1d	-C_6H_5	-$CH_2C_6H_5$
1e	-C_6H_5	-CH_2CH_3
1f	-C_6H_5	-CH_3

Fig. 1. Series **1** ligands. The C=O and C=S groups adopt a “U”-shaped conformation.

$CdCl_2$–1a: yield: 48%. Calc. for $Cd_2Cl_4C_{11}H_{14}O_2N_2S$: C, 21.81; H, 2.31; N, 4.63; S, 5.29; Cd, 37.2. Found: C, 21.33; H, 2.47; N, 5.70; S, 4.79; Cd, 36.4. Cd:S, 1.70; ***$HgCl_2$–1a***: yield: 45%. Calc. for $HgCl_2C_{11}H_{14}O_2N_2S$: C, 25.89; H, 2.74; N, 5.49; S, 6.28; Hg, 39.3. Found: C, 29.10; H, 2.85; N, 6.08; S, 7.11; Hg, 33.9. Hg:S, 0.66; ***$CdCl_2$–1b***: yield: 39%.



No.	R
2b	-C_6H_{11}
2c	-$CH_2C_4H_3O$
2d	-$CH_2C_6H_5$
2f	-C_6H_5
2g	-(o)$C_6H_5CH_3$
2h	-(o) $C_6H_5NO_2$
2j	-2-C_5H_5N
2k	-(m)$C_6H_5CF_3$

Fig. 2. Series **2** ligands. The C=O and C=S groups adopt an “S”-shaped conformation due to the intra-molecular N_3—H···O=C— hydrogen bond bridge.

Calc. for $Cd_2Cl_4C_{10}H_{14}O_2N_2S$: C, 20.23; H, 2.36; N, 4.72; S, 5.40; Cd, 37.9. Found: C, 18.90; H, 2.59; N, 5.29; S, 4.90; Cd, 38.1. Cd:S, 2.00; ***$HgCl_2$–1b***: yield: 62%; Hg, 38.9. Hg:S, 0.60; ***$HgCl_2$–1c***: yield: 42%. Calc. for $HgCl_2C_{18}H_{14}O_2N_2S$: C, 36.36; H, 2.36; N, 4.71; S, 5.38; Hg, 33.8. Found: C, 41.11; H, 2.83; N, 5.25; S, 6.60; Hg, 34.3. Hg:S, 0.65; ***$HgCl_2$–1d***: yield: 60%. Calc. for $HgCl_2C_{19}H_{16}O_2N_2S$: C, 37.50; H, 2.63; N, 4.60; S, 5.26; Hg, 33.0. Found: C, 36.84; H, 2.99; N, 4.64; S, 5.27; Hg, 37.7. Hg:S, 0.85; ***$HgCl_2$–1e***: yield: 56%. Calc. for $HgCl_2C_{14}H_{14}O_2N_2S$: C, 30.78; H, 2.56; N, 5.13; S, 5.86; Hg, 36.7. Found: C, 30.62; H, 2.47; N, 5.24; S, 6.11; Hg, 33.7. Hg:S, 0.87; ***Cd_2Cl_4–1f***: yield: 55%. Calc. for $Cd_2Cl_4C_{13}H_{12}O_2N_2S$: C, 24.88; H, 1.91; N, 4.47; S, 5.10; Cd, 37.8. Found: C, 23.75; H, 1.97; N, 4.08; S, 4.72; Cd, 36.9. Cd:S, 2.15; ***$HgCl_2$–1f***: yield: 32%. Calc. for $HgCl_2C_{13}H_{12}O_2N_2S$: C, 29.33; H, 2.25; N, 5.26; S, 6.02; Hg, 37.7. Found: C, 30.83; H, 2.80; N, 5.56; S, 6.89; Hg, 39.7. Hg:S, 0.67; ***Cd_2Cl_4–2b***: Yield: 47%. Calc. for $Cd_2Cl_4C_{12}H_{16}O_2N_2S$: C, 23.26; H, 2.58; N, 4.52; S, 5.17; Cd, 37.2. Found: C, 22.71; H, 2.97; N, 4.42; S, 5.12; Cd, 36.4. Cd:S, 1.98; ***$HgCl_2$–2b***:yield: 81%. Calc. for $HgCl_2C_{12}H_{16}O_2N_2S$: C, 27.49; H, 3.05; N, 5.34; S, 6.11; Hg, 38.3. Found: C, 27.91; H, 3.06; N, 5.52; S, 6.34; Hg, 40.8. Hg:S, 0.78; ***$CdCl_2$–2c***: yield: 69%. Calc. for $CdCl_2C_{11}H_{10}O_3N_2S$: C, 30.44; H, 2.31; N, 6.46; S, 7.38; Cd, 25.9. Found: C, 31.49; H, 2.68; N, 6.34; S, 7.28; Cd, 26.1. Cd:S, 0.98; ***$HgCl_2$–2c***: yield: 75%. Calc. for $HgCl_2C_{11}H_{10}O_3N_2S$: C, 25.29; H, 1.92; N, 5.37; S, 6.43; Hg, 38.4. Found: C, 27.47; H, 3.33; N, 5.51; S, 6.60; Hg, 36.9. Hg:S, 0.77; ***$CdCl_2$–2d***: yield: 71%. Calc. for $CdCl_2C_{13}H_{12}O_2N_2S$: C, 35.16; H, 2.31; N, 4.63; S, 5.29; Cd, 25.3. Found: C, 33.96; H, 2.47; N, 5.89; S, 6.77; Cd, 27.6. Cd:S, 0.93; ***$HgCl_2$–2d***: yield: 79%. Calc. for $HgCl_2C_{13}H_{12}O_2N_2S$: C, 29.33; H, 2.25; N, 5.26; S, 6.02; Hg, 37.7. Found: C, 29.76; H, 2.39; N, 5.47; S, 6.26; Hg, 40.1. Hg:S, 0.70; ***$CdCl_2$–2f***: yield: 81%. Calc. for $Cd_3Cl_6C_{24}H_{20}O_4N_4S_2$: C, 27.62; H, 1.92; N, 5.37; S, 6.14; Cd, 32.3. Found: C, 27.05; H, 2.17; N, 5.22; S, 6.01; Cd, 32.1. Cd:S, 1.58; ***$HgCl_2$–2f***: yield: 80%. Calc. for $HgCl_2C_{12}H_{10}O_2N_2S$: C, 27.80; H, 1.93; N, 5.41; S, 6.18; Hg, 38.7. Found: C, 27.53; H, 2.06; N, 5.45; S, 6.36; Hg, 36.7. Hg:S, 0.81; ***$CdCl_2$–2g***: yield: 77%. Calc. for $Cd_3Cl_6C_{26}H_{24}O_4N_4S_2$: C, 29.14; H, 2.24; N, 5.23; S, 5.98; Cd, 31.5. Found: C, 28.41; H, 2.52; N, 5.11; S, 5.85; Cd, 31.3. Cd:S, 1.63; ***$HgCl_2$–2g***: yield: 88%. Calc. for $HgCl_2C_{13}H_{12}O_2N_2S$: C, 29.33; H, 2.26; N, 5.26; S, 6.02; Hg, 37.7. Found: C, 29.48; H, 2.49; N, 5.34; S, 6.19; Hg, 39.3. Hg:S, 0.83; ***$CdCl_2$–2h***: yield: 95%. Calc. for $CdCl_2C_{12}H_9O_4N_3S$: C, 30.33; H, 1.90; N, 8.85; S, 6.74; Cd, 23.7. Found: C, 29.92; H, 2.17; N, 8.73; S, 6.67; Cd, 23.7. Cd:S, 1.17; ***$HgCl_2$–2h***: yield: 70%. Calc. for $HgCl_2C_{24}H_{18}O_8N_6S_2$: C, 33.72; H, 2.11; N, 9.83; S, 7.49; Hg, 23.5. Found: C, 33.11; H, 2.20; N, 9.82; S, 7.75; Hg, 23.7. Hg:S, 0.56; ***$CdCl_2$–2j***: yield: 86%. Calc. for $Cd_3Cl_6C_{22}H_{18}O_4N_6S_2$: C, 25.27; H, 1.72; N, 8.04; S, 6.13; Cd, 32.3. Found: C, 26.05; H, 2.10; N, 8.30; S, 6.40; Cd, 30.1. Cd:S, 1.36; ***$HgCl_2$–2j***: yield: 89%. Calc. for $HgCl_2C_{11}H_9O_2N_3S$: C, 25.44; H, 1.73; N, 8.09; S, 6.17; Hg, 38.7. Found: C, 25.69; H, 1.99; N, 8.22; S, 6.50; Hg, 37.5. Hg:S, 0.78; ***$CdCl_2$–2k***: yield: 44%. Calc. for $Cd_3Cl_6C_{26}H_{18}O_4N_4S_2F_6$: C, 26.47; H, 1.53; N, 4.75; S, 5.43; Cd, 28.6. Found: C, 26.09; H, 1.70; N, 4.71; S, 5.42; Cd, 27.8. Cd:S, 1.68; ***$HgCl_2$–2k***: yield: 72%. Calc. for $HgCl_2C_{13}H_9O_2N_2SF_3$: C, 26.63; H, 1.54; N, 4.78; S, 5.46; Hg, 34.2. Found: C, 25.82; H, 1.78; N, 4.71; S, 5.67; Hg, 32.5. Hg:S, 0.80.

2.2. Physical measurements

The EDS spectra were collected using an EDAX microanalyzer coupled to a scanning electronic microscope (SEM) Quanta 200 (FEY) operated at 20 keV. Elemental analyses were performed with a Leco automatic analyzer CHNS 932 model. ICP metal analyses were carried out with a plasma spectrometer Iris Intrepid from Thermo Elemental. The melting points were determined with a Reichert-Jung rheostat coupled to a Reichert-Thermovar binoculars and a RS-3.722 digital thermometer. The measured melting point values were compared with the corresponding thermogravimetric (TG) curves, which were collected under a nitrogen flow in a TA instrument thermobalance (TG-2950 model) operated in the high-resolution mode. ^{13}C CPMAS NMR spectra of both, ligands and complexes were recorded in a Bruker ASX300 (300 MHz) spectrometer.

Infrared spectra were recorded on a FT-IR spectrophotometer (from Atti Mattson, Genesis Series) in the 4000–400 cm^{-1} spectral range using Nujol mulls to avoid mechano-chemical reactions with the KBr [14]. IR spectra recorded in pressed KBr disks and of the compound dispersed on a KBr window were not similar. Raman spectra were collected by a capillary sample technique using 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 was used with an incidence angle of 60° on the metal surface when taking surface-enhanced Raman scattering (SERS) spectra.

3. Results and discussion

3.1. On the structure of the used ligands

The considered ligands are neutral molecules with acidic and basic sites. The interaction of these reactive sites within a given molecule determines its conformation (Fig. 2). Such interaction, when it takes place between neighboring molecules, serves to maintain the ligand in a condensed state, for instance, in the solid state [15] or to form complexes with other analog molecules and salts (discussed below).

Since Series **2** ligands concerns 3-monosubstituted 1-furoylthioureas, the available proton on N_3 is involved in an intra-molecular hydrogen bond interaction with the carbonyl group (Fig. 2). This has been confirmed by ^{1}H NMR data [13], Raman and IR spectra [2] and from the crystal structure of ligand **2b** [1]. Such interaction stabilizes an “S”-shaped conformation of C=S and C=O groups related to a maximum value of the O–S distance, two donor sites rich in electron density. This conformer could be appropriate for complex formation through the S atom because it remains practically free of steric impediment from the substituent groups and excludes the possibility of a chelating effect of both donor sites in the coordination process. The exception within this Series probably corresponds to compound **2j** due to the pyridyl nitrogen participation in a hydrogen bonding interaction with the N_1 proton, which forces the C=S and C=O groups to adopt an "U"-shaped conformation. This is supported by the ligand ^{1}H NMR spectrum in DMSO-d_6 solution [13] and its Raman and IR spectra in the solid state [2]. Another similar exception could be present in compound **2h** due to a bifurcated hydrogen bond of the N_3 proton with the $-NO_2$ and $-CO$ groups [16].

For Series **1** ligands, which concerns 3,3-disubstituted furoylthioureas, without proton available on N_3 to participate in hydrogen bonding intra-molecular interactions, an "U"-shaped conformation for the C=O and C=S groups (Fig. 1) is favored. Such conformation has been confirmed for compound **1e**, from its crystal structure [1].

In the formation of complexes between neutral ligands and salts the role of the salt anion is commonly ignored because the ligand-anion interaction is usually weak [17], except for highly polarizing anions [18]. While the metal ion interacts with the nucleophilic centers of the ligand molecule, the anion interaction takes place with the most positive ligand region [17]. For chloride such interaction could involve formation hydrogen bonds, in this case with the ligand acidic NH protons. Such hydrogen bonds involving the Cl^- anion have been observed, from the crystal structure, for some thiourea derivatives complexes with Cd chloride [19]. For the studied ligand–salt systems, the ligand reactivity might be dominated by its nucleophilic centers with a minor effect from the salt anion. This anion contributes to the complex stability as a whole through the formation of a hydrogen bonds network which link neighboring ligand molecules. From these considerations, the complexes to be studied could be considered as resulting from the ligand–salt interaction as a whole and not only through the involved metal atom.

3.2. *General features of the formed complexes*

When ethanolic solutions of the considered ligands and of $CdCl_2$ or $HgCl_2$ are mixed a slow advance of the complexation reaction is observed with formation of a precipitate. For some ligand–cadmium salt mixtures no formation of precipitate was observed. For these mixtures the ligand–salt interaction could be too weak to stabilize the complex in the solid state. Once separated and the excess of ethanol evaporated, the resulting precipitated complexes show morphologies that are characteristic of the involved ligand, according to their SEM images. For Series **2** ligands the solid complex usually appears as small needles, while with ligands from Series **1** it appears as globular particles (Fig. 3). This is observed for both $CdCl_2$ and $HgCl_2$ complexes. The mercury complexes were insoluble in common organic solvents while the cadmium ones were soluble in DMF and DMSO. The re-crystallization of the formed precipitates to obtain single crystals of good quality for XRD crystal structure determination is now in progress. From the gravimetric data the ligand–salt stoichiometry was preliminarily established (see Section 2.1).

In Table 1 are collected the values obtained for the metal to S atomic ratio, estimated from both elemental chemical-ICP metal analyses and a quantitative evaluation of EDS spectra. All the $HgCl_2$ complexes show a 1:1 metal–ligand ratio. The exception is the complex **$HgCl_2$–2h** (1:2 ratio). These values of metal–ligand ratio are similar to those reported for other complexes of metal salts with thiourea derivatives [20]. For the $CdCl_2$ complexes we obtained more varied metal–ligand ratios, probably related to the nature of the involved ligand (3-monosubstituted or disubstituted, N_3 substituents). Thus, the $CdCl_2$ complexes with ligands from Series **1** exhibit, without exception, the 2:1 metal–ligand ratio. However, those with ligands from Series **2** show the 3:2 ratio when the N_3 substituent is aromatic (except **$CdCl_2$–2h**, 1:1) and 1:1 when it is aliphatic. The exception in this last behavior corresponds to the **$CdCl_2$–2b** complex with a ligand–metal ratio of 2:1. The 2:1 ratio (four compounds) and the 3:2 one (four compounds) are quite atypical, but it is remarkable that they are present in eight of the eleven complexes obtained. There are reported polinuclear structures and clusters for complexes of cadmium salts with thiourea derivatives [19]. It seems, these complexes show certain trend to form polymorphic structures. A precise understanding of these metal–ligand ratios requires determination of the crystal structure for the formed complexes.

Table 1 also collects the chemical yield (%), estimated from the synthesis and the melting point for both ligands and complexes (°C). To those complexes obtained with high yields

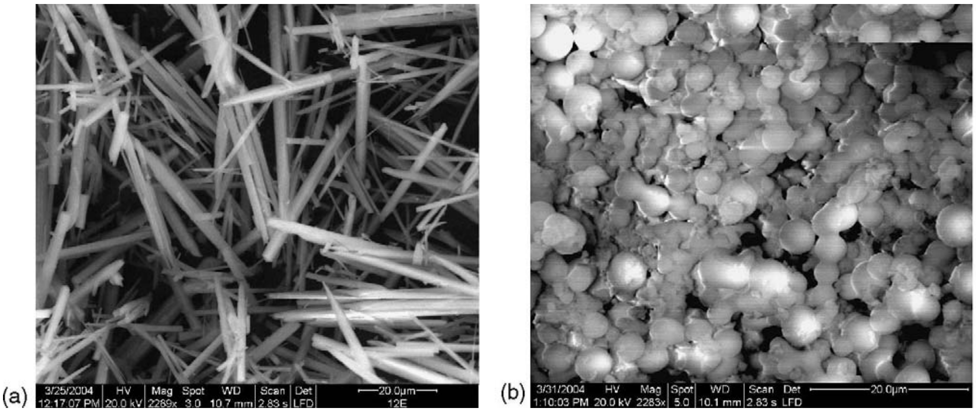


Fig. 3. SEM images of complexes **$CdCl_2$–2h** (a) and **$HgCl_2$–1c** (b). The obtained Series **2** complexes show an acicular morphology while Series **1** complexes appear as globular particles.

Table 1
$CdCl_2$ and $HgCl_2$ complexes with Series **1** and **2** ligands: chemical yield and physical data

Complex	Synthesis yield (%)	Melting point (°C)	Ligand complex	Colour	M:S atomic ratio
$CdCl_2$–1a	48	120–121	Decomposes at 163	White	2:1
$HgCl_2$–1a	45		71–72	Light yellow	1:1
$CdCl_2$–1b	39	78–79	Decomposes at 155	White	2:1
$HgCl_2$–1b	40		Melts at room temp.	Yellow ochre	1:1
$HgCl_2$–1c	42	140–141	98–99	Yellow	1:1
$HgCl_2$–1d	60	127–128	142–143	Cream	1:1
$HgCl_2$–1e	56	132–133	139–140	Cream	1:1
$CdCl_2$–1f	55	101–102	Decomposes at 166	White	2:1
$HgCl_2$–1f	32		83–84	Light yellow	1:1
$CdCl_2$–2b	47	70–71	Decomposes at 198	White	2:1
$HgCl_2$–2b	81		145–146	White	1:1
$CdCl_2$–2c	69	79–80	Decomposes at 183	Cream	1:1
$HgCl_2$–2c	75		110–111	Cream	1:1
$CdCl_2$–2d	71	129–130	Decomposes at 180	White	1:1
$HgCl_2$–2d	79		138–139	White	1:1
$CdCl_2$–2f	81	114–115	Decomposes at 221	White	3:2
$HgCl_2$–2f	80		124–125	White	1:1
$CdCl_2$–2g	77	114–115	Decomposes at 210	White	3:2
$HgCl_2$–2g	88		149–150	White	1:1
$CdCl_2$–2h	95	162–163	Decomposes at 235	Yellow	1:1
$HgCl_2$–2h	70		Decomposes at 250	Yellow	1:2
$CdCl_2$–2j	86	150–151	Decomposes at 205	White	3:2
$HgCl_2$–2j	89		Decomposes at 280	White	1:1
$CdCl_2$–2k	44	112–113	Decomposes at 215	White	3:2
$HgCl_2$–2k	72		114–115	White	1:1

usually the higher decomposition or melting temperatures were observed, except for **$CdCl_2$–2k**. It is remarkable that the ^{1}H NMR spectrum in DMSO of the free ligand **2k** [13] suggests the absence of the intra-molecular hydrogen bridge typical for the Series **2** ligands. These two parameters could be taken as indicators of the stability of the complex in the solid state. From these qualitative criteria, the complexes of higher stability are those formed with ligands from Series **2**. The complexes within this series are more stable, on heating, than the corresponding free ligand, which was attributed to the coordination bond with the metal and also to the formation of a network of hydrogen bonds through the salt anion. Complexes from Series **1** ligands show a less regular behavior. **$HgCl_2$–1b**, **–1c** and **–1f** melt at temperatures lower than that estimated for the corresponding free ligands. These three complexes are obtained with the lowest yields, 40, 42 and 32%, respectively, within the two series of considered complexes. As already mentioned, for some ligand–$CdCl_2$ mixtures within Series **1** no solid precipitate are obtained, suggesting a low stability of the corresponding complexes. Such behavior could be attributed to the structure adopted by the complex (polymeric or monomeric, discussed below) and other structural features as steric hindering and the nature (aliphatic or aromatic) of the N_3 substituents.

On heating, the ligands melt, preserving their composition and only at a higher temperature their decomposition takes place in a single step (Fig. 4). The melting point corresponds to the rupture temperature of inter-molecular interactions that maintain the ligand molecules together and ordered in the solid state. On complex formation, the coordination bond to the metal, and probably also the hydrogen bonds of neighboring ligand molecules with the salt anion appear as the main driving force for the complex stability in the solid state. On heating, the rupture of such hydrogen bonds is facilitated, however, the ligand molecules can remain bridged through the coordination bond to the metal atom, hindering, in some cases, the sample melting. This could explain why the formed complexes with $CdCl_2$, decompose without melt, which suggests that the complex crystallizes with a polymeric structure where neighboring ligand molecules remain bridged by both salt anion and cation. Well different features were observed for complexes with $HgCl_2$. They show, in general, a definite melting point followed of

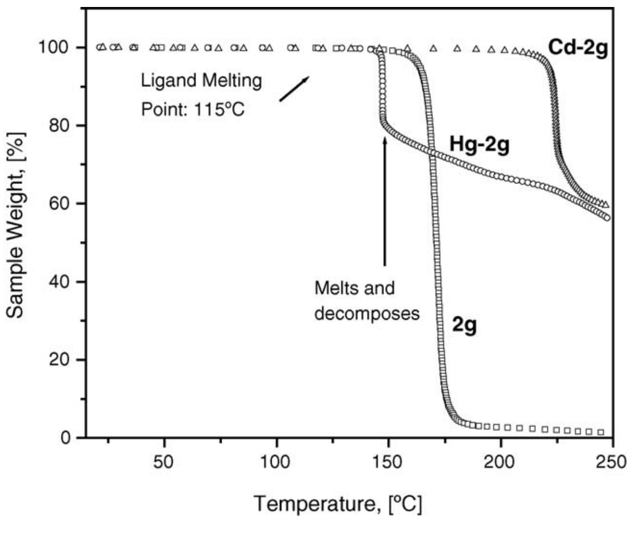


Fig. 4. TG curves of 1-furoyl-3-*o*-tolylthiourea (**2g**) and their $CdCl_2$ and $HgCl_2$ complexes. Complexes of the studied thiourea derivatives with $CdCl_2$ decompose without melt.

their thermal decomposition. This fact, together with their relatively low melting point, below 150 °C, suggests that the complexes involving $HgCl_2$ adopt a monomeric structure where the salt also serves to maintain the ligand molecules together but forming small clusters, which remain aggregated in the solid state through relatively weak interactions between them. On heating, such weak interactions are disrupted and the complex melts.

The TG curves provide additional and valuable information on the complex behavior on heating. For the free ligands, the sample melts without mass loss associated to decomposition, and at a higher temperature, it practically evaporates through a quasi-isothermic process (Fig. 4). For $CdCl_2$ the complex formation leads to certain ligand stabilization relative to its free state. Compared to the free ligand, the complex decomposes at higher temperature, suggesting the existence of a polymeric structure mediated by the salt, previously mentioned. However, for $HgCl_2$ both complex and ligand decompose at a similar temperature, which reveals a marked structural difference between these two families of complexes. Once the decomposition process begins, complexes of both $CdCl_2$ and $HgCl_2$, show similar features (Fig. 4), with successive mass loss related to the rupture of bonds around the N_2–C=S–M core. The first mass loss during the complex decomposition elapses through a quasi-isothermic process, in analogy with the free ligand behavior. In this first decomposition step the most volatile fraction of the substituent groups is lost, with formation of a pale yellow solid. The following steps in the decomposition process on heating are similar to those already reported for other thiourea derivatives complexes with salts [19]; procedure that has been used to obtain small (nanometric) particles of CdS and related semiconducting materials.

3.3. Vibrations used as sensor for the complex formation

Raman and IR spectra of thiourea and its derivatives usually result from a pronounced coupling of elemental motions within the molecule. On complex formation the most affected vibrations must be those involving motions of the N–C and C=S bonds and probably also the carbonyl stretching, ν(CO), which has proved to be a vibration very sensitive to the ligand conformation [2]. For N–C and C=S bonds the observed fundamentals involve six different of such 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; π(CS): out-of-plane bend. In compounds containing the thioamide group (HNCS) these fundamentals are known as “thioamide” bands: I–IV [20–22]. These bands have a large contribution from: ν(C–N) (I), ν(C–N) + ν(C=S) (II), ν(C–N) + ν(C=S) (III) and ν(C=S) (IV) motions and are usually reported around 1470, 1250, 1080 and 750 cm^{-1}, respectively [22]. The assignment of the bending modes usually is less conclusive and sometimes ignored. For thiourea, for instance, δ(NCN) has been estimated [23] and assigned [24] at different frequency values within the 610–400 cm^{-1} interval. For δ(C=S) the estimated and assigned values are close to 400 cm^{-1} [24], while π(CS) has been reported as a medium intensity band in the 636–570 cm^{-1} region [19,23].

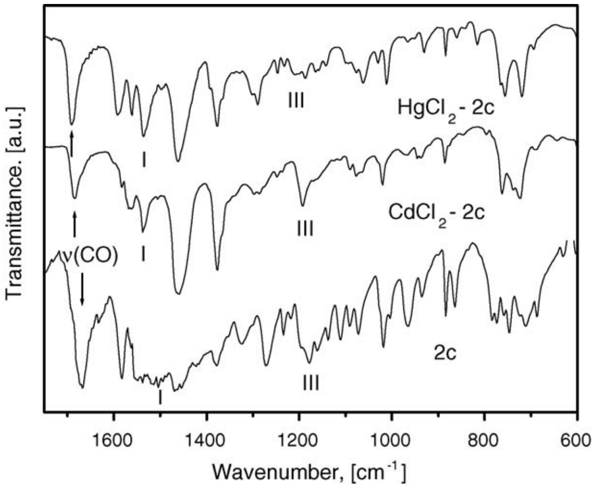


Fig. 5. FT-IR spectra of 1-furoyl-3-furfurylthiourea (**2c**) and their $CdCl_2$ and $HgCl_2$ complexes in the 1800–600 cm^{-1} region. Indicated are the carbonyl vibration, ν(CO), and the thioureido bands I and III.

The complex formation results from the interaction of the ligand with the metal salt as a whole, producing a global change of the electronic structure of both, particularly in the ligand. It is observed in the IR and Raman spectra as displacements and variations in the relative intensity of numerous bands (Figs. 5–7). On a metal coordination at S atom of a thiourea derivative a charge transfer from the ligand to the metal must be observed reducing the double bond character of the C=S bond. This charge transfer is usually related to the observed frequency shift of band IV on complex formation [5,6,21,22,25]. The coordination bond at the S atom induces a re-ordering of the electronic density within the ligand, which mainly affects the N_2–C–S core. In addition to the band IV displacement, the N–C bond gains in electron density, raising its bond character and changing the frequency of those fundamentals involving its stretching motion (thioamide bands I–III) (Fig. 5).

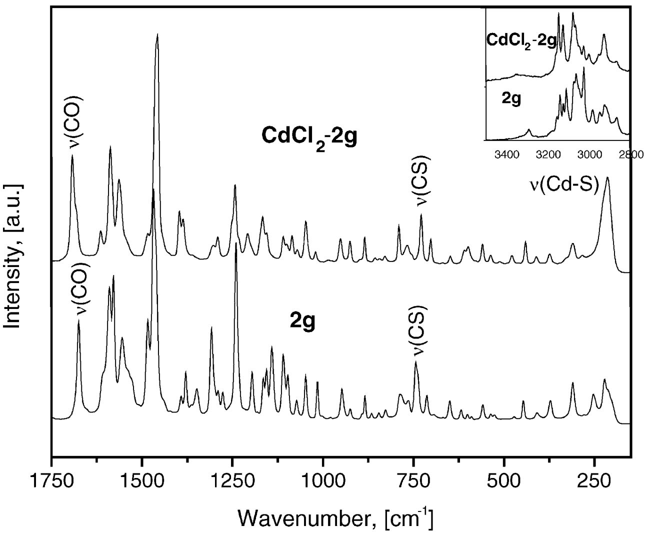


Fig. 6. FT-Raman spectra of 1-furoyl-3-*o*-tolylthiourea (**2g**) and its $CdCl_2$ complex in the 1800–200 cm^{-1} region. Inset: 3400–2800 cm^{-1} region, where the N—H stretching vibration appears.

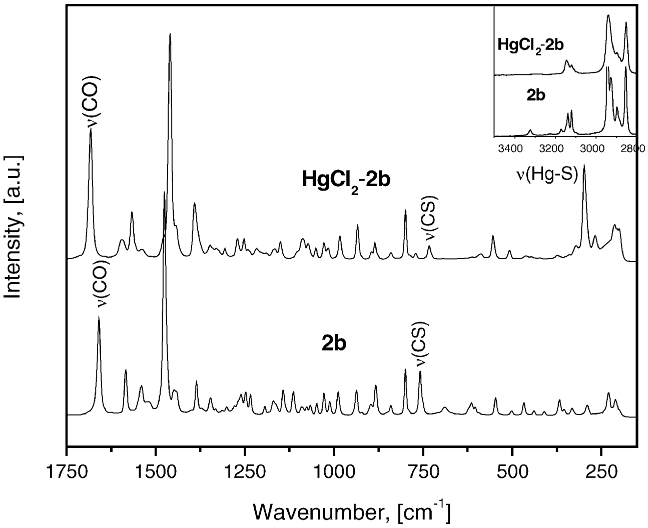


Fig. 7. FT-Raman spectra of 1-furoyl-3-cyclohexylthiourea (**2b**) and its $HgCl_2$ complex in the 1800–200 cm^{-1} region. Inset: 3400–2800 cm^{-1} region, where the N—H stretching vibration appears.

Probably the best sensor for the metal coordination at S atom of the thiocarbonyl group in the studied ligand–salt systems is the appearance of the metal–ligand stretching vibration, ν(M–S). This vibration has been found between 300 and 200 cm^{-1} for metal salts complexes with thiourea and related analogs [6,26]. Its absorption frequency could be used to evaluate the ligand–metal bond strength.

In principle, the ν(N—H) and δ(N—H) vibrations could be used as sensor of the complexation process, despite, their absorption frequency results from a combination of two opposite effects: (a) an increase in the N atom electronegativity when the thiocarbonyl group forms a coordination bond with the salt cation; (b) the participation of acidic NH protons in hydrogen bonds with the salt anion. This could explain the reported complexity for the vibrational spectra of thiourea and its complexes with salts in the spectral region where the ν(N—H) vibration falls and also the observed spectra dependence of the used salt anion [27].

In Raman and IR spectra of thiourea derivatives and their complexes a pronounced band overlapping appears, mainly due to vibrations from substituent groups. Despite the complexity of the spectra, those bands of higher sensitivity to the complex formation could be assigned comparing Raman and IR spectra from both, the ligand and the complex. In Raman spectra vibrations involving motions of heavy atoms (with an easily polarizable electronic structure, S and metal atoms, for instance), produce Raman dispersion peaks of relatively high intensity, while vibrations from light atoms are related to weak Raman signals. The inverse is valid for IR spectra where the band intensity is dominated by the dipole moment from the vibrating bonds. In this sense Raman and IR spectroscopies are complementary techniques. Comparing Raman and IR spectra the vibrational pattern of the studied series of 1-furoylthioureas (Series **1** and **2**) has been evaluated and the main bands related to motions within the N_2—C—S core assigned [2]. Such procedure is now used in the study of their complexes with $CdCl_2$ and $HgCl_2$. Particularly, IR spectra were used to evaluate the variation in those vibrations involving the motion of light atoms while the low frequency region, below 800 cm^{-1} was studied from Raman spectra. In this region fall those vibrations containing motions involving the heavy atoms.

3.4. IR spectra of the complexes

Fig. 5 shows typical IR spectra of the free ligand and of their complexes with $CdCl_2$ and $HgCl_2$. The IR spectra obtained are rich in absorption bands from vibrations within the substituent groups. In Table 2 are reported the absorption frequency of those IR bands that serve as sensor for the complex formation. The frequency values for bands I–III correspond to previous assignment of those fundamentals for the free ligands [2]. There are not significant variations in the IR frequencies of these bands related to the observed metal–ligand ratio and nature of the N_3 substitution in the thioureido core. The region of the N—H stretching vibrations appears with a pronounced overlapping due to intermolecular hydrogen bond interactions and interference with the C—H stretching modes from the sample support (Nujol) and also from δ(N—H) overtones. For that reason we have made the ν(N—H) assignments on base both spectra, IR and Raman (Figs. 6 and 7, insets). In Raman spectra, although the N—H stretching vibrations appear as week peaks, this region practically remains free of interferences. On complex formation the absorption pattern above 3200 cm^{-1}, assigned to weakly associated N—H protons shows a definite trend to a high frequency shift, which is interpreted as a weakening of their hydrogen bond interaction on complex formation. A positive shift of these absorptions is usually regarded as signifying that the ligand is not N-bonded [20]. The observed frequency shift is also accompanied by a lowering in the band intensities (Figs. 6 and 7, insets), probably related to the interaction of the weakly associated N—H with the salt anion. The absorption region 3159–3102 cm^{-1} assigned to the ν(N—H) motion from strongly associated N—H protons does not show a regular variation, probably related to the above-mentioned competitive effects of a higher N_1 electronegativity and the weakening of their hydrogen bond interaction on complex formation. For Series **2** ligands, for instance, the intra-molecular bridge N_3—H· · ·O=C— results slightly weaken but the S-shaped conformation for the ligand remains on the formed complex.

The observed absorption frequency for the carbonyl vibration, ν(CO) (Table 2) discards the possibility of metal coordination through the C=O group. The participation of the carbonyl group in the coordination process supposes a pronounced decrease in the ν(CO) absorption frequency, which was not observed except for **$CdCl_2$–2k**. It seems that the interaction between the ligand and the $CdCl_2$ in this complex is different with respect to the rest of the ligands of Series **2** (see Section 3.2). For the remaining ligands of both series, on complex formation the ν(CO) vibration increases its absorption frequency, which was attributed to a strong induced effect related to the metal coordination at S atom. The above-mentioned weakening of the N_3—H· · ·O=C— bridge for Series **2** ligands probably is related to this coordination induced effect. For free ligands, compounds

Table 2
Series **1** and **2** ligands and their CdCl$_2$ and HgCl$_2$ complexes: frequency of IR bands in 3400–1100 cm^{-1} region

Sample	ν_{NH}		$\nu_{\mathrm{C=O}}$	Thioureido bands		
				I	II	III
1a	3354(w), 3213(w)	3147(w), 3131(w)	1657(s)	1522(s)	[a]	1176(s)
CdCl$_2$–1a	3364(w), 3216(w)	3144(w), 3119(w)	1694(m)	1531(s)	[a]	1186(m)
HgCl$_2$–1a	3220(w)	3131(w), 3115(w)	1694(s)	1541(s)	[a]	1180(m)
1b	3361(w)	3137(w)	1667(s)	1531(s)	1353(w)	1177(s)
CdCl$_2$–1b	3367(w), 3282(w)	3118(w)	1693(m)	1538(s)	1349(w)	1186(s)
HgCl$_2$–1b	[a]	3131(w)	1698(s)	1545(s)	1353(w)	1182(m)
1c	3300(w)	3129(w), 3115(w)	1697(s)	1502(s)	[a]	[a]
HgCl$_2$–1c	3308(w)	3146(w), 3119(w)	1709(s)	1504(s)	[a]	[a]
1d	3371(w)	3136(w), 3117(w)	1709(s)	1525(s)	1348(w)	1195(m)
HgCl$_2$–1d	3385(w)	3129(w)	1718(s)	1527(s)	1344(w)	1204(m)
1e	3378(w)	3148(w), 3109(w)	1666(s)	1507(s)	1351(w)	1185(m)
HgCl$_2$–1e	3384(w)	3135(w), 3116(w)	1714(s)	1512(s)	1331(w)	1207(m)
1f	3371(w)	3151(w), 3111(w)	1674(s)	1507(s)	[a]	1187(s)
CdCl$_2$–1f	[a]	3149(w), 3114(w)	1693(m)	1522(s)	[a]	1187(s)
HgCl$_2$–1b	3374(w)	3145(w), 3115(w)	1703(s)	1536(s)	[a]	1219(m)
2b	3318(w)	3139(w), 3121(w)	1666(s)	1515(s)	1345(w)	1193(s)
CdCl$_2$–2b	3339(w)	3140(w), 3114(w)	1681(s)	1517(s)	1349(w)	1199(s)
HgCl$_2$–2b	3325(w)	3145(w), 3121(w)	1688(s)	1531(s)	1349(w)	1215(m)
2c	3270(w)	3133(w), 3114(w)	1667(s)	1507(s)	[a]	1178(s)
CdCl$_2$–2c	3318(w) 3266(w)	3148(w), 3121(w)	1685(s)	1537(s)	[a]	1192(s)
HgCl$_2$–2c	3261(w)	3147(w), 3123(w)	1691(s)	1537(s)	[a]	1209(s)
2d	3271(w)	3129(w), 3115(w)	1667(s)	1504(s)	1329(w)	1178(s)
CdCl$_2$–2d	3279(w)	3121(w), 3102(w)	1682(s)	1537(s)	1331(w)	1188(m)
HgCl$_2$–2d	3275(w)	3124(w)	1693(s)	1537(s)	[a]	1198(m)
2f	3355(w), 3293(w)	3142(w), 3122(w)	1669(s)	1525(s)	1354(w)	1166(s)
CdCl$_2$–2f	3348(w), 3302(w)	3148(w), 3124(w)	1681(s)	1536(s)	1352(w)	1176(m)
HgCl$_2$–2f	3350(w), 3301(w)	3147(w), 3119(w)	1692(s)	1538(s)	1339(w)	1169(m)
2g	3289(w)	3142(w), 3126(w)	1672(s)	1522(s)	[a]	1165(s)
CdCl$_2$–2g	3349(w), 3289(w)	3147(w), 3128(w)	1688(s)	1536(s)	[a]	1171(m)
HgCl$_2$–2g	3294(w)	3138(w), 3122(w)	1688(s)	1536(s)	[a]	1171(m)
2h	3399(w), 3255(w)	3147(w), 3129(w)	1681(s)	1507(s)	1352(w)	1165(m)
CdCl$_2$–2h	3405(w), 3255(w)	3150(w), 3125(w)	1701(s)	1522(s)	1351(w)	1179(m)
HgCl$_2$–2h	3391(w), 3259(w)	3136(w)	1694(s)	1531(s)	1346(w)	1181(m)
2j	3249(w)	3138(w), 3119(w)	1701(s)	1527(s)	1319(w)	1208(s)
CdCl$_2$–2j	3254(w)	3128(w)	1709(s)	1527(s)	1322(w)	1213(m)
HgCl$_2$–2j	3256(w)	3128(w), 3113(w)	1725(s)	1532(s)	1325(w)	1223(m)
2k	3321(w), 3274(w)	3151(w), 3129(w)	1667(s)	1531(s)	1336(w)	1179(s)
CdCl$_2$–2k	3322(w), 3275(w)	3159(w), 3129(w)	1649(s)	1535(s)	1333(w)	1200(s)
HgCl$_2$–2k	3323(w), 3277(w)	3163(w), 3139(w)	1692(s)	1536(s)	1333(w)	1190(s)

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

from Series **1** and **2** have the ν(CO) absorption in well-separated region due to the existence of that intra-molecular bridge. For Series **1** this vibration falls at the 1704–1652 cm^{-1} interval. While for Series **2** it is observed at relatively narrow spectral region, from 1675 to 1659 cm^{-1} [2]. For the formed complexes such regularity remains but with certain shift to higher frequencies (Table 2). Within Series **2** ligands the exception is found in the complexes formed with **2j**, which have its ν(CO) absorption above 1700 cm^{-1} (Table 2). This ligand adopts an “U”-shaped conformation of the C=S and C=O groups due to formation of a hydrogen bridge between pyridyl nitrogen and the N$_3$ proton. It seems, such intra-molecular bridge remains in the formed complex.

Below 1600 cm^{-1} fall the thioamide bands I–III (Fig. 5), which are particularly intense in IR spectra. This facilitates their identification within a region rich in IR absorptions. These bands contain the contribution from the ν(C–N) motion but strongly mixed with other vibrations, mainly from N–H bending and C=S stretching motions. In Table 2 are collected the observed frequency values for these bands. Since IR spectra were recorded on samples supported in paraffin (Nujol), in some cases band II was interfered by a band from paraffin around 1380 cm^{-1} and was not properly assigned. The bands I and III are found at higher frequencies in the IR spectra of the complexes respect to the free ligand. This expected increase in frequency can be explained as resulting from a higher double bond character of the ν(N–C) vibration upon complex formation. The positive frequency shifts are bigger for HgCl$_2$ complexes, due to the stronger bond with the mercury salt, and particularly, the strength of the Hg–S bond respect to the Cd–S one (discussed below).

Table 3
Series **1** and **2** ligands and their $CdCl_2$ and $HgCl_2$ complexes: frequency of Raman bands in 800–200 cm^{-1} region

Sample	Thioureido band IV	π(CS)	δ(CS)	δ(NCN)	$\nu_{\mathrm{Cd-S}}$
1a	699(m)	598(w)	369(w)	[a]	–
$CdCl_2$–1a	693(m)	607(w)	[a]	[a]	231(w)
$HgCl_2$–1a	690(m)	[a]	[a]	[a]	[a]
1b[b]	693(m)	530(w)	358(w)	305(w)	–
$CdCl_2$–1b	686(m)	[a]	[a]	[a]	235(w)
1c	710(m)	565(w)	356(w)	310(w)	–
$HgCl_2$–1c	702(m)	[a]	[a]	[a]	266(m)
1d	713(m)	551(w)	360(w)	292(w)	–
$HgCl_2$–1d	692(m)	546(w)	360(w)	322(w)	288(m)
1e	701(m)	557(w)	351(w)	291(w)	–
$HgCl_2$–1e	685(m)	557(w)	351(w)	[a]	290(m)
1f	709(m)	548(w)	357(w)	291(w)	–
$CdCl_2$–1f	709(m)	544(w)	358(w)	303(w)	228(w)
$HgCl_2$–1f	702(m)	534(w)	[a]	[a]	290(m)
2b	759(m)	547(w)	367(w)	289(w)	–
$CdCl_2$–2b	750(m)	549(w)	366(w)	305(w)	208(w)
$HgCl_2$–2b	733(m)	554(w)	[a]	[a]	298(m)
2c	749(m)	595(w)	355(w)	295(w)	–
$CdCl_2$–2c	736(m)	599(w)	359(w)	305(w)	221(m)
$HgCl_2$–2c	723(m)	599(w)	366(w)	[a]	297(m)
2d	750(m)	596(w)	356(w)	310(w)	–
$CdCl_2$–2d	737(m)	615(w)	[a]	307(w)	219(m)
$HgCl_2$–2d	724(m)	[a]	[a]	[a]	295(m)
2f	743(m)	535(w)	378(w)	340(w)	–
$CdCl_2$–2f	726(m)	536(w)	382(w)	357(w)	212(m)
$HgCl_2$–2f	710(m)	535(w)	379(w)	[a]	302(m)
2g	744(m)	558(w)	372(w)	310(w)	–
$CdCl_2$–2g	728(m)	559(w)	373(w)	310(w)	214(m)
$HgCl_2$–2g	721(m)	565(w)	374(w)	326(w)	298(m)
2h	760(m)	530(w)	363(w)	301(w)	–
$CdCl_2$–2h	747(w)	531(w)	367(w)	293(w)	229(m)
$HgCl_2$–2h	746(m)	536(w)	370(w)	[a]	260(m)
2j	796(m)	593(w)	358(w)	305(w)	–
$CdCl_2$–2j	791(w)	604(w)	360(w)	312(w)	207(m)
$HgCl_2$–2j	782(m)	[a]	360(w)	307(w)	285(m)
2k	748(m)	537(w)	375(w)	311(w)	–
$CdCl_2$–2k	737(m)	544(w)	372(w)	317(w)	222(m)
$HgCl_2$–2k	719(m)	540(w)	379(w)	326(w)	300(m)

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

[a] Not assigned.

[b] The Raman spectrum of its complex with $HgCl_2$ was not possible to be recorded.

3.5. Raman spectra of the complexes

Figs. 6 and 7 show typical Raman spectra for the studied thiourea derivatives and their complexes with $CdCl_2$ and $HgCl_2$. Table 3 contains the frequency of the main Raman dispersion lines observed in the 800–200 cm^{-1} spectral region, for both ligands and complexes, and their assignment. These Raman lines correspond to thioamide band IV (with a dominant contribution from ν(C=S)), π(C=S), δ(C=S), δ(N–C–N) and ν(M–S). This last vibration appears as the most conclusive evidence on the metal coordination to the thiocarbonyl group and its frequency results particularly informative on the strength of the metal–ligand bond. These absorption frequency values agree with those reported in the literature [26]. The assignment proposed in Table 3 has a relatively high level of certainty, particularly for ν(C=S) (band IV) and ν(M–S) vibrations, which produce medium intensity Raman signals, well resolved from the spectra background. In Raman spectra this region remains practically free of vibrations from the substituent groups.

On complex formation, band IV shows the expected frequency downshift, which amounts, on average, 9 and 19 cm^{-1} for $CdCl_2$ and $HgCl_2$, respectively. Similar shifts have been reported for analogous complexes with other thiourea derivatives [5,22,25]. This difference in frequency displacement between these two salts is probably related to a best ligand–salt softness coupling for $HgCl_2$, between Hg(II) (a soft acid) and the S atom from the thiocarbonyl group (a soft base). The low energy unoccupied orbitals on the mercury ion appear particularly appropriate to receive electrons from the thiocarbonyl group through the S atom, removing a relatively large electron density from the C=S bond and lowering the ν(CS) stretching frequency. This vibration falls in slightly different spectral region for the free ligands. It was observed at 713–693 cm^{-1} and 796–723 cm^{-1} intervals for Series **1** and **2**, respectively [2]. Such regularity prevails in the formed complexes where for Series **1** this vibration is observed from 709 to 683 cm^{-1} while for Series **2** it is found from 747 to 706 cm^{-1} (Table 3). The exception corresponds to 2j where in the free ligand and its complexes, the band IV is observed at relatively high frequency. It seems that the hydrogen bond bridge between N_1 proton and the pyridyl nitrogen leads to a higher electronegativity of N_1, restricting the thioamide resonance and favoring the retention of a high electron density in the C=S double bond, even in the formed complex. An analogous interpretation can be used to understand the relatively high frequency values of this vibration (band IV) in the remaining complexes from Series **2** ligands due to the bridge formed between the carbonyl group and the N_3 proton. Within the complexes formed with a given series of ligands, certain substituent dependence was observed. For instance, within Series **1** the complex formation with $HgCl_2$ is related to a relatively small ν(CS) frequency shift, particularly for aromatic substituent at N_3 (**1c–f**) and with $CdCl_2$ no solid complexes were obtained except for **1f** but without a definite band IV frequency displacement (Table 3). For an aliphatic substituent at N_3 (**1a** and **b**) the ligand forms a solid precipitate also with $CdCl_2$.

The frequency shift of band IV on complex formation is usually accompanied of a reduction in its intensity (Figs. 6 and 7) which could be attributed to the charge removing from the C=S bond due to the coordination bond with the metal. This effect is more pronounced for those complexes formed with $HgCl_2$ corroborating the higher softness coupling between this salt and the studied ligands. The intensity reduction of this band by the formation of a coordination bond at S atom provides an additional criterion for its assignment.

According to the ν(M–S) vibration, the complexes formed with $CdCl_2$ are weaker than those obtained with $HgCl_2$, for both Series **1** and **2** ligands. For complexes from Series **2** ligands and $CdCl_2$ this vibration is observed from 229 to 207 cm^{-1} while for $HgCl_2$ it is found at higher frequencies, from 302 to 260 cm^{-1}. In average, these complexes have their ν(M–S) vibration at 216 and at 292 cm^{-1}, respectively, which means a frequency difference of 76 cm^{-1}. It seems that the absorption frequency of this vibration depends of the fitting between the softness of the involved basic and acidic species. In accordance with this criterion, the most stable complexes at the S site must be those formed with $HgCl_2$. For this salt and Series **1** ligands the ν(M–S) motion for the formed complexes appears at a high frequency, on average at 283 cm^{-1}. Within a given series this metal–ligand stretching also shows certain dependence on the substituent at N_3 (Table 3), confirming that the ligand nucleophilic character at the S atom results modulated by the substituent nature. The peaks from the ν(M–S) motion results more intense for complexes formed with $HgCl_2$ as a consequence of the great electronic density of the mercury atom that acts as a strong center of dispersion.

Below 600 cm^{-1} the Raman spectra show several low intensity peaks (Figs. 6 and 7). For the free ligand, comparing IR and Raman spectra, those peaks with a dominant contribution from π(CS), δ(CS) and δ(NCN) motions were tentatively assigned [2]. Such assignment is now extended to their complexes with $CdCl_2$ and $HgCl_2$. Unlike thioamide band IV and the ν(M–S) motion, these bending modes do not show a regular variation on complex formation, probably due to their mixture with other low frequency motions.

As in the IR spectra, some other Raman peaks of the ligands vary their position and intensity on the complexation. This fact supports the above-mentioned hypothesis regarding to some global change generated in the electronic structure of the ligand on complex formation with the salt.

3.6. ^{13}C CPMAS NMR spectra

The free ligands are soluble in DMSO facilitating their ^{1}H and ^{13}C NMR study in DMSO-d_6 [13]. However, their complexes with $CdCl_2$ and $HgCl_2$ are unstable in this solvent, probably due to its interaction with the salt, inducing the complex decomposition. From this fact, representative samples of complexes with $CdCl_2$ were studied using ^{13}C CPMAS NMR spectra. These spectra appear as a set of broad peaks, with certain overlapping in some spectral regions. Fortunately, those peaks corresponding to carbonyl and thiocarbonyl groups can be unequivocally identified, and their chemical shift estimated. In Table 4 are collected the ^{13}C chemical shift for these two groups, before and after the complex formation. Data for the free ligands in DMSO-d_6 solution [13] have been included for comparison. The ^{13}C chemical shifts for the free ligand, both in solution and in the solid state are similar, suggesting that the aggregation state has a minor effect on the electronic structure of the ligand. It seems, those conformers present in DMSO solution, related to certain intra-molecular interactions, prevail in the solid state.

Upon complexation with $CdCl_2$ the ^{13}C signal from C=S carbon shifts to low frequency compared to the free ligand (Table 4). That shift is attributed to the charge re-distribution within the thiourea core on formation of the coordination bond. The electron donation from the ligand to the metal leads to a decrease in the electron density in the C=S bond, which induces an N→C charge movement, favoring certain double bond character for the N–C bond. However, the observed shifts are relatively small, which was interpreted as formation of a relatively weak coordination bond. This result agrees with the above-discussed information derived from Raman spectra of both free ligands and complexes. The higher shifts of this signal are observed for complexes with **2h** and **2j** ligands. For these ligands, the $-NO_2$ and pyridyl group, respectively, are involved in a hydrogen bond interaction with the N_1 proton. This favors an increase in the electronegativity of this nitrogen atom affecting the electron density around the thiocarbonyl carbon. The ^{13}C NMR signal from the carbonyl group appears with a low sensitivity to the coordination bond at the S atom, with an irregular variation within the studied ligands and complexes, unlike the observed behavior from IR and Raman spectra.

Table 4
Series **1** and **2** ligands and some of their complexes with $CdCl_2$: ^{13}C CPMAS NMR chemical shifts (δ), in ppm for C=O and C=S groups

Sample	^{13}C CPMAS NMR (ppm)		^{13}C NMR in DMSO-d_6[a] (ppm)	
	δ(C=O)	δ(C=S)	δ(C=O)	δ(C=S)
1a	155.9	176.9	153.8	177.5
$CdCl_2$–1a	156.3	176.4	–	–
1b	153.9	178.7	154.4	179.1
$CdCl_2$–1b	157.8	176.9	–	–
2c	158.0	179.8	157.3	179.9
$CdCl_2$–2c	158.2	179.3	–	–
2f	157.0	175.7	157.2	178.4
$CdCl_2$–2f	158.1	175.6	–	–
2g	156.5	176.3	157.4	179.3
$CdCl_2$–2g	157.9	175.5	–	–
2h	157.3	181.2	157.3	180.3
$CdCl_2$–2h	156.9	177.2	–	–
2j	153.6	178.9	157.3	178.0
$CdCl_2$–2j	153.3	175.1	–	–

[a] For comparison, data for the free ligands in DMSO-d_6 solution [13] have been included.

3.7. Correlation of Raman and IR spectra of the complexes with the reported behavior of the ligands as ionophores

The studied thiourea derivatives have been tested as ionophores in ion selective electrodes for Cd(II) and Hg(II) [1]. The best performance is reported for compounds of Series **2**, according to their sensitivity. This result agrees with those observed in Raman spectra, because the change in the ν(CS) stretching frequency of the ligand on complex formation appears more significant (a stronger complex is probably formed) for compounds of this Series. Thus, the obtained complexes of $HgCl_2$ with ligands of Series **2** exhibit double negative shift of the band IV respect to those formed with ligands from Series **1** (average from 24 to 12 cm^{-1}). For $CdCl_2$ complexes the same regularity is observed (average from 12 to 4 cm^{-1}). This also agrees with the higher chemical yield during the complex synthesis for the two salts with ligands from Series **2**.

According to the above-discussed experimental facts, the suitability of a given thiourea derivative, within the studied series of ligands, as ionophore in ISEs applications, could be estimated from the following parameters on complex formation: (a) frequency and intensity of the ν(C=S) and ν(M–S) vibrations in the Raman spectra; (b) frequency displacement of the bands I–III; (c) chemical yield obtained during the complex synthesis, but with a minor predictive value because this parameter shows certain dependence of other ligand features (e.g. steric factor, solubility). Such information could be used for a preliminary selection of a given ligand as ionophores for the studied metal ions (Cd(II) and Hg(II)).

4. Conclusions

The studied series of 3-monosubstituted and 3,3-disubstituted 1-furoylthioureas behave as neutral ligands to form complexes with $CdCl_2$ and $HgCl_2$. These ligands are neutral molecules with acidic and basic sites, which favor their interaction with both, the salt anion and cation, stabilizing the formed complexes. According to IR and Raman spectra the strongest metal–ligand interaction is observed for complexes with $HgCl_2$, probably related to an optimal fitting between the softness of the involved acidic and basic species. The relatively low thermal stability of $HgCl_2$ complexes, compared with those formed with $CdCl_2$ could be attributed to a different packing in the solid state, for instance, as monomeric units, instead of the polymeric structure expected for these last ones. On complex formation those intra-molecular hydrogen bridges observed in the free ligand in solution are preserved reducing the possibility of the carbonyl group participation in the complexation process. The IR, Raman and NMR data obtained corroborate this ligand behavior. The obtained structural information on the studied $CdCl_2$ and $HgCl_2$ complexes with 1-furoylthioureas helps to understand the reported behavior of these ligands in ion selective electrodes.

Acknowledgements

O.E.H. thanks Faculty of Sciences (University of Cadiz, Spain), through its PhD program, the access to experimental facilities. E.R. acknowledges the financial support provided by CLAF to carry out research activities on molecular materials. E.O.S acknowledges PROMEP project given by Hidalgo State Autonomous University (Mexico). The authors thank C. Vazquez from IIM (UNAM, Mexico) for TGA data acquisition.

References

[1] E. Otazo-Sánchez, L. Pérez-Marín, O. Estévez-Hernández, S. Rojas-Lima, J. Alonso-Chamarro, J. Chem. Soc., Perkin Trans. 2 (2001) 2211.
[2] O. Estévez-Hernández, E. Otazo-Sánchez, J.L. Hidalgo-Hidalgo de Cisneros, I. Naranjo-Rodríguez, E. Reguera, Spectrochim. Acta A 62 (2005) 966.
[3] L. Beyer, E. Hoyer, H. Hartman, J. Liebscher, Z. Chem. 21 (1981) 81.
[4] P. Muhl, K. Gloe, F. Dietze, E. Hoyer, L. Beyer, Z. Chem. 26 (1986) 81.
[5] V. Carcu, M. Negoiu, T. Rosu, S. Serban, J. Therm. Anal. Calorim. 61 (2000) 935.
[6] D. Gambino, E. Kremer, E.J. Baran, Spectrochim. Acta A 58 (2002) 3085.
[7] K.R. Koch, Coord. Chem. Rev. 216–217 (2001) 473.
[8] L.C.R. dos Santos, J.Q. Caluete, A.G. de Souza, Thermochim. Acta 292 (1997) 71.
[9] V. Venkataramanan, M.R. Srinivasan, H.L. Bhat, J. Raman Spectrosc. 25 (1994) 805.
[10] V. Venkataramanan, H.L. Bhat, M.R. Srinivasan, P. Ayyub, M.S. Multan, J. Raman Spectrosc. 28 (1997) 779.
[11] M. Stoev, S. Ruseva, B. Keremidchieva, Monatsh. Chem. 125 (1994) 1215.
[12] M. Stoev, S. Ruseva, Monatsh. Chem. 125 (1994) 599.
[13] E. Otazo-Sánchez, P. Ortiz-del-Toro, O. Estévez-Hernández, L. Pérez-Marín, I. Goicochea, A. Cerón-Beltrán, J.R. Villagomez-Ibarra, Spectrochim. Acta A 58 (2002) 2281.
[14] J.E. Stewart, J. Chem. Phys. 26 (1957) 248.
[15] P. Bombicz, I. Mutikainen, M. Krunks, T. Leskelä, J. Madarász, L. Niinistö, Inorg. Chim. Acta 357 (2004) 513.
[16] A. Dago, M.A. Simonov, E.A. Pobedimskaya, A. Martin, A. Macías, Kristallografiya 32 (1987) 1024.
[17] P. Ortiz, J. Fernández-Bertrán, E. Reguera, Spectrochim. Acta A 61 (2005) 1977.
[18] J. Fernández, E. Reguera, P. Ortiz, Spectrochim. Acta A 57 (2001) 2607.
[19] M.J. Moloto, M.A. Malik, P. OïBrien, M. Motevalli, G.A. Kolawole, Polyhedron 22 (2003) 595.
[20] Z. Popovic, D. Matkovic-Calogivic, Z. Soldin, G. Pavlovic, N. Davidovic, D. Vikic-Topic, Inorg. Chim. Acta 294 (1999) 35.
[21] A. Moshen, M.E. Omar, S.A. Osman, Pharmazie 28 (1973) 30.
[22] E.S. Raper, J.R. Creighton, N.R. Bell, W. Cleg, L. Cucurull-Sánchez, Inorg. Chim. Acta 277 (1998) 14.
[23] Y. Mido, I. Kitagawa, M. Hashimoto, H. Matsura, Spectrochim. Acta A 55 (1999) 2623.
[24] A. Vijay, D.N. Sathyanarayana, Spectrochim. Acta A 49 (1993) 1565.
[25] G.M.S. El-Bahy, B.A. El-Sayed, A.A. Shabana, Vib. Spectrosc. 31 (2003) 101.
[26] R.H. Prince, Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, p. 56.
[27] J.M. Alía, H.G.M. Edwards, M.D. Stoev, Spectrochim. Acta A 55 (1999) 2423.