New Complexes of Zn(II), Cd(II) and Hg(II) with Ligand Derived from 1-(3,5-diiodo, 2 -hydroxy, 4- methyl phenyl), 2-phenyl sulfanyl ethanone

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In this paper are presented the conditions to obtain several new complexes through the interaction of Zn(II), Cd(II) and Hg(II) with 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone in the molar ratio of 1:2. Also, their characterization was performed by chemical analysis, thermogravimetry, X-ray diffraction and IR absorption spectroscopy. The new complexes crystallize in the monoclinic system with Zn(II), Cd(II) or Hg(II) tetracoordinated as central atoms in tetrahedral structures. The obtaining reactions of these complexes can be used in gravimetric determination of Zn(II), Cd(II) and Hg(II) with an error of ± 0.25%.

Keywords: zinc(II), cadmium(II), mercury(II), 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone, precipitating reagent

Complexes obtained through the interaction of Zn(II), Cd(II) or Hg(II) with 1-(3,5- diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone belong to the category of coordination compounds achieved through the coordinative bonds of the functional group of $\rangle C=O$ and *-0H* bound to the benzene nucleus in α position. Having functional groups through which the coordinative bonds can be achieved, these complexes present various practical applications especially in gravimetric determination of some metallic cations [1-7].

In this paper is presented the synthesis and the study of the complex compounds obtained from the reactions between 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone and each one of Zn(II), Cd(II) and Hg(II) cations in a 2:1 combination ratio of the reactants. The obtained reaction products were investigated by chemical analysis, thermogravimetry, IR absorption spectroscopy and X-ray diffraction. Based on the reactions between ligand and Zn(II), Cd(II) or Hg(II) in the molar ratio of 2:1, complex compounds were obtained. These compounds have as central atoms cations tetracoordinated with oxygen atoms provided by the groups >C=O and -OH from the ligand molecule. The studied compounds present relatively high thermal stability due to begining to decompose at temperatures very close to 200°C. Based on the X-ray diffractograms, it was determined that the studied new compounds crystallize in monoclinic system.

Given the reactions of 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone ligand with Zn(II), Cd(II) or Hg(II) cations yield insoluble and stable compounds up to near 200°C, these reactions can be applied for determining quantitatively the respective cations. Moreover, their reactions take place under normal conditions with 100% efficiency, and the formed precipitates can be easily separated by filtration.

Experimental part

The coordinative compounds presented in this work were obtained according to the methods described in literature [6-12]. Thus there were prepared 0.2 M solutions of reactants using water as solvent for $ZnCl_2$, $CdCl_2$ and $HgCl_2$, and respectively a 1:1 (in volumes) mixture of ethylic alcohol (98%) and water for 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone (HL).

The synthesis of the studied compounds was carried out by mixing and stirring 200 mL solution of HL ligand with 100 mL solution of $ZnCl_2$, $CdCl_2$ or $HgCl_2$.

Being insoluble, the reaction products were separated by filtration, washed on the funnel vacuum nozzle and then dried at room temperature in an exicator.

Under the mentioned conditions, the efficiencies of reactions are practically 100%. All the obtained compounds are white-colored solids. Contents of C, H, S and Zn(II), Cd(II), Hg(II) respectively were determined for each obtained compound by using the appropriate chemical method [1, 2].

The thermal stability of the studied compounds was determined by means of a Q1500D (MOM Budapesta) derivatograph that records simultaneously the weight-loss curve (TG) and its derivative curve (DTG) as well as the temperature variation curve (T).

A 100 mg quantity of each investigated compound was introduced into a ceramic crucible and heated up to a temperature of 1000°C in air atmosphere. The heating rate was 10°C/min. The recorder was set at the following values: TG - 50μV, DTG-2.5 mV and T-500 μV. Al_2O_3 calcinated at 1200°C was used as reference material.

The absorption spectra in the IR range of solid samples of the synthesized compounds and HL ligand were recorded between 200 and 4000 cm^{-1} using a FTIR 660 Plus spectrometer and KBr pellet technique.

X-ray diffractograms were obtained using solid samples in the angular range of 2θ between 5 and 60^0 and a step of 0.1°/s, at room temperature by means of a Siemens D-500 diffractometer using Cu (K_α) radiation filtered by Ni. The anode voltage and current intensity were 40 KV and 100 mA respectively. The diffractometer is provided with data acquisition system and specialized software. Thus, the index of diffractograms and data processing were

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processed with Treor, Difrac-at, Crystal softwares according to the literature.

Results and discussions

According to the stoichiometry of the synthesis reaction and the chemical analysis of the investigated compounds, to each central atom, such as Zn(II), Cd(II) or Hg(II), correspond two anions of 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone ligand. The elemental composition of the studied compounds determined with a maximal error of ±0.32% is presented in table 1 and corresponds to the formula $M(C_{15}H_{11}O_2SI_2)_2$.

Reactions of thermal decomposition of the coordinative compounds presented in this work are of the following type:

$$A(s) \rightarrow B(s) + C(g) \quad (1)$$

In the derivatograms of the investigated compounds can be observed that the thermal decomposition take place on several stages forming some instable intermediary products that pass finally in more stable products, such as oxides in case of ZnL_2 and CdL_2, respectively metallic mercury that passes in vapor state in case of HgL_2. The stages of the thermal decomposition of the investigated compounds are presented in table 2.

The kinetic studies of the heterogeneous thermal decomposition reactions can be performed by several methods, such as thermogravimetric methods that employ the data obtained by recording T, TG and DTG curves with the aim of a derivatograph [13-15].

In contrast to the thermal isotherms, thermogravimetric methods need a continuous heating, the temperature of the investigated system increases in time according to a linear function, $dT/dt = \beta$ [13].

Freeman-Carrol method [14] was employed to determine the reaction order and activation energy. Values of reaction order and activation energy corresponding to the thermal decomposition of ZnL_2 and CdL_2 compounds are presented in table 3.

We mention that in case of HgL_2 thermal decomposition the values of reaction order and activation energy cannot be calculated because of TG and especially DTG curves, which present very high slopes that, do not allow the application of Freeman-Carrol method.

Thermal decomposition processes in gas-solid system are generally characterized by reaction order values ranged between 0 and 1. Numerous examples of this kind are mentioned in literature [3, 5, 6, 12-16]. Reaction order values between 0.75 and 0.88 (table 3) were obtained for the thermal decomposition of the coordinated compounds presented in this work.

The fractional values of reaction order are due to the fact that proper chemical reactions are not favored by mass transport phenomena of the volatile compounds through solid, interphase phenomena or vaporization phenomena of the volatile component, taking place at the free surface of the solid compound. The chemical reaction could take place with no influence from the above-mentioned factors only at the highest dispersion – molecular dispersion. Thus, increasing the dispersion degree, the reaction order tends to higher values, going to the value 1. In case of multi-stage thermal decomposition of the investigated compounds, the increase of the dispersion degree is achieved by the chemical reaction itself by eliminating the volatile component, which means, in fact, a thinning of the layer gases have to pass through. Hence, the reaction order of the first stage of thermal decomposition must be lower than in the following stages. This conclusion is in good agreement with the values of reaction order reported also here by other authors [5, 12-16].

IR absorption spectra of the studied ligand and complexes allow one to obtain important information on the chemical bonds of the central atoms Zn(II), Cd(II), Hg(II)) with some atoms of the ligand.

In the region of low frequencies of the spectra (400–1500 cm^{-1}) occur both bands corresponding to valence vibrations of simple bonds, such as C-C, C-O, Zn-O, Cd-O, Hg-O and bands corresponding to deformation vibrations of various bonds. Bands with frequencies of 475 cm^{-1}, 460 cm^{-1} and 430 cm^{-1} are attributed to the stretch frequencies: ν_{Zn-O}, ν_{Cd-O}, and ν_{Hg-O} respectively.

Observed in the region 1228-1285 cm^{-1} in the ligand spectrum, the bands of vibration frequencies belonging to

Table 1
ELEMENTAL COMPOSITION OF STUDIED COMPOUNDS (%)

Compound	C		H		S		M(II)		Molecular mass	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
ZnL_2	33.16	33.30	2.31	2.22	5.83	5.92	5.93	5.86	1083.19	1081.0
CdL_2	31.62	31.85	2.21	2.12	5.75	5.66	9.82	9.94	1132.9	1130.2
HgL_2	24.53	24.63	1.97	1.97	5.33	5.25	16.31	16.46	1216.8	1218.3

Table 2
STAGES OF THERMAL DECOMPOSITION OF THE INVESTIGATED COMPOUNDS

Compound	Range temperatures of thermal decomposition stages (°C)	
	Stage I	Stage II
ZnL_2	210-340	340-510
CdL_2	225-355	355-545
HgL_2	195-360	-

Table 3
VALUES OF ORDER REACTION AND ACTIVATION ENERGY

Compound	Reaction order		Activation energy (kJ/mol)	
	Stage I	Stage II	Stage I	Stage II
ZnL_2	0.75	0.88	129.5	168.5
CdL_2	0.80	0.85	138.9	186.8

C-O group shift towards higher wavelengths, and become less intense in the spectra of the investigated complexes.

Stretch (valence) vibrations of carbonyl group correspond to an intense characteristic band having its maximum at 1720 cm^{-1} in ligand. The maximum occurs in the investigated compounds at 1660 cm^{-1}, 1645 cm^{-1} and 1620cm^{-1} corresponding to ZnL_2, CdL_2 and HgL_2 respectively. This supports that the central atom of Zn(II), Cd(II) or Hg(II) coordinates with the oxygen atom in the carbonyl group: M←O=C.

Due to the fact that IR absorption spectra of ZnL_2, CdL_2 and HgL_2 complexes are very similar; we present here only the spectrum of ZnL_2 complex (fig. 1).

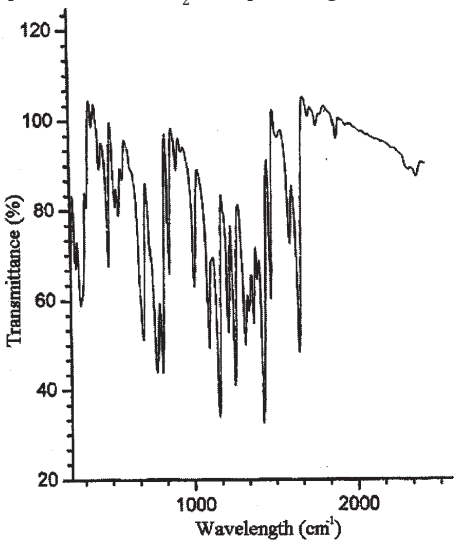

Fig. 1. IR absorption spectrum of ZnL_2 complex.

Absorption bands in the range 1225-1282 cm^{-1} result from stretch vibrations of the phenolic group (C-O). OH phenolic group absorption in *orto* position is located at 3284-3275 cm^{-1} and disappears in the investigated complexes.

For phenols, the most important band [17-21] is located within the range of 1140-1230 cm^{-1} (ν_{C-OH}) and disappears in the investigated compounds due to the substitution of hydrogen atom with a central atom, such as Zn(II), Cd(II) or Hg (II).

In conclusion, it can be stated that each central atom is bound by an oxygen atom in the phenolic group by substituting the hydrogen atom with Zn(II), Cd(II) or Hg (II), and further these central atoms coordinate with carbonyl group, M←O=C, resulting in stable cycles of 6 atoms. Due to the fact that each central atom is bound to two ligands, it results that these central atoms are tetracoordinated (two bonds to each ligand are achieved). Taking into account the external electronic structure of central Zn^{2+}, Cd^{2+} or Hg^{2+} atoms as $(n-1)d^{10}ns^0np^0$, the four bonds are achieved through the sp^3 hybrid orbitals oriented toward the corners of a tetrahedron [3]. This means the structure of the investigated compounds corresponds to that represented in figure 2.

Ligand diffractogram shows that this presents an orthorhombic symmetry having the values of *b* and *c* parameters of the elemental cell very close in comparison with *a* parameter that is higher (table 4), [22, 23].

By indexing the diffractograms of the coordination compounds ZnL_2, CdL_2, and HgL_2, the type of crystalline systems and values of elemental cell parameters were determined (figs. 3-5), [22, 23].

In table 5 are listed the values of elemental cell parameters corresponding to the investigated complexes (ZnL_2, CdL_2 and HgL_2).

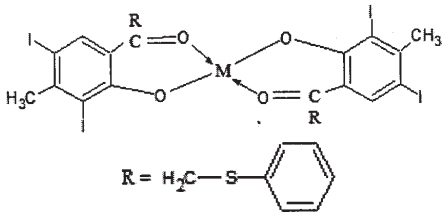

Fig. 2. Structure of complexes M[1-(3,5-diiodo, 2-oxo, 4-methyl phenyl), 2-phenyl sulfanyl ethanone]$_2$, M = Zn(II), Cd(II), Hg(II)

Table 4
PARAMETER VALUES OF ELEMENTAL CELL OF 1-(3,5-DIIODO, 2-HYDROXY, 4-METHYL PHENYL), 2-PHENYL SULFANYL ETHANONE LIGAND

Elemental cell parameters	Values obtained by indexation
a (Å)	13.0134
b (Å)	9.5810
c (Å)	9.7968
α	90°
β	90°
γ	90°
Elemental cell volume (Å^3)	1221.4

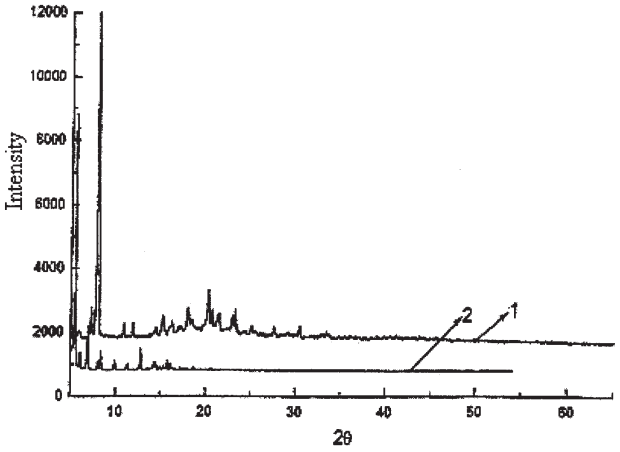

Fig. 3. Difractograms of HL (1) and ZnL_2 (2) complexes.

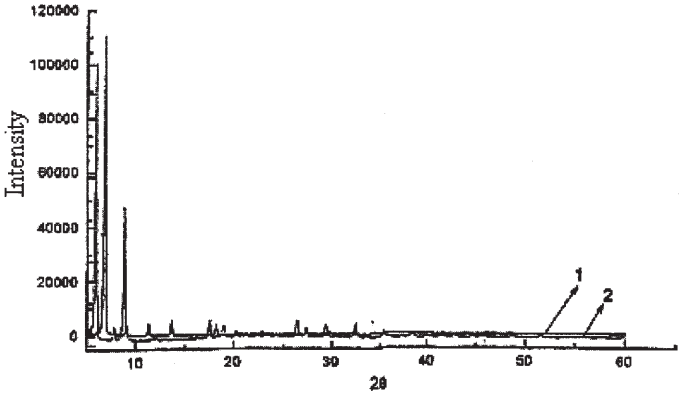

Fig. 4. Difractograms of HL (1) and CdL_2 (2) complexes.

Given the experimental data concerning the indexation of diffractograms, as regards the formation of the chemical bonds, it can be concluded that the coordination compounds of metallic cations Zn(II), Cd(II) and Hg(II)) are influenced by the crystallographic characteristics of ligands. The coordination process is achieved due to the similarity of two parameters of elemental cells of complexes related to those of the ligand. Thus, it can be noted that the investigated complexes crystallize in

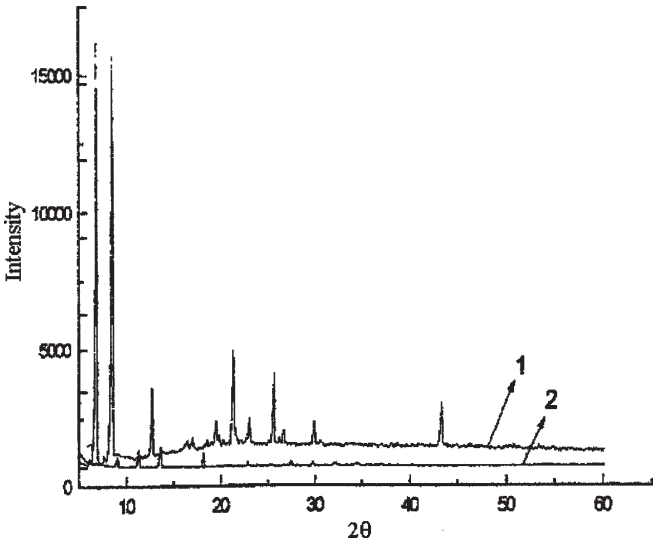

Fig. 5. Difractograms of HL (1) and HgL_2 (2) complexes

Table 5
PARAMETER VALUES OF ELEMENTAL CELLS FOR EACH INVESTIGATED COMPLEX

Elemental cell parameter	Value determined by indexation		
	ZnL_2	CdL_2	HgL_2
a (Å)	14.3619	14.5562	14.8626
b (Å)	6.2505	6.5002.	6.8001
c (Å)	11.2602	11.6080	11.8160
α	90°	90°	90°
β	92.60°	101.35°	112.25°
γ	90°	90°	90°
Elemental cell volume ($Å^3$)	1010.8	1098.3	1194.2

monoclinic system having very close values of *a* and *c* parameters of elemental cells, but much different and lower than those of *b* parameter.

At the formation of the studied complexes, it was observed an increase of the packing degree, the volume of their elemental cells being smaller than that of the ligand due to the bonds achieved with the central atoms: Zn(II), Cd(II), Hg(II).

Gravimetric determination of Zn(II), Cd(II) and Hg(II)
Reagents:

1. 10^{-2} M aqueous solutions of $ZnCl_2$, $CdCl_2$ or $HgCl_2$.
2. 10^{-2} M solution of 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone.

Working procedure

10 – 20 mL solution of $ZnCl_2$, $CdCl_2$ or $HgCl_2$ with 10^{-2} M concentration is diluted with water at 100 mL, mixed with 10^{-2} M solution of 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone, in excess, under stirring. The mixture pH is adjusted to a value of 4.5 using a solution of 0.1 N NaOH (controlled with universal indicator paper).

After one hour, the white-colored precipitate is filtered and washed with a mixture of ethylic alcohol – water (volume ratio 1:1). Then the precipitate is dried under vacuum conditions until a constant weight is reached. The precipitate is described by the molecular formula of $Zn(C_{15}H_{11}O_2SI_2)$. The gravimetric factor is 0.058 g. The mean relative error is ± 0.25%.

Analogous, Cd(II) and Hg(II) can be gravimetrically dosed with the same relative error as in case of Zn(II) determination.

Conclusions

In this paper was presented the study of some new compounds of Zn(II), Cd(II) and Hg(II) with the ligand 1-(3,5-diiodo, 2-hydroxy, 4-methyl phenyl), 2-phenyl sulfanyl ethanone, synthesized in the molar ratio central atom:ligand of 1:2.

The investigated complexes were characterized using modern methods, such as chemical analysis, thermal analysis, IR absorption spectroscopy and X-ray diffraction.

The new complexes crystallize in monoclinic system with central atoms like Zn(II), Cd(II) or Hg(II) tetracoordinated in tetrahedral structures.

The obtaining reaction of the new complexes can be employed in order to determine gravimetrically Zn(II), Cd(II) and Hg(II).

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