

INVESTIGATION OF Zn(II), Cd(II) AND Hg(II) WITH ISONICOTINIC ACID-1-H-INDOL-2,3-DIONE HYDRAZIDE SYSTEM

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Six new complexes of isatin isonicotinoyl hydrazone with Zn(II), Cd(II) and Hg(II) have been synthesised and characterised.

Following the synthesis conditions, two types of complexes were obtained: $[M(LH)Cl_2(H_2O)]$; $[M(L)Cl(H_2O)_2]$, where: LH = isatin isonicotinoyl hydrazone; M = Zn(II), Cd(II) and Hg(II).

The complexes have been characterised by elemental analyses, molar conductivity measurements, electronic and IR spectroscopy and TG studies. The experimental data suggest that the ligand acts as tridentate, and in function of pH of the reaction system, can coordinate in two different tautomeric forms: enol and ceto.

Introduction

Hydrazone derivatives from isonicotinic acid and their complexes are known for their antibacterial properties [1-3]. Some hydrazones of 1-H-indol-2,3-dione have an antitubercular activity [4,5]. Also, since the special coordinating potential of the metallic ions, depending on the synthesis way, have been already reported [6], it seemed desirable to investigate the coordination ability of the isatin isonicotinoyl hydrazone; the results and the discussion are presented bellow.

On the basis of elemental analysis, we have been suggested the following stoichiometric formula: $[M(LH)Cl_2(H_2O)]$ without the pH adjusted and $[MLCl(H_2O)_2]$ with the pH adjusted, where LH = isatin isonicotinoyl hydrazone; M = Zn(II), Cd(II) and Hg(II).

Experimental

All chemicals used are of p.a. produced by Merck.

Metallic content in complexes were determined by gravimetrically analysis. The electronic diffuse spectra with MgO powder were recorded between 380-1100 nm with an VSU-2P Zeiss-Jena Spectrophotometer, and the IR spectra (KBr, pellets) were measured on a BIO-RAD FTS-135 Spectrometer. The molar conductivity measurements were obtained through a conductivity bridge Elico CM-82. TG studies were carried out with a Q-1500 D MOM Derivatograph.

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Complexes synthesis: [M(LH)Cl₂(H₂O)]

To the ethanol solution of a equimolecular mixture of isatin and isonicotinic acid hydrazide is added by continuously stirring an ethanol solution of metal chloride in molar ratio metal / ligand 1:1. A precipitate appears immediately. This is filtered, washed, and dried under vacuum.

Analysis for ZnC₁₄H₁₂O₃N₄Cl₂: calculated: Zn 15,55; C 39,96; Cl 16,89; found: Zn 14,76; C 38,72; Cl 16,32

Analysis for CdC₁₄H₁₂O₃N₄Cl₂: calculated: Cd 24,05; C 35,94; Cl 15,19; found: Cd 23,57; C 35,02; Cl 14,86

Analysis for HgC₁₄H₁₂O₃N₄Cl₂: calculated: Hg 36,10; C 30,24; Cl 12,77; found: Hg 35,88; C 29,34; Cl 12,10

Complexes synthesis: [MLCl(H₂O)₂]

To the ethanol solution of an equimolecular mixture of isatin and isonicotinic acid hydrazide adjusted to the pH ~ 7 with NaOH 0,1M is added under continuous stirring an ethanol solution of metal chloride in molar ratio metal / ligand 1:1. After few minutes a precipitate appears. This is filtered, washed, and finally dried over in vacuum.

Analysis for ZnC₁₄H₁₃O₄N₄Cl: calculated: Zn 16,27; C 41,80; Cl 8,83; found: Zn 15,99; C 41,20; Cl 8,16

Analysis for CdC₁₄H₁₃O₄N₄Cl: calculated: Cd 25,04; C 37,42; Cl 7,91; found: Cd 24,86; C 36,98; Cl 7,12

Analysis for HgC₁₄H₁₃O₄N₄Cl: calculated: Hg 37,35; C 31,28; Cl 6,61; found: Hg 36,92; C 30,78; Cl 6,32

Results and discussion

The compound is insoluble in most common organic solvents and soluble in coordinating solvents such as DMF and DMSO.

The low values of the molar conductivity in DMF 10⁻³ M solutions (45-50 Ω⁻¹cm²mol⁻¹) indicate the non-electrolytic nature of those complexes.

A summary of the most important IR absorption bands corresponding to the ligand and the complexes, together with their proposed assignments, are given in the Table 1.

In the ligand IR spectra, at 3231, 3163 and 3032 cm⁻¹ respectively, appear three absorption bands, assigned to the isonicotinic N-H bond, isatinic N-H bond stretching vibrations respectively.

The absorption bands characteristic to the C=O vibrations of the isatinic and isonicotinic acid hydrazide fragments appear at 1719 respectively 1673 cm⁻¹ in the ligand IR spectra [7] and their behaviour after coordination differs on the pH of the synthesis.

In the case of the complexes [M(LH)Cl₂(H₂O)], the both bands are shifted towards lower frequencies. These data indicates the implication of the oxygen atom in coordination.

Table 1. Spectral IR data of the ligand and of the metal-complexes and their assignments (cm⁻¹)

Ligand/complexes	V _{O-H} water	V _{C=O} isatin	V _{C=O} hydrazide	V _{C=N} azomethine	V _{C-O}	V _{N-N}	V _{O-H} water	V _{M-O}	V _{M-N}
Ligand	–	1719	1673	1630	–	990	–	–	–
[Zn(LH)Cl ₂ H ₂ O]	3450	1709	1640	1612	–	999	870	554	449
[Cd(LH)Cl ₂ H ₂ O]	3400	1688	1656	1609	–	1009	889	560	447
[Hg(LH)Cl ₂ H ₂ O]	3500	1698	1651	1605	–	1014	876	595	445
[ZnLCl(H ₂ O) ₂]	3495	1694	–	1614	1188	1015	862	580	467
[CdLCl(H ₂ O) ₂]	3411	1709	–	1616	1191	1002	846	594	443
[HgLCl(H ₂ O) ₂]	3419	1688	–	1606	1186	1004	837	590	436

In the IR spectra of the complexes [MLCl(H₂O)₂], the hydrazidic C=O band disappears. Moreover, in the IR spectra are observed new absorption bands at 1188÷1191 cm⁻¹; these new bands are assigned to the vibrations of the C-O-M bonds. These data indicates that the tautomeric form of the ligand in complexes is an enolic one.

The ligand shows in the IR spectra, an absorption band of medium intensity, at 1630 cm⁻¹, attributed to the stretching vibration of C=N (azomethine). In the complex compounds IR spectra, this band appears between 1600÷1616 cm⁻¹, shifted to lower frequencies, which indicates the implication of the nitrogen atom of the azomethinic group in the coordination of the metallic ions. This supposition is also sustained by the fact that the band assigned to the N-N bond vibrations (appearing at 990 cm⁻¹ in the IR spectra of the free ligand) shifts to the higher frequencies after coordination.

In the IR spectrum of the free ligand, at 1546 and 1276 cm⁻¹, appear the absorption bands due to the amido II, respectively amido III vibrations. In the IR spectra of the complexes, the first band is shifted to lower frequencies and the second one to higher frequencies. These data support the implication of the amidic oxygen atoms in the coordination of the metallic ions.

In the IR spectra of the complexes, the absorption bands localized in the range 3350÷3600 cm⁻¹ can be assigned to the vibration of the coordinated water molecules. Besides, the presence of the weak bands in the range 870÷890 cm⁻¹, attributed to the distortion vibration of the O-H bond, indicates the same coordinating water molecules.

In the IR spectra of the complexes appear also new absorption bands, assigned to the vibration of the M-L bonds; M-N at 430÷470 cm⁻¹, M-O at 550÷595 cm⁻¹ respectively.

Because of the d¹⁰ electronic configuration of the metallic ions, the diffuse electronic spectra of the complexes have a very small relevance. But, the weak modification of the bands frequencies of the ligand in the UV-VIS spectra of the compounds indicates the coordination of the ligand and the obtaining of the complexes.

The TG studies indicate a loss in mass between 90÷160°C, corresponding to one or respectively two coordinating water molecules for the complexes [M(LH)Cl₂(H₂O)], respectively [MLCl(H₂O)₂]. At the higher temperature, one observes a constant decrease in

the molecular mass, due to the decomposition of the organic ligand, followed finally by the formation of the metal oxide.

Conclusions

On the basis of the elemental analysis, molar conductivity measurements, TG studies and IR spectra, we suggest that the most probable geometry of the obtained complexes is octahedral (Fig. 1).

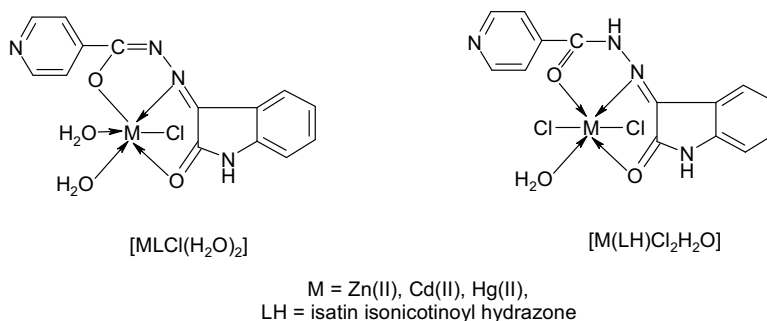


Fig. 1.

The ligand is ONO tridentate, coordinates the metallic ions through the oxygen (isatinic), nitrogen (azomethinic) and oxygen (hydrazidic) atoms. The ligand is in the cetolic form in the complexes without the pH adjustment and in enolic form in the complexes resulted with the pH adjustment.

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