

# THERMAL BEHAVIOUR OF Co(II), Ni(II), Cu(II), Zn(II), Hg(II) AND Pd(II) COMPLEXES WITH ISATIN- $\beta$ -THIOSEMICARBAZONE

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The isatin- $\beta$ -thiosemicarbazone (ITC) complexes of Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pd(II) were prepared and characterized by elemental analysis, as well as molar conductivity, magnetic susceptibility, FTIR, UV-Vis and <sup>1</sup>H NMR spectroscopic methods. The complexes were also studied for its thermal stability. They all behaviour as anhydrous complexes and its thermolysis passes through the stages of deamination (517–547 K) and complete thermal decomposition (619–735 K).

**Keywords:** Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pd(II) complexes, isatin- $\beta$ -thiosemicarbazone, thermal stability

## Introduction

The synthetic versatility of isatin has led to an extensive use of this compound in organic synthesis [1]. Thiosemicarbazones of various aldehydes and ketones occupy a special place among organic ligands, since they contain various donor atoms and are able to change denticity depending on the starting reagents and their reaction conditions. This class of Schiff bases can react metal ions to give chelate coordination compounds. Thiosemicarbazone derivatives are of considerable interest because of their chemistry and potentially beneficial biological activities, such as antitumor, antibacterial, antiviral and antimalarial activities [2]. Many coordination compounds of transition metals with isatin derivatives show greater activity than the ligands alone.

In this context experimental data on synthesis, physicochemical properties, composition and structure of these compounds hold interest both from scientific and practical points of view.

In this paper, we describe the thermal behaviour observed in isatin- $\beta$ -thiosemicarbazone complexes of Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pd(II). Structural representation of ligand and its complexes are given in Fig. 1.

## Experimental

### Preparation of samples

C<sub>9</sub>H<sub>8</sub>N<sub>4</sub>SO (ITC). Isatin-2,3-indolinedione and thiosemicarbazide, taken with 1:1 molar ratio, were dissolved in aqueous ethanol in presence of a few

drops of acetic acid. The mixture was refluxed over water bath for 1 h. After cooling at room temperature, the yellow microcrystalline solid was separated, washed with ethanol, diethylether and dried over silica gel [3]. UV-Vis (DMF,  $\nu(\text{cm}^{-1}/\epsilon \cdot 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm})$ ): 28.6/0.946  $\pi \rightarrow \pi^*$ , 27.3/1.325  $n \rightarrow \pi^*$ . IR (KBr,  $\text{cm}^{-1}$ ): 3422, 3290, 3229, 3141  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1699  $\nu_{\text{C=O}}$ , 1607  $\nu_{\text{C=N}}$ , 854  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.9–7.6 (m, 4H, Ar), 8.69, 9.04 (s, 2H, NH<sub>2</sub>), 11.21 (2, 1H, NH), 12.47 (s, 1H, NH).

Ni(ITC)<sub>2</sub>Cl<sub>2</sub>. A hot ethanol solution of ligand (40 cm<sup>3</sup>, 1.0 mmol) was added to the solution of equimolar amount of nickel chloride (20 cm<sup>3</sup>, 1 mmol). The solution was refluxed for 8 h. A brown solid was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu(\text{cm}^{-1}/\epsilon \cdot 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm})$ ): 28.7/1.622  $\pi \rightarrow \pi^*$ , 27.2/1.704  $n \rightarrow \pi^*$ , 22.2/1.223 <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (P), 18.7/0.226 <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (F), 13.5/0.02 <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> (F). IR (KBr,  $\text{cm}^{-1}$ ): 3418, 3282, 3236, 3161  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1659  $\nu_{\text{C=O}}$ , 1554  $\nu_{\text{C=N}}$ , 814  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.91–7.57 (m, 4H, Ar), 8.71, 9.07 (s, 2H, NH<sub>2</sub>), 11.25 (2, 1H, NH), 12.52 (s, 1H, NH).

Co(ITC)<sub>2</sub>Cl<sub>2</sub>. In a hot ethanol solution of ligand (30 cm<sup>3</sup>, 0.5 mmol) was added to the solution of equimolar amount of cobalt chloride (20 cm<sup>3</sup>, 0.5 mmol). The solution was refluxed for 6 h. A dark pink was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu(\text{cm}^{-1}/\epsilon \cdot 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm})$ ): 28.9/3.195  $\pi \rightarrow \pi^*$ , 27.1/3.580  $n \rightarrow \pi^*$ , 19.5/0.817 <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (P), 16.7/0.013 <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> (F), 14.7/0.005 <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>. IR (KBr,  $\text{cm}^{-1}$ ): 3418, 3306, 3221, 3137  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1651  $\nu_{\text{C=O}}$ , 1551  $\nu_{\text{C=N}}$ , 838  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.91–7.67 (m, 4H, Ar), 8.72, 9.09 (s, 2H, NH<sub>2</sub>), 11.24 (2, 1H, NH), 12.46 (s, 1H, NH).

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Cu(ITC)Cl<sub>2</sub>. To the hot ethanol solution of the ligand (40 cm<sup>3</sup>, 0.8 mmol) was added an equimolar amount of copper chloride (20 cm<sup>3</sup>, 0.8 mmol). The solution was refluxed for 5 h. A green solid was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu$  (cm<sup>-1</sup>/ε·10<sup>3</sup> mol<sup>-1</sup> dm<sup>3</sup> cm): 28.8/0.568  $\pi \rightarrow \pi^*$ , 26.9/0.528  $n \rightarrow \pi^*$ , 25.3/0.451 <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub>, 19.8/0.176 <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub>, 13.4/0.02 <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>. IR (KBr, cm<sup>-1</sup>): 3407, 3270, 3229, 3125  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1700  $\nu_{\text{C=O}}$ , 1511  $\nu_{\text{C=N}}$ , 833  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.92–7.67 (m, 4H, Ar), 8.72, 9.10 (s, 2H, NH<sub>2</sub>), 11.28 (2, 1H, NH), 12.41 (s, 1H, NH).

Zn(ITC)Cl<sub>2</sub>. To the hot ethanol solution of the ligand (35 cm<sup>3</sup>, 1.5 mmol) was added an equimolar amount of zinc chloride (25 cm<sup>3</sup>, 1.5 mmol). The solution was refluxed for 7 h. A dark yellow solid was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu$  (cm<sup>-1</sup>/ε·10<sup>3</sup> mol<sup>-1</sup> dm<sup>3</sup> cm): 28.9/2.851  $\pi \rightarrow \pi^*$ , 27.2/2.967  $n \rightarrow \pi^*$ , 18.2/0.058 CT-transfer, 17.1/0.055  $d \rightarrow d^*$ . IR (KBr, cm<sup>-1</sup>): 3407, 3262, 3233, 3129  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1700  $\nu_{\text{C=O}}$ , 1511  $\nu_{\text{C=N}}$ , 838  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.9–7.6 (m, 4H, Ar), 8.75, 9.11 (s, 2H, NH<sub>2</sub>), 11.28 (2, 1H, NH), 12.41 (s, 1H, NH).

Hg(ITC)Cl<sub>2</sub>. In a hot ethanol solution of ligand (40 cm<sup>3</sup>, 2 mmol) was added to the solution of equimolar amount of mercury chloride (20 cm<sup>3</sup>, 2 mmol). The solution was refluxed for 10 h. An orange was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu$  (cm<sup>-1</sup>/ε·10<sup>3</sup> mol<sup>-1</sup> dm<sup>3</sup> cm): 28.7/2.921  $\pi \rightarrow \pi^*$ , 27.1/3.479  $n \rightarrow \pi^*$ , 24.5/3.435 CT-transfer, 17.0/0.029  $d \rightarrow d^*$ . IR (KBr, cm<sup>-1</sup>): 3411, 3298, 3229, 3161  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1700  $\nu_{\text{C=O}}$ , 1510  $\nu_{\text{C=N}}$ , 838  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.9–7.6 (m, 4H, Ar), 8.77, 9.11 (s, 2H, NH<sub>2</sub>), 11.28 (2, 1H, NH), 12.41 (s, 1H, NH).

Pd(ITC)Cl<sub>2</sub>. In a hot ethanol solution of ligand (40 cm<sup>3</sup>, 2 mmol) was added to the solution of equimolar amount of palladium chloride (20 cm<sup>3</sup>, 2 mmol). The solution was refluxed for 3 h. An orange was isolated and washed with 95% ethanol. UV-Vis (DMF,  $\nu$  (cm<sup>-1</sup>/ε·10<sup>3</sup> mol<sup>-1</sup> dm<sup>3</sup> cm): 27.2/3.195  $\pi \rightarrow \pi^*$ , 34.1/3.589  $n \rightarrow \pi^*$ , 19.5/0.817 CT-transfer, 16.7/0.01  $d \rightarrow d^*$ . IR (KBr, cm<sup>-1</sup>): 3411, 3266, 3233, 3125  $\nu_{\text{NH}+\nu_{\text{NH}_2}}$ , 1700  $\nu_{\text{C=O}}$ , 1511  $\nu_{\text{C=N}}$ , 834  $\nu_{\text{C=S}}$ . <sup>1</sup>H NMR (DMSO,  $\delta$ , ppm) 6.9–7.6 (m, 4H, Ar), 8.72, 9.09 (s, 2H, NH<sub>2</sub>), 11.25 (2, 1H, NH), 12.39 (s, 1H, NH). All complexes are soluble in DMF and DMSO, and slightly soluble in hot ethanol and methanol.

## Methods

The chemical used were of AR grade. Microanalysis for carbon, hydrogen and nitrogen was carried out with Carlo Erba 1106 microanalyser. The

chlorid content was determined potentiometric. The metal contents determined by a Virial AA-457 Double beam spectrometer.

Molar conductivity of the complexes ( $c=10^{-3}$  mol dm<sup>-3</sup>) was measured at room temperature by an Iskra Conductivity Meter 0.67 using solutions in DMF. The magnetic measurement was carried out at room temperature (292 K) with a magnetic balance MSB-MKI, Sherwood Scientific Ltd., Cambridge, England, using HgCo(NCS)<sub>4</sub> for calibration. The data were corrected for diamagnetic susceptibilities by using the Pascal's constants. The Fourier transformation infrared spectra (FTIR) were recorded with a Michaelson Bomen MB-series spectrophotometer, using the potassium bromide KBr pellet (1 mg/100 mg) technique. The electronic spectra (UV-Vis) were recorded on a Varian Cary-100 UV-Vis spectrophotometer using 10<sup>-3</sup> mol dm<sup>-3</sup> solutions in DMF. The nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were obtained in DMSO solution with a Gemini-200 'HF NMR'. The residues and intermediates of thermal decomposition were characterised by their X-ray diffraction patterns, powder method, taken on a Philips X'PERT diffractometer using Ni filtered CuK<sub>α</sub> radiation  $\lambda=1.54178$  Å. The measurements were made within the range  $2\theta=9-65^\circ$ , with step of 0.05° and time between 10 s.

TG/DTA curves of the complexes were studied in the air atmosphere with sample mass of 150–200 mg and temperature gradient 2.5 K min<sup>-1</sup>, using derivatograph Q 1500 (MOM, Hungary). The measurements were made at a heating rate of 10 K min<sup>-1</sup>, at a temperature range 323–773 K, using Perkin Elmer TGS-2 Thermogravimetric system.

## Results and discussion

All the complexes were isolated in high yields and are air-stable both in the solid-state and in solution. The results of elemental analysis are consistent with a proposed structure of the obtained complex. The analytical data established different stoichiometries, mainly influenced by the nature of the inorganic anion. In fact, two kinds of stoichiometries, M(ITC)<sub>2</sub>Cl<sub>2</sub> ( $M=\text{Co, Ni}$ ) and M(ITC)Cl<sub>2</sub> ( $M=\text{Cu, Zn, Hg and Pd}$ ) are found.

Molar conductances of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the complexes in DMF are in correlation with their structure. It indicates that the Ni(II) and Co(II) complexes behave as electrolytes [4] since chloride ions are present in outer space of compounds. In the other hand, the complexes of Cu(II), Zn(II), Hg(II) and Pd(II) behave as non-electrolytes. This suggests that the chloride ion is involved in the coordination by its presence in the inner space of the complexes (Fig. 1).

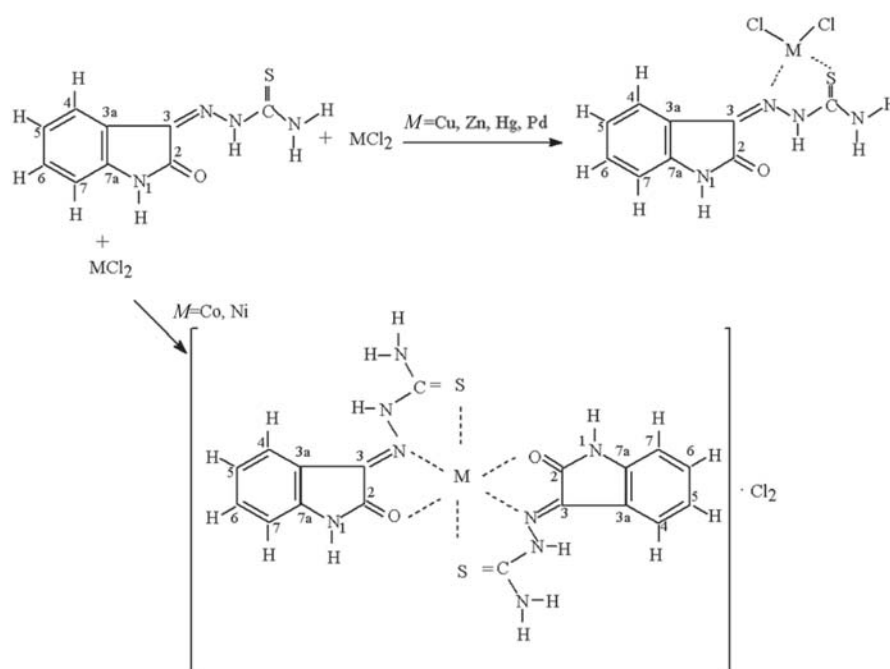


Fig. 1 Reaction scheme of complexes formation

Table 1 Analytical and physical data of the investigated compounds

Compound	Color	<i>m.p.</i> /°C	Analysis/% found (calcd.)					Mol. cond./ S cm <sup>2</sup> mol <sup>-1</sup>	$\mu_{\text{eff}}$ /MB
			C	H	N	Cl	<i>M</i>		
ITC	yellow	239–241	48.95 (49.08)	3.75 (3.66)	25.30 (25.44)	–	–	–	–
Ni(ITC) <sub>2</sub> Cl <sub>2</sub>	brown	297	39.10 (37.99)	2.69 (2.8)	22.1 (19.7)	12.15 (12.46)	10.06 (10.30)	110	3.39
Co(ITC) <sub>2</sub> Cl <sub>2</sub>	light violet	264	42.1 (42.7)	2.99 (3.2)	22.3 (22.1)	12.32 (12.46)	10.43 (10.34)	108	4.82
Cu(ITC) <sub>2</sub> Cl <sub>2</sub>	green	291	36.7 (36.9)	2.6 (2.5)	17.3 (17.5)	11.20 (11.13)	19.86 (19.93)	15	1.85
Zn(ITC) <sub>2</sub> Cl <sub>2</sub>	dark yellow	259	30.32 (30.30)	2.41 (2.3)	15.5 (15.7)	19.85 (19.92)	18.35 (18.35)	10	diamagnetic
Hg(ITC) <sub>2</sub> Cl <sub>2</sub>	orange	292	22.62 (22.71)	1.58 (1.69)	11.65 (11.77)	14.85 (14.93)	–	8	diamagnetic
Pd(ITC) <sub>2</sub> Cl <sub>2</sub>	orange	286	28.55 (28.35)	2.07 (2.09)	14.55 (14.59)	18.56 (18.64)	–	10	diamagnetic

The analytical and physical data of the investigated compounds are presented in Table 1.

#### Infrared and <sup>1</sup>H NMR spectra

As all thiosemicarbazones, isatin- $\beta$ -thiosemicarbazone can exhibit thione-thiol tautomerism, since it contains a thioamide –NH–C=S functional group. There is no IR band at 2500–2600 cm<sup>-1</sup> in the spectrum of the free ligand as well as complexes, and this indicates the absence of S–H grouping in the ligand. This is supported by the <sup>1</sup>H NMR spectrum, which does not show any peak at 4 ppm attributable to the

S–H proton [2]. The resonance at 11.21 ppm in the spectrum of ITC was assigned to the N–NH proton and it also appears in the spectrum of the complexes. The deshielding of NH<sub>2</sub> protons upon complexation can be related to the change from an E to a Z conformation of the ligand [5]. The presence of two peaks keeps the same separation between them (0.34–0.37 ppm) as in the free ligand (0.35 ppm) is indicative of no change in the bond order for the C–N bond when coordinate to the metallic halide. It also may correspond to some electron density changes caused within the S–C–NH<sub>2</sub> substructure by formation of the metal–S bond [12]. In the 3500–3000 cm<sup>-1</sup>

region in spectra of ligand and complexes, all bands attributable to the NH<sub>2</sub> and NH stretching vibrations are present. All bands generated by nitrogen–hydrogen stretching vibrations are located on top of broad absorption starting at about 3500 cm<sup>-1</sup> and covering approximately 700 cm<sup>-1</sup> range [6]. This phenomenon, typical for hydrogen bonded systems, also strongly overlaps the ν<sub>CH</sub> vibrations expected between 3100 and 3000 cm<sup>-1</sup>. At 1700 cm<sup>-1</sup>, bands assigned to ν<sub>C=O</sub> mode were observed at similar positions in the ligand and Cu(II), Zn(II), Hg(II) and Pd(II) complexes spectra, suggesting the noninvolvement of carbonyl oxygen in complex formation. But, in the Co(II) and Ni(II) complexes the ν<sub>C=O</sub> value undergoes a negative shift (Δν=40 and 48 cm<sup>-1</sup>) upon coordination. The absorption bands ν<sub>C=N</sub> are shifted to lower frequencies (Δν=53–97 cm<sup>-1</sup>) in the spectrum of the complexes, indicate that this group is the coordinated site of the ligand. It also can be seen that absorption bands of ν<sub>C=S</sub> stretching vibrations in the spectrum of coordination compounds are shifted to the lower frequencies (Δν=16–40 cm<sup>-1</sup>) upon coordination, too. Taking into account the assignments of the vibrational absorptions, the following considerations [7] on the ligand behavior in the metal complexes can be made:

- An O, N, S tridentate ligand behavior is suggested in the Ni(II) and Co(II) complexes, with a probable octahedral coordination around the central ion and coordination number 6 of central ion.
- A N, S bidentate ligand behavior can be proposed in the Cu(II), Zn(II), Hg(II) and Pd(II) coordination compounds with a probable tetracoordination around the metal atom and coordination number 4 of central ion.

#### Electronic absorption spectra

The electronic spectra of isatin-β-thiosemicarbazone show primer absorption band of aromatic ring and thiosemicarbazone moiety due to transition of π–π\* type and an n–π\*. These transitions are found also in the spectra of the complexes, but they are shifted towards lower and higher frequencies, confirming the coordination of the ligand by the metallic ions [8]. The electronic spectrum of the nickel(II) complex shows three distinct bands at ca. 13.500 cm<sup>-1</sup> (<sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>2g</sub> (F)), 18.700 cm<sup>-1</sup>, (<sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (F)) and at ca. 22.200 cm<sup>-1</sup> (<sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (P)) which is characteristic for hexacoordinated Ni(II). Since the value of the magnetic moment μ<sub>eff</sub>=3.39 μ<sub>B</sub> lies between 3.35–3.70 μ<sub>B</sub>, it can be assumed high-spin configuration of Ni(II) with two unpaired electrons and indicate pseudo-octahedral environment around the metal ion [8–10] and coordination number 6 for Ni(II) ion. The electronic absorption spectra of the cobalt(II)

complex contain two distinct *d–d* bands. The one located at lower energy belonging to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>2g</sub> (F), and one at higher energy to the <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>1g</sub> (P) corresponding to a hexacoordinated Co(II). The third band corresponds to the forbidden two-electron transition <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>A<sub>2g</sub>, which is weaker with the majority of Co(II) complexes, and usually appears as a shoulder. Hence, those values and corresponding magnetic moment μ<sub>eff</sub>=4.82 μ<sub>B</sub> suggest octahedral geometry around Co(II) ion in this complex [9] and coordination number 6 for Co(II) ion. The electronic spectrum of the copper(II) complex exhibit bands at 13.400, 19.800 and 25.300, which can be assigned to the <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>B<sub>2g</sub>, <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub> and <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>E<sub>g</sub> transitions [7]. These transitions, as well as the measured value of the magnetic moment (μ<sub>eff</sub>=1.85 μ<sub>B</sub>) suggests a square-planar stereochemistry of the compound [8–10] and coordination number 4 for Cu(II) ion. The electronic spectrum of palladium(II) complex, exhibits bands at 16.700 and 19.500 cm<sup>-1</sup>, assigned to charge transfer and *d→d\** transitions, respectively. The comparison of similar palladium(II) compounds with this one suggests a square-planar stereochemistry of the compound [8, 10] and coordination number 4 for Pd(II) ion. The spectrum (Table 1) of diamagnetic zinc(II) and mercury(II) complexes exhibits two bands assigned to charge transfer and *d→d\** transitions. Assumption for these complexes is that they have a tetrahedral geometry [8] and coordination number 4.

#### Thermal analysis

The thermogravimetric (TG/DTA) curves corresponding to the complexes (Table 2) are presented in Fig. 2.

Mass loss (TG and calculated), temperature ranges and a description of thermal events observed in the studies are summarized in Table 1. The thermal stability of coordination compounds was studied in the air atmosphere, in the range of 323–773 K. All the complexes have no mass loss and endothermic peak under 473 K, indicating that the complexes do not contain coordinated water molecules or water of crystallization. Their thermal decompositions reveal them to be anhydrous, which is consistent with the elemental and spectral analysis. The complexes were stable in air at room temperature. The nature of the solid decomposition products was established on the basis of the TG curves and confirmed by IR and X-ray spectroscopy. The FTIR spectra of the gaseous product evolved during the decomposition of the investigated complexes reveals them to be molecules of CO<sub>2</sub> (2350, 630–800 cm<sup>-1</sup>), CO (2200 cm<sup>-1</sup>) and hydrocarbons (3000–2750, 1750 and 1050–1590 cm<sup>-1</sup>) [6, 11, 12].

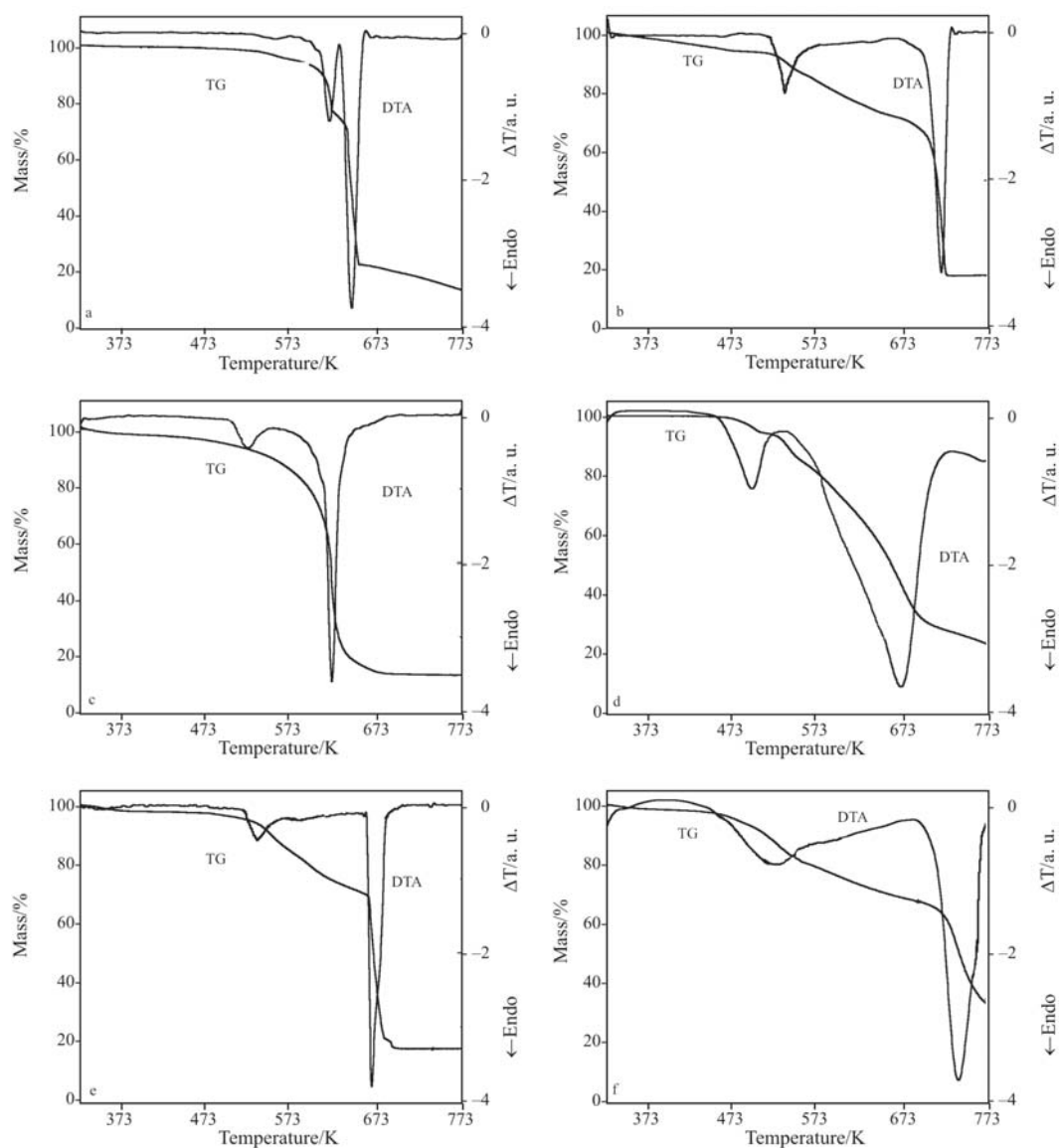
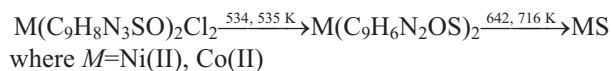
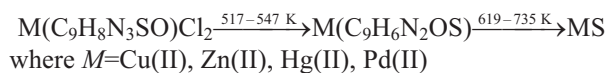


Fig. 2 Thermogravimetric curves for a – Ni(II), b – Co(II), c – Hg(II), d – Cu(II), e – Pd(II) and f – Zn(II) complexes

Table 2 Temperature range of the thermal decomposition of the investigated compounds

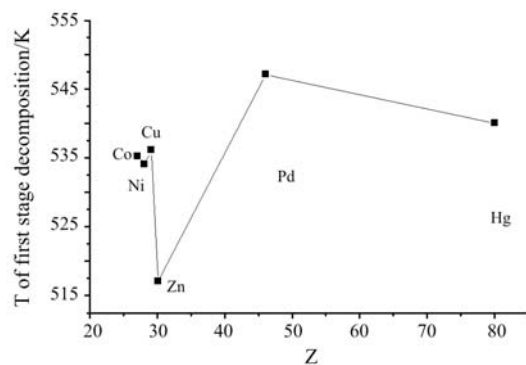
Compound	Mass of sample/mg	Temperature/K	Mass loss/%	Total mass loss/%		Final product of decomposition
				found	calcd	
Ni(ITC) <sub>2</sub> Cl <sub>2</sub>	5.684	534.15 642.26	18.198 62.30	84.59	84.07	NiS
Co(ITC) <sub>2</sub> Cl <sub>2</sub>	4.464	535.25 715.73	17.95 65.28	83.23	84.05	CoS
Cu(ITC)Cl <sub>2</sub>	4.989	536.17 668.45	15.59 57.06	73.62	73.62	CuS
Zn(ITC)Cl <sub>2</sub>	3.431	517.13 735.12	15.05 58.44	73.49	72.67	ZnS
Pd(ITC)Cl <sub>2</sub>	5.320	547.17 665.25	12.05 53.52	65.57	65.17	PdS
Hg(ITC)Cl <sub>2</sub>	1.577	540.10 619.07	10.05 43.11	53.16	52.69	HgS

From the thermal investigation (TG/DTA) it is possible to observe that the decomposition proceeds in two stages:

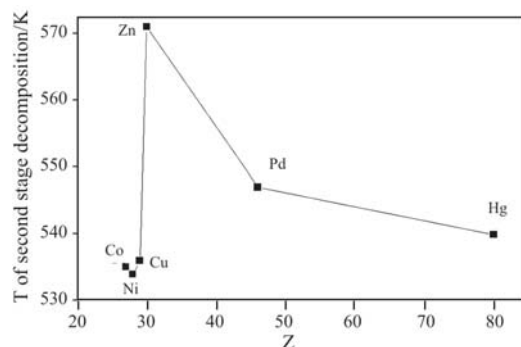


The endothermic effect observed for compounds ~523 K corresponds, judging from the observed mass loss, corresponds to deamination of the initial complexes [11–13]. The subsequent exothermicity at 640–713 K is apparently related to thermooxidative destruction of the coordinated ligand. The mass loss for Co(II) complex calculated from the TG curve is equal to 83.23% (theoretical value is 84.05%); the mass loss for Ni(II) complex is equal to 84.59% (theoretical value is 84.07%); the mass loss for Cu(II) complex is equal to 73.62% (theoretical value is 73.62%); the mass loss for Zn(II) complex is equal to 73.49% (theoretical value is 72.67%); the mass loss for Pd(II) complex is equal to 65.57% (theoretical value is 65.17%) and the mass loss for Hg(II) complex is equal to 53.16% (theoretical value is 52.69%).

In the first stage of decomposition, the most stable complex is Pd(II), while the least thermally stable is Zn(II) complex [11, 13–15].



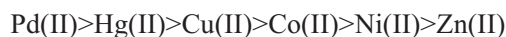
**Fig. 3** Dependence of the temperature of the first stage of complex decomposition



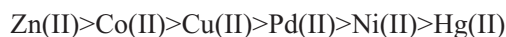
**Fig. 4** Dependence of the temperatures of the second stage of complex decomposition

In the second stage of decomposition, the most stable complexes are Zn(II) and Co(II), while the least thermally stable are Ni(II) and Hg(II) complexes. The decomposition is complete at 620–735 K, giving the respective metal sulfides.

As it can be seen, the thermal stability in the first stage decreases in order:



In the second stage, the thermal stability decreases in order:



The results show that thermal stability of coordination compounds do not change regularly with increasing atomic number of the element (Figs 2 and 3). It is also interesting, that Zn(II) complex as the most unstable in the first stage of decomposition, is the most stable in the second stage of thermal decomposition. The temperature of the maximum of this effect probably depends on the nature of coordinated metal [11, 13–15].

## Conclusions

A series of complexes of isatin- $\beta$ -thiosemicarbazone with Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pd(II) were prepared. The spectral studies indicated the octahedral geometry for Ni(II) and Co(II), square-planar for Cu(II) and Pd(II) and tetrahedral for Zn(II) and Hg(II) complexes. Their thermal decompositions reveal them to be anhydrous, which is consistent with the elemental and spectral analysis. Thermolysis of complexes proceeds through the stages of deamination and complete thermooxidative decomposition. Thermal stability of coordination compounds do not change regularly with increasing atomic number of the element.

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