

Spectrophotometric study of Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Hg(II) complexes with isatin- β -thiosemicarbazone

SANDRA S. KONSTANTINOVIĆ^{1*}, BLAGA C. RADOVANOVIĆ²,
ZORAN B. TODOROVIĆ^{1#} and SLAVICA B. ILIĆ¹

¹Faculty of Technology, Bulevar Oslobođenja 124, 16000 Leskovac and ²Faculty of Science,
Department of Chemistry, Višegradaska 33, 18000 Niš, Serbia

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Abstract: The composition and stability of the complexes of isatin- β -thiosemicarbazone with Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Hg(II) have been investigated using spectrophotometric method at 30 °C and constant ionic strength of 0.1 mol dm⁻³ (KNO₃) in 70 % ethanol. Experimental results indicate the formation of MeL and MeL₂ complexes for Ni(II) and Co(II), and MeL for Cu(II), Zn(II), Pd(II) and Hg(II) complexes, whose stability constants, β_n , have been calculated using a computerized iterative method of successive approximation.

Keywords: isatin- β -thiosemicarbazone, complexes, spectrophotometric study, stability constant.

INTRODUCTION

It is known that aromatic azo and azomethine compounds (Schiff bases) are widely used because of their very good chelatogenic characteristics. In addition to the commercially available compounds, there are a large number of new synthesized ones which are of interest for the study of their complexation reactions and practical applications.¹ The synthetic versatility of isatin has led to an extensive use of this compound in organic synthesis. It stemmed from the interest in the biological and pharmacological properties of its derivatives.^{2–6} Also, thiosemicarbazones are of considerable interest because of their chemistry and potentially beneficial biological activities, such as anti-tumor, antibacterial, antiviral and anti-malarial activities.^{2–6} The activity of thiosemicarbazones is thought to be due to their power of chelation with traces of metal ions present in biological systems. In recent thermodynamic studies of some metal complexes, potentiometric methods were used.^{7,8} Also thermodynamic studies on transition metal ion complexes of some thiosemicarbazones using a spectrophotometric method have been reported.^{7,8}

* Corresponding author. E-mail: andjelkovic_s@yahoo.com

Serbian Chemical Society member.

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In this study, isatin- β -thiosemicarbazone (ITC) was synthesized and the stability constants of the complexes of this ligand with Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Hg(II) were evaluated by spectrophotometry.

EXPERIMENTAL

Preparation of isatin- β -thiosemicarbazone, C₉H₈N₄SO, (ITC)

Isatin-2,3-indolinedione and thiosemicarbazide, in a 1:1 molar ratio were dissolved in 95 % ethanol. The mixture was refluxed over a water bath for 1 h. After cooling to room temperature, the yellow microcrystalline solid was separated, washed with ethanol, diethyl ether and dried over silica gel.⁹

UV/VIS (DMF, $\nu(\text{cm}^{-1}/\epsilon \times 10^3 (\text{mol}^{-1} \text{dm}^3 \text{cm}))$): 28.6/0.946 $\pi \rightarrow \pi^*$, 27.3/1.325 $n \rightarrow \pi^*$; IR (KBr, cm^{-1}): 3422, 3290, 3229, 3141 $\nu(\text{NH}) + \nu(\text{NH}_2)$, 1699 $\nu(\text{C}=\text{O})$, 1607 $\nu(\text{C}=\text{N})$, 854 $\nu(\text{C}=\text{S})$. ¹H-NMR (DMSO, δ / ppm) 6.9–7.6 (*m*, 4H, Ar), 8.69, 9.04 (*s*, 2H, NH₂), 11.21 (2, 1H, NH), 12.47 (*s*, 1H, NH). Analysis: Calculated: 49.08 % C, 3.66 % H, 25.44 % N, 14.56 % S. Found: 48.95 % C, 3.75 % H, 25.30 % N, 14.61 % S; m.p. 239–241 °C.

Solutions

All reagents and solvents were of analytical grade.

ITC solutions were prepared by dissolving an exactly weighted amount of the substances in 70 % ethanol and in buffers prepared with 70 % ethanol.

Stock solutions of metal ions, $c_M = 0.1 \text{ mol dm}^{-3}$ were prepared by dissolving metal(II) chloride in doubly distilled water. The copper(II) solution was standardized iodometrically, while solutions of the other metals were standardized gravimetrically. Solutions of required concentrations were obtained by precisely diluting the stock solutions with the solvent.

The ionic strength, $I = 0.1 \text{ mol dm}^{-3}$, of the ligand and metal salt solutions was adjusted with potassium nitrate (1 M, prepared in distilled water). The following buffer solutions were prepared: pH 3.9, by mixing CH₃COOH (0.2 mol dm⁻³) and CH₃COONa (0.2 mol dm⁻³) in the required ratios; pH 5.8, 6.9, 7.6, 8.1 and 9.0, by mixing in different ratios a solution containing 0.2 mol dm⁻³ H₃BO₃, 0.05 mol dm⁻³ H₂C₄H₄O₆ and 0.05 mol dm⁻³ Na₂SO₄ with a solution containing 0.05 mol dm⁻³ Na₂B₄O₇; pH 9.9, by mixing the required volumes of a 0.05 mol dm⁻³ solution of Na₂B₄O₇ and a 0.05 mol dm⁻³ solution of Na₂CO₃; pH 11 and 12, by mixing 0.05 mol dm⁻³ solutions of tris-HCl.

Determination of pH

The actual pH values of the buffers prepared in 70 % ethanol, as well as the pH of solutions of the ligand and its complexes without buffers, were measured with a combined pH electrode calibrated using pH standard solutions prepared in 70 % ethanol. Since the solvent has a relative permittivity different to that of pure water, all pH values are relative and valid only for the solvent used (70 % ethanol).

UV/Vis Spectroscopy

Absorption spectra of isatin- β -thiosemicarbazone and its complexes with metal(II) ions were investigated in the solvent with the buffers, at pH 3.9–9.9, and the ionic strength of 0.1 mol dm⁻³ (KNO₃). UV/Vis Spectra were recorded on a Varian Cary-100 UV/VIS spectrophotometer using adequate solutions. A blank for the spectrophotometric measurement of the ligand was prepared with the solvent and the corresponding buffer. The absorbance of solutions with complexes was measured against the blank having the same composition as the complex solutions except for the metal ion. In order to prove the stability of the absorbance, measurements were repeated after 30, 60 and 90 min.

RESULTS AND DISCUSSION

Absorption spectra

The electronic spectra of isatin- β -thiosemicarbazone (Fig. 1) show reference absorption bands ($\lambda_1 = 251 \text{ nm}$ and $\lambda_2 = 281 \text{ nm}$) of the aromatic ring and the

indole moiety due to transitions of the $\pi-\pi^*$ type and an absorption band at $\lambda_3 = 355$ nm, also due to a transition of the $\pi-\pi^*$ type but from the thiosemicarbazone part of the molecule. No transitions which could be assigned to an $n-\pi^*$ type were observed in the spectra, since they are covered with the more intensive $\pi-\pi^*$ type. The absorption spectra of isatin-3-thiosemicarbazone at different values of pH exhibit one isobestic point at 325 nm (Fig. 1). This reveals that at last two species (thione–thiol tautomerism) exist in equilibrium in a solution of isatin- β -thiosemicarbazone depending on the pH of the medium (Scheme 1). Species B is present at high pH values and has a bathochromic shift, as a result of the increased extent of chain conjugation.⁸

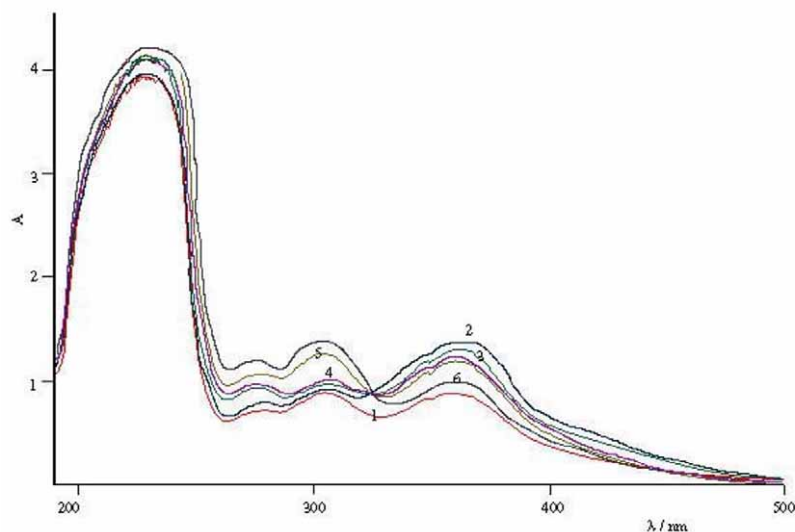
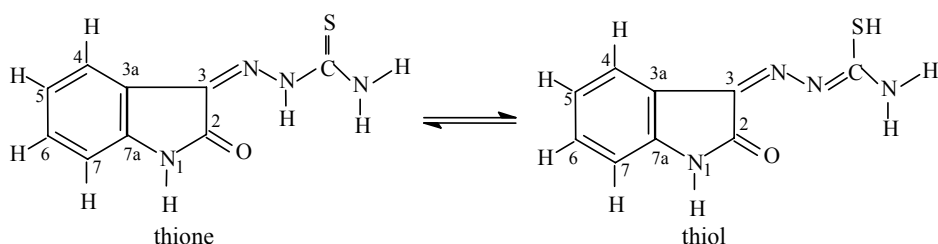


Fig. 1. UV/Vis spectra of isatin- β -thiosemicarbazone (10^{-4} mol dm $^{-3}$ in 70 % ethanol) at pH 6.89 without buffer (1), and at pH 8.1 (2), pH 9.0 (3), pH 9.9 (4), pH 11.0 (5) and pH 12.0 (6).



Scheme 1.

The absorption spectra of the ITC complex with Co(II) in solutions of different pH values are shown in Fig. 2. The optimal pH value for the formation of the Co(II) and Ni(II) complexes ($c_M = c_L = 1.0 \times 10^{-4}$ mol dm $^{-3}$) is 7.3 with buffer, whereas without buffer it is 7.5 for Ni(II) and 7.1 for Co(II). The maximum absorbance at 412 nm for Co(II) and 455 nm for Ni(II) decreases at higher pH values than these.

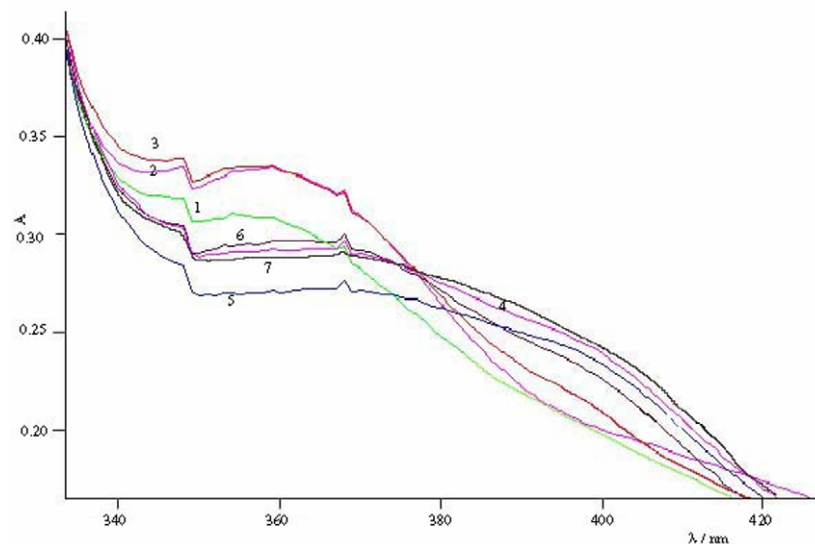


Fig. 2. Absorption spectra of the Co(II) complex in 70 % ethanol at pH 7.1 without buffer (7), and at pH 3.9 (1), 5.5 (2), 6.9 (3), 7.3 (4), 8.1 (5) and 9.9 (6) with buffer.

The best pH value for the formation of the Zn(II) and Hg(II) complexes ($c_M = c_L = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) is at 6.2 and 6.1 without buffer, respectively, and at 6.3 with buffer. The maximum absorbance at 402 nm for the Zn(II) complex does not change uniformly, while the maximum absorbance at 398 nm for the Hg(II) complex decreases at higher pH than these.

Absorption spectra of the ITC complex with Cu(II) in solutions of different pH values are shown in Fig. 3. The optimal pH values for the formation of the Cu(II) and Pd(II) complexes ($c_M = c_L = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$) formation are at 4.9 for Cu(II) and 5.1 for Pd(II) without buffer and at 5.5 with buffer. Maximum absorbance at 450 nm for Cu(II) and 378 nm for Pd(II) decreases at higher pH than these.

The dependence of the absorbance of the complexes on pH is shown in Fig. 4. An analysis of the curves shows the optimal for complex formation. These pH values are in good agreement with those obtained from the absorption spectra of the complexes.

Under the optimum conditions, using a constant concentration of ITC ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) and the varying the Ni(II), Co(II), Cu(II), Zn(II), Pd(II) and Hg(II) concentrations in ethanol–water solutions, it was found that the system obeys the Beer law with standard deviations of 0.002, 0.003, 0.002, 0.004, 0.003, and 0.006, respectively, within the metal concentration range 1.0×10^{-5} – 2×10^{-4} for the Ni(II) and Co(II) complexes, 1.0×10^{-5} – 4×10^{-4} for the Cu(II) and Pd(II) complexes, 0.40×10^{-4} – 2.0×10^{-4} for the Zn(II) complex and 0.20×10^{-5} – 1.00×10^{-4} for the Hg(II) complex. The molar absorptivity (ϵ) values at 455 nm for Ni(II) was $1.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, at 415 nm for Co(II) was $0.39 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, at

402 nm for Zn(II) was $0.29 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, at 450 nm for Cu(II) was $0.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, at 378 nm for Pd(II) was $0.35 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and at 398 nm for Hg(II) was $0.37 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, indicating that ITC can be readily utilized as a sensitive reagent for the micro-analytical determination of these metal ions.

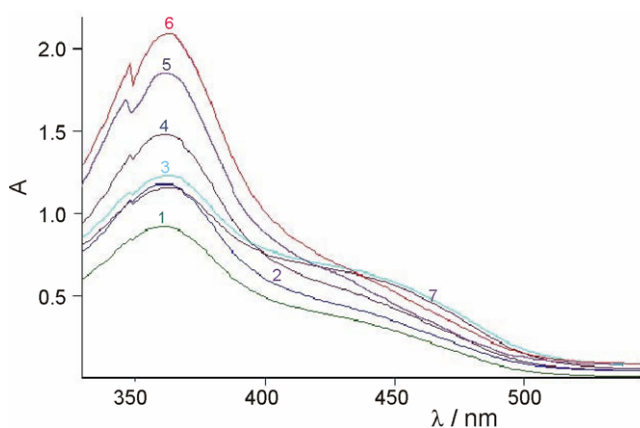


Fig. 3. Absorption spectra of the Cu(II) complex in 70 % ethanol at pH 4.9 without buffer (7), and at pH 3.9 (1), 5.5 (2), 6.9 (3), 7.3 (4), 8.1 (5) and 9.9 (6) with buffer.

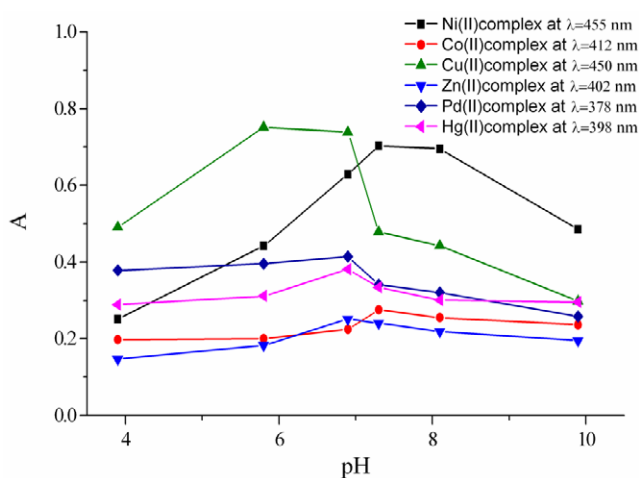


Fig. 4 Absorbance vs. pH of a mixture of ITC with metal ions in 70 % ethanol solution and $I = 0.10 \text{ mol dm}^{-3}$ with KNO_3 .

Composition and stability of the complexes

The composition and values of the stability constant of the formed complexes were determined in 70 % ethanol at $I = 0.10 \text{ mol dm}^{-3}$ (KNO_3) and at a constant temperature of $30 \text{ }^\circ\text{C}$ using a modified Job's method.¹⁰

The Job's curves (Fig. 5) were obtained using equimolar solutions of metal(II) ions and ITC in solutions without buffer. As can be seen, the observed maxima indicate the formation of MeL and MeL_2 complexes for Ni(II) and Co(II), and MeL for Cu(II), Zn(II), Pd(II) and Hg(II) complexes.

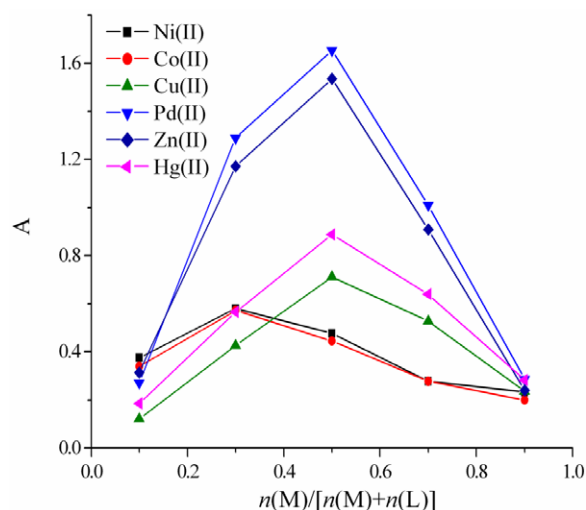


Fig. 5 Job curves for the complexes at pH 7.1 and $\lambda = 412$ nm for Co(II), at pH 7.5 and $\lambda = 455$ nm for Ni(II), at pH 4.9 and $\lambda = 450$ nm for Cu(II), at pH 6.2 and $\lambda = 402$ nm for Zn(II), at pH 5.2 and $\lambda = 378$ nm for Pd(II) and at pH 6.1 and $\lambda = 398$ nm for Hg(II).

The stability constants of the complexes predominant in solution were calculated according to a computerized iterative method of successive approximations.^{11,12} The obtained composition and $\log \beta_n$ values with standard errors are presented in Table I. The values of the stability constants are relative, since the dissociation of the ligand was not taken into consideration.

TABLE I. Composition and stability of the complex of metal(II) ions with ITC in 70 % ethanol ($t = 30$ °C)

Complex	Me:L	$\beta_n / 10^6 \text{ dm}^3 \text{ mol}^{-1}$	$\log \beta_n$	$-\Delta G / \text{kJ mol}^{-1}$
Cu(ITC)Cl ₂	1:1	27.1	7.43	43.13
Zn(ITC)Cl ₂		1.76	6.24	36.24
Pd(ITC)Cl ₂		0.341	5.53	32.08
Hg(ITC)Cl ₂		5.85	6.76	39.27
$\beta_n / 10^5 \text{ dm}^6 \text{ mol}^{-2}$				
Co(ITC) ₂ Cl ₂	1:2	6.39	6.98	40.51
Ni(ITC) ₂ Cl ₂		8.40	7.00	40.63

Thus, the trend of the stability of the complexes follows the order Cu > Ni > Co > Hg > Zn > Pd. This order agrees with the conclusions reached by Irving and William.¹³

The Cu(II) complex is the most stable of the studied complexes, probably due to its 3d⁹ configuration and well-known Jahn–Teller effect.^{14,15} The complexes formed by Ni(II) and Co(II) ions in 1:2 stoichiometry with ITS are more stable than the coordination compounds of a 1:1 type of mercury, zinc and palladium. The information gained from the values of ΔG at 30 °C indicates that the formation of the complexes is spontaneous, exothermic and follows the order of decreasing complex stability.

ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО ПРОУЧАВАЊЕ И АНАЛИТИЧКА ПРИМЕНА
КОМПЛЕКСА Co(II), Ni(II), Cu(II), Zn(II), Pd(II) И Hg(II) СА
ИЗАТИН- β -ТИОСЕМИКАРБАЗОНОМ

САНДРА С. КОНСТАНТИНОВИЋ¹, БЛАГА Ц. РАДОВАНОВИЋ², ЗОРАН Б. ТОДОРОВИЋ¹ И СЛАВИЦА Б. ИЛИЋ¹

¹ Tehnološki fakultet, Bulevar oslobođenja 124, 16000 Leskovac i ² Prirodno-matematički fakultet, Odsek za hemiju, Višegradska 33, 18000 Niš

Састав и стабилност наведених комплекса су испитани коришћењем спектрофотометријске методе при температури од 30 °C и константној јонској јачини 70 % раствора етанола 0,1 mol dm⁻³ (KNO₃). Резултати сугеришу формирање MeL и MeL₂ код Ni(II) и Co(II), и MeL код Cu(II), Zn(II), Pd(II) и Hg(II) комплекса, чије су константе стабилности β_n одређене коришћењем рачунарске итеративне методе sukcesivних апроксимација. Испитана је и могућност примене истраживаног азометина као реагенса за спектрофотометријска одређивања микроколичина метала.

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