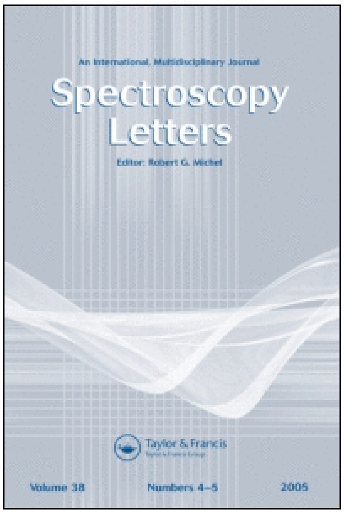

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Synthesis and spectral characterization of N-[5-nitro-2-furfurylidene]-N^2-[β-isatin]azine and its Zn(II), Cu(II) and Ni(II) complexes

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Synthesis and spectral characterization of N[1]-[5-nitro- 2-furfurylidene]-N[2]-[β-isatin]azine and its Zn(II), Cu(II) and Ni(II) complexes

Key words: azine, Zn(II), Cu(II) and Ni(II) complexes, spectral characterization, antibacterial activity.

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Abstract

Coordination compounds of Zn(II), Cu(II) and Ni(II) with N^1-[5-nitro-furfurylidene]-N^2-[β-isatin]azine were prepared. Using elemental analysis, atomic absorption (AA), molar conductances, Fourier transform infrared (FTIR), electronic (UV/VIS) spectroscopics methods, their structure were established to be [ZnLCl$_2$]·H$_2$O, [CuLCl$_2$]·H$_2$O and [NiL$_2$Cl$_2$]·2H$_2$O. Spectral studies indicate complexation through nitrogen atom and oxygen atom of isatin part of ligand. Coordination compounds were tested for antibacterial activity against *Staphylococcus aureus*, *Enterococcus D*, *Proteus vulgaris and Escherichia coli*.

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Introduction

It is known that large number of isatin products have great activity against some microorganisms. Also, many hydrazine products have wide application in medicine as active physiological preparations, due to their activities against tuberkulosis, certain types of cancers and microorganisms[1,2,4].

It is also known that many furan derivatives have wide hemotherapeutic applications in clinical and veterinary medecine[9].

Dodd and Stillman(8) stated that the presence of a nitro-group in position 5 of the furan ring conferred appreciable bacteriostatic action. Thus, the 5-nitrofuran derivatives generally exhibited considerable antibacterial activity, primarly *in vitro* against gram-negative and gram-positive organisms[9]. Some of this type, e.g. Nitrofurazol, Nitrofurantoin and Furazolidon, are applied therapeutically in the treatment of bacterial infective of the urinary tract[13].

It is established that many coordination compounds of transition metals with Schiff bases as ligands, have selective activities and it's showed that complexes have greater activity than ligands[3,6].

Considering all this, it was interesting to try synthesis of compounds with potential biological activity.

The present paper describes the synthesis of N^1-[5-nitro-2-furfurylidene]-N^2-[β-isatin]azine from β-hydrazone of isatin and 5-nitro-2-furancarboxaldehyde. It also describes the preparation of Zn(II), Cu(II) and Ni(II) complexes with N^1-[5-nitro-2-furfurylidene]-N^2-[β-isatin]-azine and their spectral characterization.

Synthesized compounds were tested for antibacterial activity against *Staphylococcus aureus, Enterococcus D, Proteus vulgaris and Escherichia coli* in a standard minimum inhibitory concentration (MIC) serial dilution test.

Experimental

Materials

The chemical used were of the AR grade.

Methods and instruments

Microanalysis of carbon, hydrogen and nitrogen was carried out with a Carlo Erba 1106 microanalyzer. Chloride was determined by Mohr's method. The content of metals was determined by Virial AA-457 Double Beam spectrometer.

Molar conduntance of the complexes were measured with the help of a Iskra Conductivity Meter 0.67 using the 10^{-3}M solutions of DMF.

The electronic spectra (UV/VIS) were recorded on a Perkin - Elmer Lambda 15 UV/VIS spectrophotometer in 95% solutions of ethanol .

The Fourier transformation infrared spectra (FTIR) were recorded with Michaelson Bomen MB-series spectrophotometers, using the potassium bromide KBr pellet (1mg/100mg KBr) technique.

The antimicrobial activity was determined by following the bacterial growth at 37°C in the nutrition medium for 24 hours. The concentration of a compounds tested at which ni increase in optical density was observed after incubation of 24 hours, were accepted as the minimal inhibitory concentration (MIC).

Synthesis of ligand and complexes

(a) Synthesis of β-hydrazone of isatin

β - hydrazone of isatin was prepared by refluxing equimolar amounts of isatin and hydrazone in 95% solution of ethanol for about 1.08×10^5s. The resultant yellow solid products were filtered, washed with ethanol and dried with $CaCl_2$.

(b) Synthesis of N^1-[5-nitro-2-furfurylidene]-N^2-[β-isatin]azine

For the synthesis of N^1-[5-nitro-2-furfurylidene]-N^2-[β-isatin]azine, β - hydrazone of isatin was dissolved in a minimum amount of 95% ethanol. To this refluxing solution, a 5-nitro-2-

furancarboxaldehyde was added in equimolar amounts with continuous refluxing for about 1.62×10^5s. The mixture were acidified with H_2SO_4 to reach pH 4-4.5. The resultant yellow orange coloured solid product was filtered, washed with 95% ethanol and dried with $CaCl_2$.

(c) Synthesis of complexes

For the synthesis of complexes, β - hydrazone of isatin was dissolved in a minimum amount of 95% solution of ethanol. To this refluxing solution, a 5-nitro-2-furancarboxaldehyde was added in equimolar amount together with metal (II) chloride, continuous refluxing for about 2.16×10^5s. The mixture were acidified with H_2SO_4 to reach pH 4-4.5. A coloured crystalline products were filtered, washed with 95% ethanol and dried with $CaCl_2$.

Results and discussion

Synthesis

N^1-[5-nitro-2-furfurylidene]-N^2-[β-isatin]azine were synthesized by the condensation reaction of β-hydrazone of isatin and 5-nitro-2-furancarboxaldehyde in 95% solution of ethanol at pH 4-4.5. Since ligand is partly soluble in 95% solution of ethanol, coordination compounds of Zn(II), Cu(II) and Ni(II) were synthesized by the template reaction of β-hydrazone of isatin and 5-nitro-2-furancarboxaldehyde in the presence of metal(II) chloride in 95% solution of ethanol at pH 4-4.5. The reaction of the formation of complexes, is shown at Figure 1.

Elemental analysis and molar conduntaces

Although the synthesis of complexes were done using molar ratio 1:1 of all reactives,the elemental analysis (Table I) of the complexes indicate 1:1 metal to ligand stoichiometry for Zn(II) and Cu(II) and 1:2 for Ni(II). These complexes are coloured solids, and they are insoluble in water and ether, partly soluble in ethanol and soluble in DMF and DMSO.

Molar conduntances of 10^{-3} molar solutions of the complexes in DMF are found in the range of 10-28 $\mu ohm^{-1}cm^2mol^{-1}$ (Table I). The results of molar conduntance of all the complexes show their nonelectrolytic behaviour[12]. This indicate that chloride ions are also involved in the coordination by presence in the innerspace of complexes.

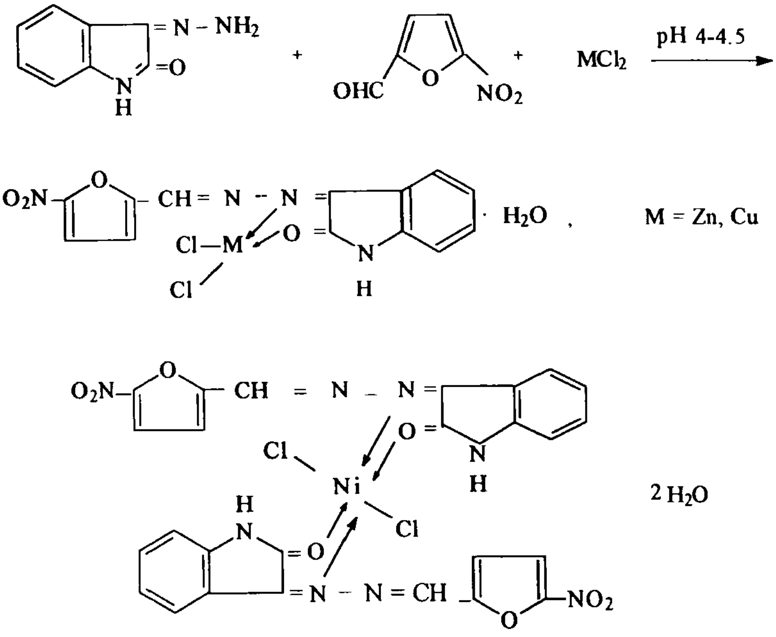

Figure 1. The reaction scheme of the formation of the complexes

Table I. Analytical and physical data of investigated compounds

No.	Compound	Yield (%)	Decom. t.(°C)	Colour	Analysis (%)					Molar. condun. (μohm^{-1} cm^{2}mol^{-1})
					C	H	N Found (Calcd.)	Cl	Me	
1.	β-hydrazone of isatin	90.00	>250	yellow	59.55 (59.62)	4.41 (4.37)	26.15 (26.09)	-	-	-
2.	ligand	46.27	>250	orange	54.88 (54.93)	2.89 (2.82)	19.76 (19.72)	-	-	-
3.	$[ZnLCl_2]\cdot H_2O$	44.02	>250	dark brown	35.50 (35.58)	2.15 (2.28)	12.75 (12.77)	16.29 (16.19)	16.55 (14.92)	16
4.	$[CuLCl_2]\cdot H_2O$	19.35	>250	dark red	35.80 (35.73)	2.09 (2.29)	12.79 (12.83)	16.11 (16.29)	15.03 (14.56)	28
5.	$[NiL_2Cl_2]\cdot 2H_2O$	20.25	>250	light brown	42.52 (42.62)	3.15 (3.11)	17.40 (17.39)	9.54 (9.36)	8.14 (8.00)	10

Electronic absorption spectra

The electronic spectra of compounds were recorded in 95% solution of ethanol (Table II). The electronic spectra of the compounds, shows absorbtion bands due to transitions of the π-π^* type. None of the observed bands can be assigned to a n-π^*transition, since any such transition would be completely exhibit by overlapping π-π^* bands with much greater intesities[9]The transitions of π-π^* type are mainly located on the C=N and C=O groups. The shift of III band to the higher frequency and shift of II band to the lower frequency at complexes, indicate coordination of metal(II) and ligand through C=N and C=O[10,11]. Also, electronic spectra of complexes shows a new band (IV) derived from coordinated metals in coordination compounds.

Infrared spectra

However, the FTIR spectrum is more informative about the possible coordination sites of the ligand. Also, the bidentante nature of ligand is established on the basis of frequency shifts of corresponding absorptions in the FTIR spectrum of the complexes (Table III). The absorption bands ν (C = N) in the spectrum of complexes are shifted to lower frequencies ($\Delta\nu = 3 - 12\ \text{cm}^{-1}$) indicating the formation of a bond between the nitrogen atom of isatin part of the ligand and metal ion. This absorption band can't be found in the spectra of complex of cooper, since overlapping by other bands in this area. The absorption bands of ν(C = O) stretching vibrations are shifted to lower frequencies ($\Delta\nu = 27 - 13\ \text{cm}^{-1}$) in the spectrum of complexes. This indicates that C = O group is the second coordination site of the ligand. In the spectrum of complexes are also observed a vibrations ν(OH) corresponding to lattice water in regio 3357 - 3364cm^{-1}. Lattice water is in outer sphere of complexes and it's became during the reaction of condesation[5]. In spectrum of complexes are also vibrations corresponding to M - O in regio 502 - 498 cm^{-1}, and M - N in regio 461 - 446 cm^{-1}.[1,4,7] Thus, the knowledge gained from the infrared spectrum provides clear evidence that the ligand is bonded both through the nitrogen atom and oxygen atom from isatin part in bidentante manner.

Antibacterial activity

The impact of central ion of the compounds was found on antimicrobial activity against tested gram-positive and gram-negative organisms. Experimental MIC are shown in a Table IV. As it

Table II. Electronic spectral data of investigated compounds recorded in 95% ethanol at 25°C [λ_{max} (nm) and $\varepsilon_{max} \times 10^3$ ($mol^{-1}dm^3cm^{-1}$)]

No.	Compound	I	II	III	IV
1.	β-hydrazone of isatin	_	271.2 (1.547)	326.4 (1.062)	_
2.	ligand	210.0 (0.798)	271.4 (2.914)	329.2 (2.013)	_
3.	$[ZnLCl_2]\cdot H_2O$	230.8 (0.487)	270.2 (9.220)	329.8 (7.670)	376.4 (4.290)
4.	$[CuLCl_2]\cdot H_2O$	214.0 (3.380)	264.4 (1.203)	386.0 (0.626)	458.8 (0.415)
5.	$[NiL_2Cl_2]\cdot 2H_2O$	213.0 (1.286)	271.4 (2.265)	329.4 (1.386)	379.4 (0.416)

Table III. FTIR spectral data of investigated compounds [frequency (cm^{-1})]

No	Compound	Assigment of bands[a]					
		ν(OH)	ν(C=O)	ν(C=N)[1]	ν(C=N)[2]	M - O	M - N
1.	β-hydrazone of isatin	-	1759w	1605s	–	-	-
2.	ligand	_	1759w 1716w	1605m	1589s		
3.	$[ZnLCl_2]\cdot H_2O$	3357s	1733m 1713m	1604s	1589s	498w	446m
4.	$[CuLCl_2]\cdot H_2O$	3364s	1732w 1703s	-	1577m	501m	461m
5.	$[NiL_2Cl_2]\cdot 2H_2O$	3357s	1785w -	1601s	1589s	502s	446s

[a] Relative intensity:s - strong, m - medium, w - weak

[1] Vibrations of group from β-hydrazone of isatin part of ligand

[2] Vibrations of azomethine group

Table IV. Range of minimal inhibitory concentration ($\mu g ml^{-1}$) of investigated compounds

No	Compound	S.aureus	E.group D	P.vulgaris	E.coli
1.	ligand	> 1000	> 1000	> 1000	> 1000
2.	$[ZnLCl_2]\cdot H_2O$	< 50	200 - 500	< 50	50 - 200
3.	$[CuLCl_2]\cdot H_2O$	< 50	< 50	< 50	< 50
4.	$[NiL_2Cl_2]\cdot 2H_2O$	50 - 200	200 - 500	200 - 500	50 - 200

shows, all compounds have antibacterial activity *in vitro* against test-bacterial organisms in different concentration. The results show that coordination compounds have greater activity than ligand, which indicate that coordinated biometals have influence on antibacterial effects. It also shows that metals have different activity, and it decreases in a range: Cu≥ Zn> Ni.

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