Transition Metal Complexes of Isonicotinoyl- -hydrazone-4-diphenylaminobenzaldehyde: Synthesis, Characterization and Antimicrobial Studies

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Abstract: A series of complexes of Cu(II), Ni(II), Co(II), Mn(II) and Cd(II) with isonicotinoylhydrazone-4-diphenylaminobenzaldehyde (INHDA) has been reported. The complexes have been characterized by analytical data, IR, UV-Vis, NMR spectra, magnetic susceptibility values, thermal analysis and for the Cu(II) complex the ESR spectrum has been registered. The biological activity of these complexes were investigated against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella enteritidis*, *Shigella flexneri* bacteria. The INHDA ligand is coordinate at the metallic ions by oxygen amide (O=C) and the azomethine nitrogen.

Keywords: Template synthesis, Isonicotinoylhydrazone, Complexes, Antibacterial activity

Introduction

The heterocyclic chemistry offers the results of the researches show a lot of bioactive substances. The parameters of the chemical structure, the physical and electronical characteristics of the molecule are determined factors in the manifestation of the bioactivity¹⁻³. Hydrazones and Schiff bases were the subject of many interesting studies due to their important applications in much synthetic areas especially in indicators-chemistry. Hydrazones are being used extensively in detection and quantitative determination of several metals, for the preparation of compounds having diverse structures, analytical chemistry for the identification and isolation of carbonyl compounds⁴. However, the most valuable property of hydrazones is perhaps their great physiological activity. It is well known that the

hydrazone group provides a wide range of application in biological and pharmaceutical fields. Therefore, a number of hydrazide-hydrazone derivatives have been claimed to possess interesting antibacterial-antifungal, anticonvulsant, antiinflammatory, antimalarial and antituberculosis activities⁵⁻¹². In the continuation of our earlier studies on the complexes with the ligands from the aroylhydrazone class^{13,14} we report here the synthesis and characterization of the complexes of Cu(II), Ni(II), Co(II), Mn(II), Cd(II) with the isonicotinoylhydrazone-4-diphenylaminobenzaldehyde ligand.

Experimental

All reagents and solvents used are of the type AR and were used without further purification. The metal content and chlorine was obtained by the literature methods¹⁵ and carbon, hydrogen and nitrogen were determined with an analyzer CHN-Hewlett Packard 185. The IR spectra were recorded between 4000-400 cm^{-1} on a BIORAD-FT-IR 135 FTS spectrophotometer in a disc of anhydrous KBr. The electronic spectra in reflection (300-1100 nm) were obtained on a VSU-2P Zeiss-Jena spectrophotometer using MgO as a standard. The ESR spectrum for the Cu(II) complex were registered at room temperature (293 K) on a microcrystalline powder with an ART 5 spectrophotometer. The magnetic moments were determined by the Faraday method at the room temperature. ^1H and ^{13}C NMR spectra were recorded on a device Varian Gemini 300BB in DMSO- d_6 . The molar conductivity of the complexes was measured with a HACH-sens ion 5-conductivitymeter to the solutions in DMF 10^{-3} M. The thermic analysis was realized with an MOM-Q-1500 D derivatograph in air with a heating rate of $5^\circ\text{C}/\text{min}$. The biological activity of the complexes was studied by the diffusion technic in agar plates using DMF as solvent at the concentration of 150 $\mu\text{g}/\text{mL}$.

Synthesis of ligand (INHDA B)

A solution of 0.001 mol of isonicotinoylhydrazine and 0.001 mol of 4-diphenylaminobenzaldehyde in 75 mL (MeOH + C_6H_6) was refluxed for 4 h on a water-bath. After the solution was concentrated the precipitate was filtered and recrystallized from ethanol (Figure 1).

Synthesis of complexes

A methanolic solution of metal chloride MCl_2 (0.002 mol/25 mL MeOH) was added to a mixture of isonicotinoylhydrazine (0.002 mol INH/40 mL MeOH) and 4-diphenylaminobenzaldehyde (0.002 mol DAB/60 mL MeOH + C_6H_6). The reaction mixture was refluxed on a water-bath for 4 h after which a part of the solvent was removed by distillation. The precipitated complexes were filtered, washed with methyl alcohol and then with ether and finally dried in vacuum on anhydrous CaCl_2 .

Figure 1. Isonicotinoylhydrazone-4-diphenylaminobenzaldehyde (INHDA B = HL).

Results and Discussion

The obtained complexes were coloured powders, stable for a long time in the open atmosphere, insoluble in methanol, ethanol, chloroform and acetone; the complex combinations of Ni(II), Co(II), Mn(II) are soluble in DMF but the complexes of Cu(II), Cd(II) are partly soluble. The analytical data suggest a ratio of 1:1 (metal : ligand) for the

complexes of Cu(II), Ni(II), Cd(II) and of 1:2 for the complexes of Co(II), Mn(II) (Table 1). The presence of lattice water was confirmed by TG analysis. The molar conductivity corresponding for the Ni(II), Co(II), Mn(II) complexes present low values and in this way it can be assigned a structural formula of non-electrolyte for these.

Table 1. Analytical and physical data of the complexes.

Compound	Colour / m.p, °C	Found(Calcd.), %					Λ_m^* $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
		M	C	H	N	Cl	
INHDA (HL)	Yellow /	—	76.35	4.89	14.06	—	—
$\text{C}_{25}\text{H}_{20}\text{N}_4\text{O}$	209		(76.53)	(5.10)	(14.28)		
[Cu(HL)Cl ₂]	Brown /	11.83	56.76	3.57	10.40	13.26	—
	248	(12.06)	(56.97)	(3.79)	(10.63)	(13.48)	
[Ni(HL)Cl ₂].2H ₂ O	Orange /	10.30	53.56	4.09	9.81	12.51	13.52
	226	(10.52)	(53.79)	(4.30)	(10.04)	(12.73)	
[Co(HL) ₂ Cl ₂].2H ₂ O	Brown /	5.98	62.93	4.41	11.56	7.25	10.74
	221	(6.20)	(63.16)	(4.63)	(11.79)	(7.47)	
[Mn(HL) ₂ Cl ₂]	Light	5.82	65.72	4.17	12.07	7.58	
	Yellow /	(6.03)	(65.93)	(4.39)	(12.30)	(7.80)	14.38
	> 280						
[Cd(HL)Cl ₂]	Yellow /	19.32	51.92	3.24	9.49	12.13	—
	> 280	(19.53)	(52.13)	(3.47)	(9.73)	(12.33)	

* 10^{-3} M solution in DMF

Infrared spectra

The IR spectra analysis gave information about the mode of coordination of the INHDAB ligand to the metallic ions. The characteristic bands are presented in Table 2.

Table 2. Characteristic IR bands (cm^{-1}) of the INHDAB ligand and its complexes.

Compound	ν_{OH} water	ν_{NH}	$\nu \text{ C=O}$		$\delta \text{ NH}$		$\gamma \text{ NH}$		β ring pyridine in plane	$\nu \text{ M-N}$
			Amide I	$\nu \text{ C=N}$	Amide II	Amide III	Amide III			
INHDA (HL)	-	3053	1672	1590	1554	1331	604	-	-	-
[Cu(HL)Cl ₂]	-	3058	1660	1573	1551	1357	602	443		
[Ni(HL)Cl ₂].2H ₂ O	3395	3059	1654	1577	1553	1354	597	419		
[Co(HL) ₂ Cl ₂].2H ₂ O	3358	3056	1655	1575	1550	1358	598	428		
[Mn(HL) ₂ Cl ₂]	-	3060	1657	1578	1549	1345	601	412		
[Cd(HL)Cl ₂]	-	3091	1656	1574	1556	1352	605	421		

In the ligand spectrum ν_{NH} vibration from the imide group is located at 3053 cm^{-1} . The amide band I is situated at 1672 cm^{-1} and the band at 1590 cm^{-1} is assigned to the vibration corresponding to the azomethine group^{16,17}. The amide II ($\delta \text{ NH}$) and amide III ($\gamma \text{ NH}$) vibrations give bands in spectrum situated at 1554 cm^{-1} and 1331 cm^{-1} respectively. The weak band from 604 cm^{-1} shows the “ β ” deformation in plane from the pyridinic ring. IR spectra of the complexes of Ni(II), Co(II) contain a broad band situated in the range $3400 - 3350 \text{ cm}^{-1}$; this band is associated to the lattice water from the composition of these complexes¹⁸. The imido ν_{NH} frequency appears in the region $3091-3056 \text{ cm}^{-1}$ and as consequence the imide group does not changed its structure during the coordination. The amide I vibration shift towards lower values and as a result the hydrazone ligand is

coordinated to the metal ions by mean of the amide oxygen ($\text{O}=\text{C}$)¹⁹. The azomethine frequency band $\nu\text{N}=\text{C}$ is found to the lower values suggests the azomethine nitrogen coordination in all the complexes^{20,21}. The deformation in plane for the pyridinic ring is found at close values from that of free ligand and thus suggests that the nitrogen from the pyridinic ring is not involved in the coordination²². The coordination of the azomethine nitrogen of the INHDAB ligand to the Cu(II), Ni(II), Co(II), Mn(II), Cd(II) ions was also proved by the $\nu\text{M}-\text{N}$ vibrations appearing in the range $443\text{--}412\text{ cm}^{-1}$,²³ which were absent in the spectrum of the ligand.

NMR spectra

The INHDAB ligand formation is confirmed by the singlet from δ 8.40 ppm assigned to the azomethine proton ($-\text{N}=\text{CH}-$) in ^1H NMR spectrum but also by the peak from δ 140.95 ppm associated to the azomethine carbon in the ^{13}C NMR spectrum. Beside these values in the ^1H NMR spectrum of the ligand show signal to δ 11.97; δ 8.78 ppm assigned to the protons amide $-\text{NH}-8$; H-2,6 pyridine and also peaks in the ^{13}C NMR spectrum to δ 161.19; δ 149.25 ppm corresponding to the atoms of carbon amide-7; C-2,6 pyridine. In ^1H NMR spectrum of the complex of Cd(II) the signals of the protons $-\text{NH}-8$ amide and azomethine shift with 0.34 ppm and respectively 0.41 ppm result which sustain the coordination of the ligand by the amide oxygen $\text{O}=\text{C}$ and the azomethine nitrogen. The signals of the atoms of carbon C-7 and C-10 in the ^{13}C NMR spectrum present shifts of 2.76 ppm respectively 2.48 ppm and pointed clearly the involvement of the atoms of amide oxygen and azomethine nitrogen in coordination. The atoms of carbon C-2,6 have signals in the same region of the spectrum and the shift is very small and in this way is confirmed that the pyridinic nitrogen is not involved in the coordination.

Electronic spectra, ESR and magnetic determinations

The electronic spectra (Table 3) and the magnetic moments support the stereochemistry of the complexes. The electronic spectrum of the INHDAB ligand presents a maximum of absorption at 28169 cm^{-1} assigned to the $n \rightarrow \pi^*$ transition from the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ chromophore groups. This transition could be found again in the complex combinations spectra but shifts towards lower frequencies, result which indicates the coordination of the ligand at the metallic ions²⁴.

Table 3. Reflection spectra for the ligand and complexes.

Compounds	Frequencies, cm^{-1}	Assigning
INHDAB (HL)	28169	$n \rightarrow \pi^*$
	26595	$n \rightarrow \pi^*$
[Cu(HL)Cl ₂]	19607	$^2\text{B}_{1g} \rightarrow ^2\text{E}_g$
	14492	$^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$
[Ni(HL)Cl ₂].2H ₂ O	27100	$n \rightarrow \pi^*$
	21834	$^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$
	17605	$^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$
	27472	$n \rightarrow \pi^*$
	19920	$^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g} (\text{P})$
[Co(HL) ₂ Cl ₂].2H ₂ O	15137	$^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g} (\text{F})$
	10224	$^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g} (\text{F})$
	27322	$n \rightarrow \pi^*$
[Mn(HL) ₂ Cl ₂]	24096	CT
	26385	$n \rightarrow \pi^*$
[Cd(HL)Cl ₂]	25188	CT

The Cu(II) complex displays electronic spectral bands in the region 19607 cm^{-1} and 14492 cm^{-1} , which may be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in a square-planar stereochemistry²⁵. The experimental value of the magnetic moment is of 1.83 BM and suggests a monomeric square-planar geometry. The ESR spectrum of a polycrystalline sample of the complex measured at room temperature gave $g_{\parallel}$ and $g_{\perp}$ values in the range of 2.164 and 2.073, respectively. The high intensity of the signal confirms the monomeric molecular formula. The $g_{\parallel}$ and $g_{\perp}$ values were > 2 , corresponding to an axial symmetry with all main axes disposed parallelly. The fact that $g_{\parallel} > g_{\perp} > 2.0023$ supports a ground state of the Cu(II) ion with the unpaired electron in the $d_{x^2-y^2}$ orbital and from the ESR spectrum there results an square-planar geometry²⁶. The G parameter determined as $G = [(g_{\parallel} - 2) / (g_{\perp} - 2)]$ was found to be much less than 4, suggesting considerable interaction in the solid state. For the Ni(II) complex, two absorption bands appeared at 17605 cm^{-1} and 21834 cm^{-1} . These bands could be assigned to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ which characterize the Ni(II) ion in the square-planar stereochemistry²⁷. The diamagnetism of the complex confirms this symmetry. In the spectrum of Co(II) complex, the bands at 10224 cm^{-1} , 15137 cm^{-1} and 19920 cm^{-1} are associated to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) respectively ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3). These transitions are specified to the Co(II) ion in the field of octahedral symmetry and the magnetic moment of 4.92 BM corresponds to this geometry¹⁹. The ligand field splitting energy (10 Dq), interelectronic repulsion parameter (B) and nephelauxetic ratio (β) for the Co(II) complex were calculated using the secular equations given by König²⁸ and these correspond to the 10 Dq = 11388 cm^{-1} , B = 724 cm^{-1} , $\beta = 0.74$ values.

$$10\text{ Dq} = 2\nu_1 - \nu_3 + 15B$$

$$B = 1/30 [-(2\nu_1 - \nu_3) + (-\nu_1^2 + \nu_3^2 + \nu_1 \nu_3)^{1/2}]$$

The value of the β parameter indicates a moderate covalent character for the metal–ligands bonds. In the case of the Mn(II) complex, the „*d-d*” transitions doubly forbidden from the fundamental term ${}^6A_{1g}$ towards the quartet terms ${}^4A_{1g}(G)$, ${}^4E_g(G)$, ${}^4T_{2g}(G)$, ${}^4T_{1g}(G)$ exhibit a very small intensity and are concealed by the intraligand transitions²⁹. The absorption band at 24096 cm^{-1} can be attributed to the charge transfer of ligand $\rightarrow$ metal. The magnetic moment of 5.86 BM supports an octahedral configuration of the type high spin around the Mn(II) ion. The Cd(II) complex presents an intense band situated at 25188 cm^{-1} which can be assigned to the charge transfer transition $L \rightarrow M$ ³⁰. The electronic spectroscopy doesn't permit the establish of a clear stereochemistry for the Cd(II) ion but taking into consideration the bidentate behaviour of the INHDAB (HL) ligand as well as the tendency of the Cd(II) ion for the tetrahedral geometry in the tetracoordination complexes, we propose this type of stereochemistry.

Thermal analysis

Thermal analysis by the TG and DTG techniques has proved to be very useful in determining the crystal water content in complexes and their thermal stability and decomposition mode under a controlled heating rate. The determined temperature ranges and the corresponding percent mass losses are given in Table 4. For the complexes of Ni(II), Co(II) the lattice water is eliminated in the domain $85 - 155\text{ }^{\circ}\text{C}$. At high temperatures ($t > 240\text{ }^{\circ}\text{C}$) the complexes were decomposed and the INHDAB ligand was eliminated in two steps by oxidative degradations; in the final step ($\approx 700\text{ }^{\circ}\text{C}$) results the metallic oxides as stable residue: CuO, NiO, Co_3O_4 , Mn_2O_3 and CdO. Data from the thermal analysis sustain the molecular formulas assigned for these complexes. The structural formulas assigned to the complexes are presented in Figure 2.

Table 4. Thermal analysis for the complex combinations.

Complex	Total mass losses		Temp. °C	Loss, %
	Theoretical, %	Experimental, %		
[Cu(HL)Cl ₂]	85.32	84.94	240-395	32.24
			395-650	52.70
			650-700	14.88 exp./res. 15.10 calc./res.
			85-145	6.28
[Ni(HL)Cl ₂].2H ₂ O	87.06	86.61	145-470	53.92
			470-640	26.41
			640-700	13.18 exp./res. 13.39 calc./res.
			90-155	3.61
[Co(HL) ₂ Cl ₂].2H ₂ O	91.89	91.56	155-430	41.27
			430-665	46.68
			665-700	8.25 exp./res. 8.44 calc./res.
			245-440	22.36
[Mn(HL) ₂ Cl ₂]	91.67	91.33	440-670	68.97
			670-700	8.46 exp./res. 8.67 calc./res.
			260-465	17.03
[Cd(HL)Cl ₂]	77.98	77.75	465-660	60.72
			660-700	22.09 exp./res. 22.31 calc./res.

Figure 2. The structural formula of the complexes; (a) [M(INHDAB)Cl₂].xH₂O; M = Cu(II) x = 0; M = Ni(II) x = 2; (b) [Cd(INHDAB)Cl₂]; (c) [M(INHDAB)₂Cl₂].xH₂O; M = Co(II) x = 2; M = Mn(II) x = 0

Antimicrobial activity

The antimicrobial activity of the synthesized complexes and INHDAB ligand it was evaluated on the gram-(+) bacteria *Staphylococcus aureus* and on the gram-(−) bacteria *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella enteritidis* and *Shigella flexneri*. Table 5 shows the obtained results expressed by the diameter of the inhibition zone of the growth bacteria by the tested compounds.

Table 5. Antimicrobial activity of INHDAB and its metal complexes.

Compound	Bacteria / Inhibition zone (mm)				
	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. enteritidis</i>	<i>S. flexneri</i>
	gram-(+)	gram-(−)	gram-(−)	gram-(−)	gram-(−)
	ATCC 25923	ATCC 25922	ATCC 27853	Code 10871	Code 13532
INHDAB (HL)	4	5	5	5	4
[Cu(HL)Cl ₂]	5	4	4	4	5
[Ni(HL)Cl ₂].2H ₂ O	10	12	11	10	9
[Co(HL) ₂ Cl ₂].2H ₂ O	6	5	6	6	4
[Mn(HL) ₂ Cl ₂]	11	4	10	5	12
[Cd(HL)Cl ₂]	16	18	19	6	7
Ciprofloxacin	25	30	24	28	31

The results show that INHDAB exhibited weak activity. The complexes of Cu(II), Co(II) show a weak action compared to all the germs and the complexes of Ni(II), Mn(II) are a little more active compared to *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Shigella flexneri*. The Cd(II) complex manifest maximum activity to *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* and this effect is assigned to the donor atoms which are not involved in the coordination but become more active by the formation of the complex combination²⁰. The increased activity of the chelates can be explained based on the overtone concept and the Tweedy chelation theory³¹. According to the overtone concept of cell permeability, the lipid membrane surrounding the cell favours the passage of only lipid-soluble materials, which means that liposolubility is an important factor controlling antimicrobial activity. On chelation, the polarity of metal ion is reduced to a greater extent due to overlap of the ligand orbital and partial sharing of its positive charge with the donor groups. In addition, it is also due to delocalization of the π -electrons over whole chelate ring, enhancing the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites of the enzymes of the microorganisms.

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