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Studies on the Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) with the Isonicotinoylhydrazone-3-aldehydeindole

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Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) have been synthetized with the aroylhydrazone ligand (INHAI) formed by condensation of the isonicotinoylhydrazine with 3-aldehyde-indole. The complexes have been characterized by analytical data, IR, UV-Vis, NMR spectra, magnetic susceptibility, thermal analysis and for the Cu(II) complex by ESR spectrum. The biological activity of these complexes have been investigated for the bacterias *Staphylococcus aureus, Escherichia coli* and *Proteus vulgaris*. The INHAI ligand is coordinated bidentate by the oxygen amide C=O and the azomethine nitrogen in the complexes of Cu(II), Ni(II), Co(II) and monodentate by the nitrogen of the pyridinic ring in the complexes of Mn(II), Zn(II), Cd(II).

Key Words: Isonicotinoylhydrazone, Complexes, Azomethine group, Template synthesis, Transition metal ions.

INTRODUCTION

The chemistry of the heterocycles is known for diversity of bioactive substances. More complex formation of the transitional metals with the aroylhydrazone ligands have antibacterial, antitumor, fungicidal and antioxidative activities[1-3]. The complexes of Ni(II) and Mn(II) with the isonicotinoylhydrazone-α-pyridinaldehyde exhibit antituber activity[4]. In continuation of our studies on the complexes with the ligands from the aroylhydrazone[5,6], in this paper, the synthesis and characterization of the complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) with the isonicotinoylhydrazone-3-aldehydeindole ligand have been reported.

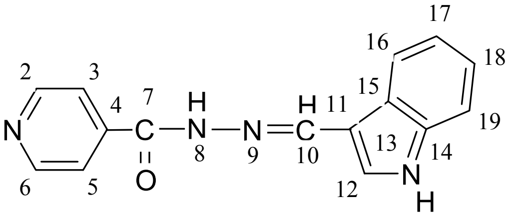

Fig. 1. Isonicotinoylhydrazone-3-aldehydeindole ($C_{15}H_{12}N_4O$) (INHAI = HL)

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 methods[7] and carbon, hydrogen and nitrogen were determined with an analyzer CHN-Hewlett Packard185. The IR spectra were recorded between 4000-400 cm^{-1} on a BIORAD-FT-IR135FTS 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 ART5 spectrophotometer. The magnetic moments were determined by Faraday method at the room temperature. ^{1}H and ^{13}C NMR spectra were recorded on a device Varian Gemini 300BB in DMSO-d_6. The molar conductivity for the complexes of Mn(II), Zn(II), Cd(II) were measured with a HACH-sens ion 5-conductivity meter to the solutions in DMF 10^{-3} M. The thermic analysis was realized with an MOM-Q-1500D derivatograph in air with a heating rate of 5 ºC/min. The biological activity of the complexes was studied by the diffusion technic in Agar plates using DMF as solvent at the concentration of 200 µg/mL. Isonicotinoylhydrazone-3-aldehydeindole (INHAI); analysis, calculated for $C_{15}H_{12}N_4O$: C, 68.18; H, 4.54; N, 21.21. Found : C, 67.97; H, 4.36; N, 21.02. The colour of the ligand is light-yellow; m.p. 147-149 ºC.

Synthesis of the complexes: A methanol solution of respective metal chloride (0.004 mol/25 mL MeOH) was added to a mixture of isonicotinoylhydrazine (0.004 mol/40 mL MeOH) and 3-aldehydeindole (0.004 mol/40 mL MeOH). The reaction mixture was refluxed on a water-bath for 3 h, after which 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 $CaCl_2$. Analysis, calculated % for $[Cu(HL)Cl_2]$: Cu, 15.94; C, 45.16; H, 3.01; N, 14.05; Cl, 17.81; Found: Cu, 15.73; C, 44.94; H, 2.78; N, 13.84; Cl, 17.59. Calculated for % $[Ni(HL)Cl_2]$: Ni, 14.90; C, 45.72; H, 3.04; N, 14.22; Cl, 18.03; Found: Ni, 14.68; C, 45.49; H, 2.83; N, 14.03; Cl, 17.81. Calculated for % $[Co(HL)Cl_2]\cdot 2H_2O$: Co, 13.70; C, 41.86; H, 3.72; N, 13.02; Cl, 16.51; Found : Co, 13.49; C, 41.65; H, 3.51; N, 12.79; Cl, 16.29. Calculated for % $[Mn(HL)_2Cl_2]$: Mn, 8.39; C, 55.05; H, 3.67; N, 17.12; Cl, 10.85; Found: Mn, 8.17; C, 54.84; H, 3.46; N, 16.89; Cl, 10.63. Calculated for % $[Zn(HL)_2Cl_2]\cdot 0.5H_2O$: Zn, 9.71; C, 53.46; H, 3.71; N, 16.63; Cl, 10.54; Found: Zn, 9.49; C, 53.23; H, 3.48; N, 16.41; Cl, 10.33. Calculated for % $[Cd(HL)_2Cl_2]$: Cd, 15.80; C, 50.60; H, 3.37; N, 15.74; Cl, 9.98; Found: Cd, 15.58; C, 50.39; H, 3.15; N, 15.53; Cl, 9.76.

RESULTS AND DISCUSSION

All the complexes are coloured powders with high melting points. These are insoluble in methyl alcohol, ethyl alcohol, chloroform, acetone, while complexes of Mn(II), Zn(II), Cd(II) are soluble in DMF and the other complexes are partially soluble.

The analytical data suggest a ratio of 1:1 (metal:ligand) for the complexes of Cu(II), Ni(II), Co(II) and of 1:2 for the complexes of Mn(II), Zn(II), Cd(II) (Table-1). The molar conductivity presents lower values in the case of the complexes of Mn(II), Zn(II), Cd(II) and hence considered as non-electrolytes.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compounds	m.p. (ºC)	Colour	μ_{eff} (BM)	Λ_m† (Ω^{-1} cm^2 mol^{-1})
[Cu(HL)Cl$_2$]	305	Dark green	2.09	–
[Ni(HL)Cl$_2$]	>340	Orange	Diamag.	–
[Co(HL)Cl$_2$]·2H$_2$O	248	Brown	2.21	–
[Mn(HL)$_2$Cl$_2$]	314	Yellow	5.83	11.26
[Zn(HL)$_2$Cl$_2$]·0.5H$_2$O	261	Yellow	Diamag.	13.08
[Cd(HL)$_2$Cl$_2$]	318	Yellow	Diamag.	12.79

†10^{-3} M solution in DMF.

The key infrared bands are presented in the Table-2. In the ligand spectrum the ν(NH)-indole vibration is found at 3398 cm^{-1} while the ν(NH)-amide vibration is situated at 3098 cm^{-1}. The amide I band is presented at 1657 cm^{-1} and the band from 1604 cm^{-1} correspounds to the valency vibration for the azomethine group[8]. The amide II band δ(NH) is situated at 1551 cm^{-1}. The weak absorption from 615 cm^{-1} is assigned to the deformation vibration in plane, β for the pyridinic ring. The IR spectra of the complexes of Co(II) and Zn(II) contain intense bands at 3450 and 3446 cm^{-1}. These bands correspond to the lattice water presented in the composition of the complexes[8]. The ν(NH)-indole vibration is found in the same region of the ligand and as a result the nitrogen from the indolic skeleton doesn't take part to the coordination. The amide I band and the band of the azomethine frequency ν(C=N) suffers negative shifts in the complexes of Cu(II), Ni(II), Co(II) and positive at the complexes of Mn(II), Zn(II), Cd(II). These results indicate the fact that the INHAI ligand is coordinated by the oxygen amide (C=O) and azomethine nitrogen atoms in the complexes of Cu(II), Ni(II), Co(II) but is not involved in the coordination by these atoms in the complexes of Mn(II), Zn(II), Cd(II). The, β deformation shifts towards higher values in the complexes of Mn(II), Zn(II), Cd(II) and presents very small variations in the complexes of Cu(II), Ni(II), Co(II) and from here result that the nitrogen from the pyridinic ring is coordinated to the Mn(II), Zn(II), Cd(II) and not in the complexes with the Cu(II), Ni(II), Co(II) ions[9].

TABLE-2
KEY IR (cm^{-1}) BANDS FOR LIGAND AND ITS METAL COMPLEXES

Compounds	ν(NH) (INH)	ν(C=O) Amide I	ν(C=N)	δ(NH) Amide II	β ring pyridine in plane	ν(M-N) Azomethine
INHAI(HL)	3098	1657	1604	1551	615	–
$[Cu(HL)Cl_2]$	3060	1613	1573	1507	614	435
$[Ni(HL)Cl_2]$	3045	1612	1574	1513	613	426
$[Co(HL)Cl_2]\cdot 2H_2O$	3050	1602	1573	1494	615	424
$[Mn(HL)_2Cl_2]$	3047	1670	1616	1551	635	–
$[Zn(HL)_2Cl_2]\cdot 0.5H_2O$	3056	1660	1610	1547	650	–
$[Cd(HL)_2Cl_2]$	3051	1669	1613	1551	637	–

The signal of the azomethine proton (-N=CH-) from δ 8.66 ppm in the ^1H NMR spectrum and also the peak from δ 146.26 ppm attributed to the azomethine carbon in the ^{13}C NMR spectrum sustain the INHAI ligand formation. In the ^1H NMR spectra of the complexes of Zn(II) and Cd(II) the signals of the protons H8-amide, H10-azomethine, H13-indole and also the peaks C7, C10, C12, C14 from the ^{13}C NMR spectra present very small shifts and thus confirmed that the oxygen amide, azomethine nitrogen, indolic nitrogen atoms are not involved in the coordination in these complexes. The signals of the C2,6 and C4 atoms shift with 2.6; 2.67 ppm, respectively 2.88; 2.83 ppm, results which put on evidence the coordination of the pyridinic nitrogen to the Zn(II), Cd(II) ions[10].

The electronic transitions (Table-3), the magnetic moments (Table-1), the analytical data indicate a tetrahedral geometry for the complexes of Cu(II), Mn(II), Zn(II), Cd(II)[11] and a square-planar configuration around the metalic ion for the complexes of Ni(II), Co(II)[11]. In the ESR spectrum the high intensity of the signal suggests a monomeric structure for the Cu(II) complex. The form of the spectrum together with the value of the, g parameter (gisotrope = 2.0567) sustain a tetrahedral stereochemistry weak distortion[12]. The complexes of Co(II), Zn(II) lose the lattice water between 80-160 ºC. All the complexes decomposed at high temperatures (> 260 ºC) and the ligand is fractionary eliminated and resulted as stable metal oxides such as CuO, NiO, Co_3O_4, Mn_2O_3, ZnO, CdO. The structures of all the complexes structures are presented in the Figs. 2-4.

TABLE-3
REFLECTION SPECTRA FOR LIGAND AND ITS METAL COMPLEXES

Compounds	Frequencies (cm^{-1})	Assignments
INHAI(HL)	27397	$n \rightarrow \pi^*$
$[Cu(HL)Cl_2]$	25641	$n \rightarrow \pi^*$
	12195	$^2T_2 \rightarrow {}^2E$
$[Ni(HL)Cl_2]$	23529	$n \rightarrow \pi^*$
	21052	$^1A_{1g} \rightarrow {}^1B_{1g}$
	19047	$^1A_{1g} \rightarrow {}^1A_{2g}$
$[Co(HL)Cl_2].2H_2O$	24096	$n \rightarrow \pi^*$
	21276	$^2A_{1g} \rightarrow {}^2E_g$
	16393	$^2A_{1g} \rightarrow {}^2B_{2g}$
$[Mn(HL)_2Cl_2]$	26315	$n \rightarrow \pi^*$
	23255	C T
$[Zn(HL)_2Cl_2].0.5H_2O$	26455	$n \rightarrow \pi^*$
	23809	C T
$[Cd(HL)_2Cl_2]$	26178	$n \rightarrow \pi^*$
	24213	C T

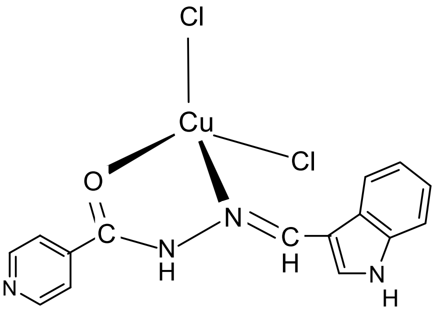

Fig. 2. Structure of the complex $[Cu(HL)Cl_2]$

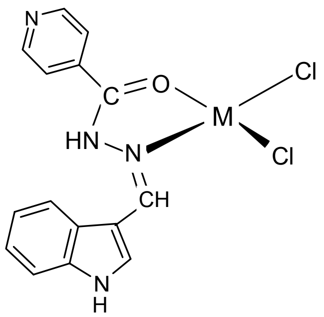

Fig. 3. Structure of the complexes $[M(HL)Cl_2]\cdot xH_2O$ [M = Ni(II), x = 0; M = Co(II), x = 2

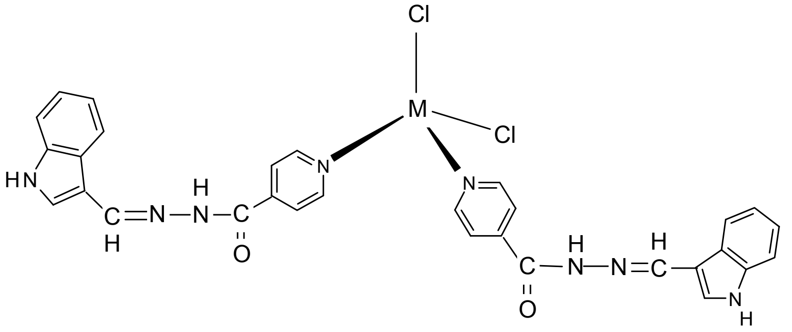

Fig. 4. Structure of the complexes $[M(HL)_2Cl_2]\cdot xH_2O$ M = Mn(II), Cd(II), x = 0; M = Zn(II), x = 0.5

The tests of the biological activity (Table-4) show the fact that for the *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) bacteria, the complexes of Cu(II), Ni(II), Co(II) which contain the bidentate INHAI ligand are less actives than the free ligand while the complexes of Mn(II), Zn(II), Cd(II) which contain the monodentate INHAI ligand present a higher activity than the ligand. For the *Proteus vulgaris* (Gram-negative) bacteria, all the complexes have a lower activity compared with the ligand.

TABLE-4
ANTIMICROBIAL ACTIVITY OF INHAI AND ITS COMPLEXES

Compounds	Bacteria/Inhibition zone (mm)		
	S. aureus Gram-positive	*E. coli* Gram-negative	*P. vulgaris* Gram-negative
INHAI(HL)	7	6	15
$[Cu(HL)Cl_2]$	5	5	12
$[Ni(HL)Cl_2]$	6	5	6
$[Co(HL)Cl_2]\cdot 2H_2O$	5	6	10
$[Mn(HL)_2Cl_2]$	10	12	13
$[Zn(HL)_2Cl_2]\cdot 0.5H_2O$	13	16	11
$[Cd(HL)_2Cl_2]$	11	13	12

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