



J. Serb. Chem. Soc. 76 (8) 1103–1115 (2011)
JSCS–4188

Synthesis and characterization of new complexes of some divalent transition metals with *N*-isonicotinamido-4-chlorobenzalaldimine

LUCICA VIORICA ABABEI^{1*}, ANGELA KRIZA², CRISTIAN ANDRONESCU³
and ADINA MAGDALENA MUSUC³

¹The House of Teaching Staff Giurgiu, 8, Nicholae Droc Barcian Street, Giurgiu,

²University of Bucharest, Faculty of Chemistry, 23 Dumbrova Rosie Street,

Bucharest and ³Romanian Academy, "Ilie Murgulescu" Institute of Physical
Chemistry, 202 Independence Avenue, 060021 Bucharest, Romania

(Received 27 October 2010, revised 2 February 2011)

Abstract: New complexes of *N*-isonicotinamido-4-chlorobenzalaldimine (INHCBA) with Cu(II), Co(II) and Cd(II), having formula of the type $[M(\text{INHCBA})(\text{ac})_2] \cdot x\text{H}_2\text{O}$ ($M = \text{Cu}^{2+}$, $x = 1$, $M = \text{Co}^{2+}$, $x = 2$, $M = \text{Cd}^{2+}$, $x = 0$, $\text{ac} = \text{CH}_3\text{COO}^-$), and with Cu(II), Mn(II) and Zn(II), having formula of the type $[M(\text{INHCBA})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot x\text{H}_2\text{O}$ ($M = \text{Cu}^{2+}$, Mn^{2+} , $x = 2$ and Zn^{2+} , $x = 2.5$) were synthesized and characterized by analytical and physico-chemical techniques, *i.e.*, elemental analyses, IR, UV–Vis–NIR and EPR spectroscopy as well as thermal analysis and the determination of the molar conductivity and magnetic moments. The thermal behaviour of complexes was studied by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The ligand behaves as bidentate NO, being coordinated through the azomethine nitrogen and carbonylic oxygen. The heats of decomposition, ΔH , associated with the exothermal effects, were also determined.

Keywords: *N*-isonicotinamido-4-chlorobenzalaldimine; template synthesis; transition metal complexes; thermal analysis.

INTRODUCTION

Schiff bases play an important role in inorganic chemistry due to their ability to form stable complexes with most transition metal ions. The coordination compounds of aroylhydrazones were reported to act as enzyme inhibitors and be useful due to their pharmacological applications.^{1–3}

The tuberculostatic activity of isonicotinic acid hydrazide and its aroylhydrazones containing azomethine nitrogen was attributed to their ability to form

* Corresponding author. E-mail: lucica_32@yahoo.com

doi: 10.2298/JSC101027097A

stable complexes with d- and f-block metal ions.⁴ Boraey presented the thermal behaviour of some aroylhydrazone Schiff bases with transition metal complexes.⁵ The chromism of these complexes was discussed in terms of change in the ligand field strength and/or coordination geometry. In the context of previous research, a number of complexes of transition metals with ligands derived from 1-naphthaldehyde isonicotinoylhydrazone⁶ and 2-(phenyl-2-pyridinylmethylene)-isonicotinohydrayide⁷ were obtained and characterized.

Thermal analysis techniques provided information concerning the stability and decomposition of these compounds in the solid state.^{8–11} The results led to information concerning the composition, dehydration and thermal behaviour of the complexes.

The synthesis and characterization of three combinations of Cu(II), Co(II) and Cd(II) acetate and three combinations of Cu(II), Mn(II) and Zn(II) sulphate with *N*-isonicotinamido-4-chlorobenzalimine are reported herein. The structural formula of the ligand is shown in Fig. 1.

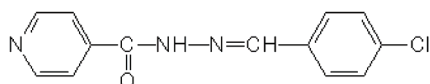


Fig. 1. The structural formula of *N*-isonicotinamido-4-chlorobenzalimine (INHCA).

EXPERIMENTAL

Materials

All chemicals were of pure analytical grade and were purchased from Sigma-Aldrich and Fluka.

Synthesis of *N*-isonicotinamido-4-chlorobenzalimine

N-Isonicotinamido-4-chlorobenzalimine was obtained by refluxing a mixture of isoniazid (0.002 mol) and 4-chlorobenzaldehyde (0.002 mol) (molar ratio 1:1) on a water bath for 5 h. Ethanol (30 mL) was used as the solvent. After cooling, a white precipitate formed which was filtered, washed with ethanol and dried under vacuum over CaCl₂.

Synthesis of complexes

To ethanolic solution of isoniazid (0.002 mol in 30 mL of ethanol) was added an ethanolic solution of 4-chlorobenzaldehyde (0.002 mol in 30 mL ethanol). The mixture was stirred at 50 °C for 30 min and then either an ethanolic solution of Cu (II), Co (II) or Cd (II) acetate (0.002 mol in 30 ml ethanol), or an ethanolic solution of Cu(II), Mn(II) or Zn(II) sulphate (0.001 mol in 15 mL ethanol) was added under stirring. The mixtures were refluxed on water bath for 2 h. On cooling, the metallic complexes precipitated. The solid products (**I–VI**) were filtered, washed with ethanol and dried under vacuum over anhydrous CaCl₂.

Techniques

Elemental analyses (C, H and N) were realised with an Elemental Combustion System CHNS-O, using a Costech device, type ECS 4010. The metal content was determined by gravimetric methods: Cu with salicylaldoxime, and Co, Mn, Zn and Cd as pyrophosphates.¹²

The melting temperatures of the complexes were directly determined using an SMPI Melting Point Apparatus (Stuart Scientific). The molar conductances of the complexes at room

temperature were measured as 10^{-3} M solutions in DMF using a Consort type C-533 conductivity instrument.

The IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded in KBr pellets using a BIO-RAD FTS-135 spectrometer. The reflectance spectra of the complexes were recorded on a JASCO V 670 spectrophotometer.

The magnetic susceptibilities were determined at room temperature using the Faraday method and the electronic paramagnetic resonance (EPR) spectra of the Cu(II) complexes were recorded at room temperature on a Jeol JESS FA 100 spectrometer, with a 100 Hz field modulation.

The thermal experiments were performed on a Mettler Toledo TGA/SDTA 851e thermal analyzer, within the temperature range 300–1300 K, and a Mettler Toledo DSC 853e differential scanning calorimeter, within the temperature range 300–900 K. The TG curves were recorded under a dynamic nitrogen atmosphere with a flow rate of 50 mL min^{-1} and at a heating rate of 10 K min^{-1} . The DSC curves were obtained under a dynamic nitrogen atmosphere with 80 mL min^{-1} flow rate and a 10 K min^{-1} heating rate. The samples were placed in aluminium crucibles for the DSC experiments and alumina crucibles for TG/SDTA experiments, with a pinhole in the lid to prevent pressure build-up due to gaseous products. The sample mass was between 0.8 and 1.5 mg for both methods. At the end of the heating process, the mass of the sample remaining after the DSC experiments represented approximately 35 % from its initial values for all the studied complexes. The TG/DTA and DSC curves were used to characterize the accompanying mass and heat changes during linear heating.

RESULTS AND DISCUSSION

A new Schiff base, named *N*-isonicotinamido-4-chlorobenzalaldimine, was obtained by condensation of *p*-chlorobenzaldehyde (CBA) with isoniazid (INH).

Complexes with INHCBA were obtained by template synthesis. The compounds were soluble in DMF and insoluble in other common organic solvents (methanol, ethanol, acetone, diethyl ether and chloroform). The molar conductivity measurements in DMF showed that the sulphate complexes were 1:1 electrolytes and the acetate complexes non-electrolytes.¹³

The analytical data showed that the complexes may be formulated as $[\text{M}(\text{INHCBA})(\text{ac})_2]$ ($\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II})$ or $\text{Cd}(\text{II})$, $\text{ac} = \text{CH}_3\text{COO}^-$), and $[\text{M}(\text{INHCBA})_2(\text{H}_2\text{O})_2]\text{SO}_4$ ($\text{M} = \text{Cu}(\text{II}), \text{Mn}(\text{II})$ or $\text{Zn}(\text{II})$).

The results of elemental analysis for the prepared complexes are listed below.

$[\text{Cu}(\text{INHCBA})(\text{ac})_2]\cdot\text{H}_2\text{O}$ (**I**). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{ClCuN}_3\text{O}_6$: C, 44.42; H, 3.954; Cu, 13.85; N, 9.146 %. Found: C, 44.16; H, 3.745; Cu, 13.46; N, 9.376 %.

$[\text{Co}(\text{INHCBA})(\text{ac})_2]\cdot 2\text{H}_2\text{O}$ (**II**). Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{ClCoN}_3\text{O}_7$: C, 43.166; H, 4.265; Co, 12.46; N, 8.887 %. Found: C, 43.421; H, 4.435; Co, 12.64; N, 8.645 %.

$[\text{Cd}(\text{INHCBA})(\text{ac})_2]$ (**III**). Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{CdClN}_3\text{O}_5$: C, 41.63; H, 3.29; Cd, 22.93; N, 8.57 %. Found: C, 41.47; H, 3.61; Cd, 22.61; N, 8.90 %.

$[Cu(INHCBA)_2(H_2O)_2](SO_4) \cdot 2H_2O$ (IV). Anal. Calcd. for $C_{26}H_{28}ClCuN_3O_{10}S$: C, 46.34; H, 4.192; Cu, 9.43; N, 6.23 %. Found: C, 46.78; H, 4.365; Cu, 9.14; N, 6.48 %.

$[Mn(INHCBA)_2(H_2O)_2](SO_4) \cdot 2H_2O$ (V). Anal. Calcd. for $C_{26}H_{28}ClMnN_3O_{10}S$: C, 46.94; H, 4.246; Mn, 8.26; N, 6.318 %. Found: C, 46.60; H, 4.564; Mn 8.41; N, 6.63 %.

$[Zn(INHCBA)_2(H_2O)_2](SO_4) \cdot 2.5H_2O$ (VI). Anal. Calcd for $C_{26}H_{29}ClN_3O_{10.5}Szn$: C, 45.60; H, 4.272; N, 6.139; Zn, 9.55 %. Found: C, 45.89; H, 4.601; N, 6.42; Zn, 9.30 %.

Some physical properties (colour, melting point, molar conductivity in DMF 10^{-3} M) of the complexes are given in Table I.

TABLE I. Analytical and physical data of the complexes (INHCBA = *N*-isonicotinamido-4-chlorobenzalaldimine; ac = CH_3COO^-)

Compound	Colour	M. p., °C	$\Lambda_M^a / \Omega^{-1} cm^2 mol^{-1}$	μ_{eff} / μ_B
$[Cu(INHCBA)(ac)_2] \cdot H_2O$ (I)	Brown	270	5.5	2.25
$[Co(INHCBA)(ac)_2] \cdot 2 H_2O$ (II)	Brown	255	4.1	5.51
$[Cd(INHCBA)(ac)_2]$ (III)	Yellow	299	2.6	Diamagnetic
$[Cu(INHCBA)_2(H_2O)_2](SO_4) \cdot 2H_2O$ (IV)	Green	239	86	2.07
$[Mn(INHCBA)_2(H_2O)_2](SO_4) \cdot 2H_2O$ (V)	White	>325	80	5.78
$[Zn(INHCBA)_2(H_2O)_2](SO_4) \cdot 2.5H_2O$ (VI)	Yellow	>325	82	Diamagnetic

^a 10^{-3} M in DMF at 20 °C

Infrared spectra

The main bands from the IR spectra of the ligand and its metal complexes are presented in Table II.

INHCBA is expected to act as tridentate ligand, the possible coordination sites being the pyridinic nitrogen, the azomethine nitrogen and the amide group. A study and a comparison of the IR spectrum of INHCBA and those of its metal complexes imply that the ligand is bidentate in nature with the carbonyl oxygen and the azomethine nitrogen as the two coordination sites.

In the IR spectrum of the ligand, an intense band appears at 1668 cm^{-1} , which is assigned to the frequency vibration $\nu(C=O)$ amide I. In the IR spectra of the complexes, the band group corresponding to amide I appear shifted by $5\text{--}69\text{ cm}^{-1}$ towards lower frequencies, which indicates the involvement of the carbonyl group in the coordination.¹⁴

The NH stretching bands of the free ligand occur at 3192 and 3091 cm^{-1} , respectively,¹⁵ and remain unaffected after complexation. This excludes the possibility of coordination through the imine nitrogen atom.

Another important band occurs at 1592 cm^{-1} , attributed to the $\nu(C=N)$ azomethine mode, appears in the IR spectrum of INHCBA.¹⁶ Shifts towards lower values of $\Delta\nu$, $6\text{--}45\text{ cm}^{-1}$, were also observed for the frequencies charac-

teristic of the azomethine group in all the spectra of the metal complexes. This suggests the involvement of the azomethine nitrogen in the coordination of INHCBA with the metal ions.¹⁷

The spectra of complexes show bands assigned to both bridging and chelating binding coordination modes of the acetate anion.¹⁸ A correlation between antisymmetric and symmetric carboxylate group infrared absorption frequencies and carboxylate group types has been developed. The acetate ion in aqueous solution is characterized by bands at 1578 and 1411 cm^{-1} , which are commonly assigned to the antisymmetric (ν_{asym}) and the symmetric (ν_{sym}) stretching vibrations of the carboxylate group. These frequencies and, in particular, their difference, $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}}$ have been used as an empirical indicator of the coordination modes of acetates. According to Deacon and Phillips,¹⁸ a difference larger than 200 cm^{-1} indicates monodentate coordination, whereas one smaller than 150 cm^{-1} indicates a bidentate coordination mode. Moreover, it is accepted that values of $\Delta\nu$ smaller than 200 cm^{-1} can indicate a bidentate coordination mode. In complexes **I–III**, the frequency of $\nu_{\text{asym}}(\text{COO})$ appears at 1490 cm^{-1} , while those characteristic of $\nu_{\text{sym}}(\text{COO})$ ranged from 1358–1414 cm^{-1} . For these complexes, $\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}} < 150 \text{ cm}^{-1}$, which is an indication of a bridge or a chelating binding mode for the coordination of the acetate group. Furthermore, an increase of ν_{asym} as compared to free acetate corresponds to acetate in a bridging coordination mode, while a decrease of ν_{asym} suggests a chelating binding mode.¹⁹

The IR spectra of the complexes **IV–VI** show a band attributed to the counter anion SO_4^{2-} .¹⁴

The bands in the domain 3479–3400 cm^{-1} and 911–902 cm^{-1} in the IR spectra of the complexes **IV–VI** suggest the presence of coordination water.²⁰

The overall IR spectral evidence suggests that INHCBA acts as a bidentate ligand and is coordinated to the metal ions by the azomethine nitrogen and the carbonyl oxygen, whereby a five-member chelate ring is formed.

Electronic and EPR spectra. Magnetic moments

The electronic spectral data and the magnetic moments of the complexes are presented in Table III.

The UV spectrum of the Schiff base presents two bands at 37037 and 28248 cm^{-1} , assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The electronic spectra of the two Cu(II) complexes exhibit bands at 14450 cm^{-1} for complex **I**, and at 13774 cm^{-1} for complex **IV**, which can be attributed to $xy \rightarrow x^2 - y^2$ transitions. These values together with the magnetic moments (2.25 and 2.07 μ_B) suggest an octahedral geometry for the Cu(II) ions.²¹

The EPR spectrum of polycrystalline $[\text{Cu}(\text{INHCBA})(\text{ac})_2] \cdot \text{H}_2\text{O}$ complex (**I**) was recorded at room temperature (Fig. 2a). This complex exhibited a broad and

TABLE II. Selected infrared absorption frequencies (cm^{-1}) of INHCBA and its complexes

Compound	$\nu(\text{OH})$	$\nu(\text{C=O})$ Amide I	$\nu(\text{C=N})$ Azomethine	$\delta(\text{H}_2\text{O})$ Coordinated	$\nu(\text{N-N})$	$\nu(\text{SO}_4^{2-})$ Ionic	$\nu(\text{COO}^-)$ ν_{asym} ν_{sym}	$\Delta\nu$
INHCBA	—	1668	1592	—	850	—	—	—
$[\text{Cu}(\text{INHCBA})(\text{ac})_2] \cdot \text{H}_2\text{O}$ (I)	—	1603	1569	—	842	—	1489 1380	109
$[\text{Co}(\text{INHCBA})(\text{ac})_2] \cdot 2\text{H}_2\text{O}$ (II)	—	1653	1569	—	855	—	1490 1414	76
$[\text{Cd}(\text{INHCBA})(\text{ac})_2]$ (III)	—	1599	1570	—	856	—	1490 1358	132
$[\text{Cu}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2\text{H}_2\text{O}$ (IV)	3400	1646	1586	911	854	1111	—	—
$[\text{Mn}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2\text{H}_2\text{O}$ (V)	3400	1662	1547	910	859	1197	—	—
$[\text{Zn}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2.5\text{H}_2\text{O}$ (VI)	3479	1663	1549	902	860	1123	—	—

TABLE III. Electronic spectral data and geometries for the ligand and complexes

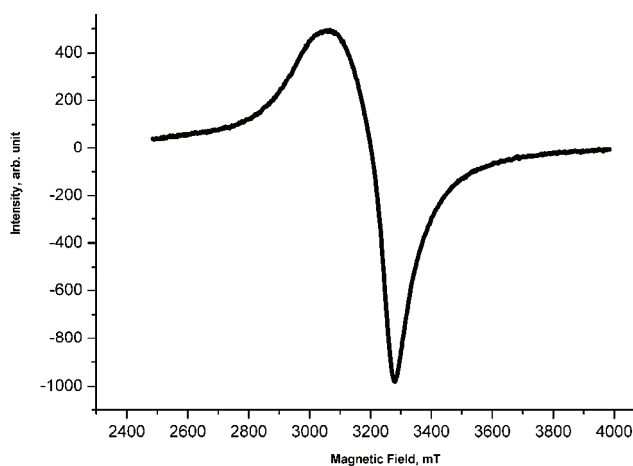
Compound	Frequency, cm^{-1}	Assignment	Geometry	$10\Delta q / \text{cm}^{-1}$	B	β
INHCBA	37037	$\pi \rightarrow \pi^*$	—	—	—	—
	28248	$n \rightarrow \pi^*$	—	—	—	—
$[\text{Cu}(\text{INHCBA})(\text{ac})_2] \cdot \text{H}_2\text{O}$ (I)	38167	$\pi \rightarrow \pi^*$	Octahedral	—	—	—
	28901	$n \rightarrow \pi^*$	—	—	—	—
	14450	$xy \rightarrow x^2 - y^2$	—	—	—	—
$[\text{Co}(\text{INHCBA})(\text{ac})_2] \cdot 2\text{H}_2\text{O}$ (II)	37878	$\pi \rightarrow \pi^*$	Octahedral	8802	860.4	0.886
	29239	$n \rightarrow \pi^*$	—	—	—	—
	21834	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$	—	—	—	—
	17667	${}^4\text{T}_{1g}(\text{F}) \rightarrow \text{A}_{2g}$	—	—	—	—
	8875	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$	—	—	—	—
$[\text{Cd}(\text{INHCBA})(\text{ac})_2]$ (III)	38062	$\pi \rightarrow \pi^*$	Octahedral	—	—	—
	30487	$n \rightarrow \pi^*$	—	—	—	—
$[\text{Cu}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2\text{H}_2\text{O}$ (IV)	38461	$\pi \rightarrow \pi^*$	Octahedral	—	—	—
	29069	$n \rightarrow \pi^*$	—	—	—	—
	13774	$xy \rightarrow x^2 - y^2$	—	—	—	—
$[\text{Mn}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2\text{H}_2\text{O}$ (V)	39370	$\pi \rightarrow \pi^*$	Octahedral	—	—	—
	34246	$n \rightarrow \pi^*$	—	—	—	—
	30487	CT	—	—	—	—
$[\text{Zn}(\text{INHCBA})_2(\text{H}_2\text{O})_2][\text{SO}_4] \cdot 2.5\text{H}_2\text{O}$ (VI)	39682	$\pi \rightarrow \pi^*$	Octahedral	—	—	—
	34482	$n \rightarrow \pi^*$	—	—	—	—

intense slightly anisotropic signal ($g_{\text{isotropic}} = 2.1096$, $H_{\text{isotropic}} = 319.971$ mT), assigned to the Cu(II) ion in a quasi-isotropic octahedral environment.²²

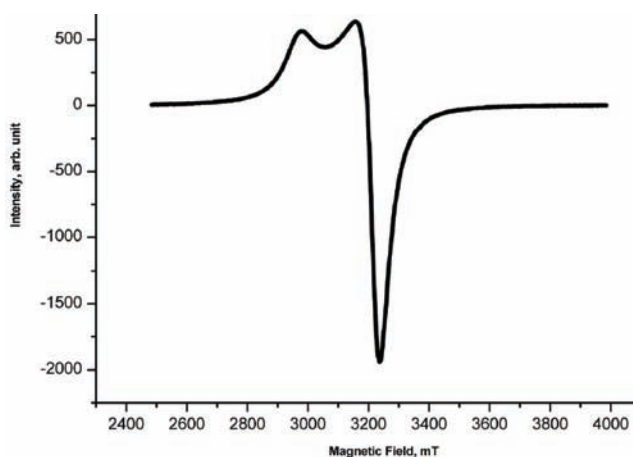
The $[\text{Cu}(\text{INHCBA})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot 2\text{H}_2\text{O}$ complex (**IV**) was also examined by EPR spectroscopy and the values for g_{\parallel} and g_{\perp} were determined for the proper magnetic field (Table IV). The EPR spectrum (Figure 2b) and the values of the magnetic field parameters require an octahedral symmetry for the Cu(II) complex **IV**.

TABLE IV. EPR data of complex **IV**

Compound	g		H / mT	
	g_{\parallel}	g_{\perp}	H_{\parallel}	H_{\perp}
$[\text{Cu}(\text{INHCBA})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (IV)	2.2648	2.1129	298.063	319.491



(a)



(b)

Fig. 2. The EPR spectra for complex **I** (a) and **IV** (b) at room temperature.

The electronic spectrum of the Co(II) complex presents three bands at 8875, 17667 and 21834 cm^{-1} , attributed to the d–d transitions ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively. These transitions and the values of the field parameters correspond to those characteristic for an octahedral geometry.²¹ For this complex, the experimentally determined magnetic moment was 5.51 μ_{B} , indicating a high-spin character and excluding oxidation to Co(III). This value is within the range of 4.3–5.7 μ_{B} corresponding to an octahedral geometry for a cobalt ion.¹⁷

The ligand field splitting energy ($10\Delta q$), the interelectronic repulsion parameter (B) and the nephelauxetic ratio (β) for the Co(II) complex were calculated using the secular equations given by König²³ and the values are presented in Table III.

In the spectra of the Cd(II) and Zn(II) complexes, the bands of the ligand appear displaced to lower values. For d^{10} ions, the UV spectrum provides no information about the environment. However, according to the IR spectra, an octahedral environment of the metallic ion is proposed.

The Cd(II) and Zn(II) complexes are diamagnetic, as expected for the d^{10} configuration.²⁴

The Mn(II) complex presents a signal in UV domain at 30487 cm^{-1} assigned to a transfer of electric load, according to the theory data for a d^5 ion. It is well known that d–d transitions occur in d^5 systems but these transitions are of very low intensity and hence no d–d bands for such transitions were observed.²⁵

The magnetic moment determined for the Mn(II) complex was 5.78 μ_{B} . This value falls in the range of 5.65–6.10 μ_{B} and it is appropriate for manganese ions in an octahedral environment.²⁵

Thermal behaviour of the complexes

The determined temperatures ranges and percent mass losses are given in Table V.

The thermal TG/DTA and DSC curves of ligand are presented in Fig. 1-S, Supplementary material. The TG/DTA curves of Schiff base ligand shows an exothermal decomposition with a maximum at $T_{\text{max}} = 603$ K on the DTG curve. The evaluation of the exothermal peak area (DSC curve) gave a value of $\Delta H = -122.5$ J g^{-1} .

The TG/DTA and DSC curves of complex I are shown in Fig. 2-S, Supplementary material. The mass loss observed between 323 and 373 K, corresponding to an endothermic peak at 310 K on DTG curve, is due to dehydration with a loss of one molecule of water (Calcd., 4.08 %; exp., 4.04 %). The thermal decomposition occurred in two steps between 373–483 K and 483–1260 K with total mass loss of 60.15 %. It can be observed from the TG curve that the decomposition process was not completed. Decomposition of the complex was

also confirmed by a strong exothermic effect on DSC curve with a maximum at 585 K. The evaluation of the exothermal peak area gave a value of $\Delta H = -9708.7 \text{ J g}^{-1}$. The final residue, estimated as CuO and unreacted compound,^{26,27} had an observed mass of 35.81 %.

TABLE V. Thermoanalytical results for the M(II) complexes

Compound	TG range, K	Mass loss found (calcd.), %	Assignment
[Cu(INHCBA)(ac) ₂] \cdot H ₂ O (I)	323–373	4.04 (4.08)	Loss of lattice water molecule
	373–483	10.15 (10.45)	Loss of CO ₂ molecule
	483–1260	50.00	Removal of the ligand (the thermal decomposition was not completed)
	>1260	35.81	Leaving CuO and unreacted compounds
[Co(INHCBA)(ac) ₂] \cdot 2H ₂ O (II)	323–460	8.27 (8.26)	Loss of lattice water molecule
	460–1260	69.16 (69.44)	Loss of CO ₂ molecules and decomposition of ligand
	>1260	22.57 (17.16)	Leaving Co ₂ O ₃
[Cd(INHCBA)(ac) ₂] (III)	500–670	72.73 (70.97)	Loss of CO ₂ molecules and decomposition of ligand
[Cu(INHCBA) ₂ (H ₂ O) ₂](SO ₄) \cdot 2H ₂ O (IV)	>670	24.48 (26.12)	Leaving CdO
	323–383	7.31 (7.34)	Loss of lattice water molecule
	383–470	6.86 (7.34)	Removal of coordinated water molecule
	470–1240	67.71 (69.13)	Removal of one molecule of SO ₃ and ligand
[Mn(INHCBA) ₂ (H ₂ O) ₂](SO ₄) \cdot 2H ₂ O (V)	>1240	18.12 (17.48)	Leaving CuO
	323–388	8.00 (7.46)	Loss of lattice water molecule
	388–523	7.83 (7.46)	Removal of coordinated water molecule
	523–653	16.31 (17.92)	Removal of molecule of SO ₃
[Zn(INHCBA) ₂ (H ₂ O) ₂](SO ₄) \cdot 2.5H ₂ O (VI)	653–1270	38.48 (43.89)	Removal of ligand
	>1270	29.38 (29.00)	Leaving MnO
	323–383	9.11 (9.05)	Loss of lattice water molecule
[Zn(INHCBA) ₂ (H ₂ O) ₂](SO ₄) \cdot 2.5H ₂ O (VI)	383–473	6.28 (6.72)	Removal of coordinated water molecule

TABLE V. Continued

Compound	TG range, K	Mass loss found (calcd.), %	Assignment
[Zn(INHCBA) ₂ (H ₂ O) ₂](SO ₄)·2.5H ₂ O (VI)	473–673	16.32 (17.51)	Removal of molecule of SO ₃
	673–1270	37.29 (38.43)	Removal of ligand
	>1270	31.00 (32.33)	Leaving ZnSO ₄

The thermal decomposition of [Co(INHCBA)(ac)₂].2H₂O proceeded in four stages (Fig. 3-S, Supplementary material). Thermal dehydration occurred between 323 and 460 K with a mass loss of 8.27 %. The subsequent steps corresponded to the total decomposition of the complex. The DSC curve had a wide range of thermal change with several exothermal superposed peaks with maxima at 580, 660, 705 and 830 K. These are correlated with the decomposition of the ligand molecules and loss of CO₂ molecules. The evaluation of the exothermal peaks area (neglecting the partial superposition) gave a value of $\Delta H = -4657.9 \text{ J g}^{-1}$ for the first peak and $\Delta H = -601.5 \text{ J g}^{-1}$ for the second one. The final decomposition process corresponded to the formation of cobalt(III) oxide as the final product.

The TG/DTA and DSC curves of [Cd(INHCBA)(ac)₂] complex are presented in Fig. 4-S, Supplementary material. The complex was stable up to 500 K. The thermal decomposition progressed in one stage, as a complex process with two superposed peaks. The end product, estimated as CdO, had an observed mass of 24.48 %, compared with the calculated value of 26.12 %.

The complexes:

[Cu(INHCBA)₂(H₂O)₂](SO₄)·2H₂O (**IV**),

[Mn(INHCBA)₂(H₂O)₂](SO₄)·2H₂O (**V**) and

[Zn(INHCBA)₂(H₂O)₂](SO₄)·2.5H₂O (**VI**)

underwent decomposition mainly in four stages (Figs. 5-S–7-S, Supplementary material). The first stage occurred in the 323–383, 323–388 and 323–383 K ranges, respectively, corresponding to dehydration process and release of two crystallization water molecules for complexes **IV** and **V**, and 2.5 molecules for complex **VI**. The second decomposition stage of the complexes corresponded to removal of coordinated water molecules. The third decomposition stage of the complexes corresponded to partial decomposition. The third stage for complex **IV** was in the 470–773 K temperature range with two strong exothermic peaks on the DSC curve with maxima at 484 K and 625 K. This correlated with the decomposition of the ligand molecule and expulsion of SO₃ molecules. The evaluation of the areas of the exothermal peaks gave a value of $\Delta H = -290.5 \text{ J g}^{-1}$, and $\Delta H = -1735.9 \text{ J g}^{-1}$, respectively.

The third decomposition stage of the complexes **V** and **VI** is in continuation of the second stage, in the 523–653 K and 473–673 K temperature ranges, respectively.

The final decomposition process for complexes **IV** and **V** corresponded to the formation of copper oxide and manganese oxide, respectively, as the final product. The final residue for complex **VI** was estimated as ZnSO_4 .

Based on the above analytical and spectral data and the thermal analysis, the structural formula and stoichiometry for complexes indicated in Fig. 3 were proposed.

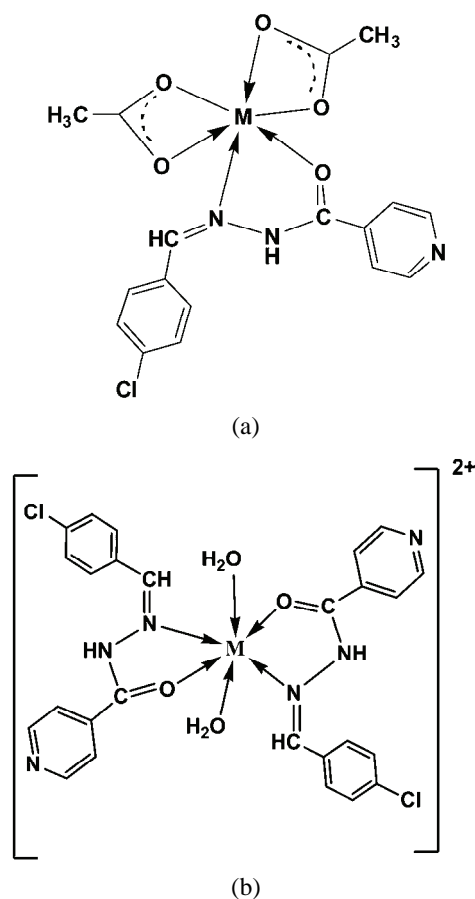


Fig. 3. Structural formula proposed for a) $[\text{M}(\text{INHCBA})(\text{ac})_2] \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, $x = 1$, $\text{M} = \text{Co}^{2+}$, $x = 2$, $\text{M} = \text{Cd}^{2+}$, $x = 0$, $\text{ac} = \text{CH}_3\text{COO}^-$) and b) $[\text{M}(\text{INHCBA})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Cu}^{2+}$, Mn^{2+} , $x = 2$ and Zn^{2+} , $x = 2.5$).

CONCLUSIONS

Six new complexes of *N*-isonicotinamido-4-chlorobenzaldehyde (INHCBA) with Cu(II), Co(II), Cd(II), Mn(II) and Zn(II), were synthesized and characterized. The spectroscopic data showed that the Schiff base ligand acted as bidentate NO, being coordinated through the azomethine nitrogen and carbonylic

oxygen. The structural formula of the complexes were proposed based on elemental analysis, molar conductance, magnetic moment values, IR, UV–Vis and EPR spectra and thermal analysis. The number of water molecules of crystallization was determined by differential thermal analysis. The thermal results allowed information concerning the stoichiometry of these compounds to be acquired.

SUPPLEMENTARY MATERIAL

The thermal TG/DTA and DSC curves of the ligand and complexes are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НОВИХ КОМПЛЕКСА НЕКИХ ДВОВАЛЕНТНИХ ЈОНА ПРЕЛАЗНИХ МЕТАЛА СА *N*-ИЗОНИКОТИНАМИДО-4-ХЛОРБЕНЗАЛЈАЛДИМИНОМ

LUCICA VIORICA ABABEI¹, ANGELA KRIZA², CRISTIAN ANDRONESCU³ и ADINA MAGDALENA MUSUC³

¹The House of Teaching Staff Giurgiu, 8, Nicholae Droc Barcian Street, Giurgiu, ²University of Bucharest, Faculty of Chemistry, 23 Dumbrava Rosie Street, Bucharest u ³Romanian Academy, "Ilie Murgulescu" Institute of Physical Chemistry, 202 Independence Avenue, 060021 Bucharest, Romania

Описана је синтеза и структурна карактеризација нових комплекса двовалентних јона прелазних метала са *N*-изоникотинамидо-4-хлорбензалјалдимином (ИНХСВА) као лигандом. Нађено је да комплекси Cu(II), Co(II) и Cd(II) имају општу формулу типа $[M(\text{INHCSVA}(\text{ac})_2) \cdot x\text{H}_2\text{O}]$ ($M = \text{Cu}^{2+}$, $x = 1$, $M = \text{Co}^{2+}$, $x = 2$, $M = \text{Cd}^{2+}$, $x = 0$, $\text{ac} = \text{CH}_3\text{COO}^-$), док је код комплекса Cu(II), Mn(II) и Zn(II) нађена општа формула типа $[M(\text{INHCSVA})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot x\text{H}_2\text{O}$ ($M = \text{Cu}^{2+}$, Mn^{2+} , $x = 2$ и Zn^{2+} , $x = 2.5$). За карактеризацију комплекса употребљене су различите аналитичке и физичко-хемијске методе, као што су елементална микроанализа, IR, UV–Vis–NIR и EPR спектроскопија, термална анализа, као и различита кондуктометријска и магнетна мерења. Термална анализа комплекса урађена је на бази термогравиметријске (TG) и диференцијалне термалне анализе (DTA), као и диференцијалне скенирајуће калориметрије (DSC). Нађено је да се испитивани лиганд бидентатно (NO) координује, и то преко азотетинског атома азота и карбонилног атома кисеоника.

(Примљено 27. октобра 2010, ревидирано 2. фебруара 2011)

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