

Synthesis and Characterization of Complexes of Mn(II), Co(II), Ni(II) and Cu(II) with an Aroylhydrazone Ligand

L. MITU* and ANGELA KRIZA

*Department of Physics and Chemistry, University of Pitești
Pitești 110040, Romania
E-mail: ktm7ro@yahoo.com*

New complexes of Mn(II), Co(II), Ni(II) and Cu(II) have been obtained with the aroylhydrazone ligand (INH2AP), formed through the condensation of isonicotinoylhydrazine with 2-aldehyde pyrrole. The complexes were characterized by elemental analysis, IR and UV-Vis, magnetic susceptibility, thermal analysis. For the complex of Cu(II) the ESR spectrum was also determined. The elemental analysis suggests a stoichiometry of 1 : 2 (metal : ligand) for the Co(II), Ni(II) and Cu(II) complexes and of 1 : 1 for the Mn(II) complex. The magnetic moments and the electronic spectra indicate an octahedral stereochemistry for all the complexes. The infrared spectra evince the fact that the ligand is coordinated to the metal ions through the atom of oxygen amide (C=O) and the azomethine nitrogen.

Key Words: Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Complexes, Isonicotinoylhydrazone, Azomethine group, "Template" synthesis.

INTRODUCTION

The hydrazones derived from isonicotinoylhydrazine and their metal complexes exhibit a particular significance for the possibilities of medical application. The literature shows that isonicotinoylhydrazine is utilized as an antituberculosis drug. Numerous research papers have emphasised a number of bactericidal or fungicidal properties of the complex combinations of some metal ions with isoniazide, not less than the complex combinations with derived hydrazones^{1,2}. The complexes of Mn(II) and Ni(II) with isonicotinoylhydrazone- α -pyridinaldehyde exhibit an antituberculosis activity³. Within the framework of prior research, complex combinations of a number of transitional metals with an indented isonicotinoylhydrazone ligand were prepared and characterized⁴. In view of the biological importance of the hydrazones derived from isonicotinoylhydrazine, as well as their complex formations with various metal ions, here the authors report the synthesis and the study of the complex combinations of Mn(II), Co(II), Ni(II) and Cu(II) with the INH2AP hydrazone, resulting through the condensation of isonicotinoylhydrazine with 2-aldehyde pyrrole.

EXPERIMENTAL

All chemicals and solvents used were purchased as AR grade and were used without further purification.

The metal contents and chlorine were obtained by means of the methods described in literature⁵ and carbon, hydrogen and nitrogen were determined with an analyser CHN-Hewlett Packard-185. The IR spectra were recorded in the region 4000–400 cm^{-1} , by means of a Biorad-FTIR 135 FTS spectrophotometer, in a disc of anhydrous KBr. The electronic spectra in reflection (300–1100 nm) were achieved with a VSU-2P Zeiss-Jena spectrophotometer, using MgO as a standard. The ESR spectrum for the Cu(II) complex was recorded at room temperature ($T = 293 \text{ K}$) on a microcrystalline powder with an ART-5 spectrophotometer. The magnetic moments were determined through the Faraday method at room temperature. The molar electric conductivity for the Mn(II) complex was measured with an HACH-sense ion 5 conductivity-meter on the DMF 10^{-3} M solution. The thermic analysis was done with an MOM-Q-1500 D derivatograph in air with a heating rate of $5^\circ\text{C}/\text{min}$.

Synthesis of the hydrazone ligand: The INH2AP (HL) ligand was prepared by following the general method. To the methanolic solution of isoniazid (0.002 mol INH/30 mL MeOH) was added a methanol solution of 2-aldehydpyrrole (0.002 mol 2AP/30 mL MeOH). The resulting solution was refluxed for 5 h on a water-bath, after which it was concentrated to less than half of its initial volume; the precipitated hydrazone was filtered under vacuum, it was washed with methyl alcohol and then with ether and dried in vacuum on anhydrous CaCl_2 .

% Analysis, Calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}$: C, 61.68; H, 4.67; N, 26.16; Found: C, 61.41; H, 4.42; N, 25.93. The colour of the ligand was greenish-white; m.p. $205\text{--}207^\circ\text{C}$.

Synthesis of the complex combinations: A methanol solution of metal chloride (0.002 mol/25 mL MeOH) was added to a mixture of isonicotinoylhydrazine (0.004 mol INH/40 mL MeOH) and 2-aldehydpyrrole (0.004 mol 2AP/40 mL MeOH). The reaction mixture was refluxed on a water-bath for 3 h, after which part of the solvent was removed through distillation. The precipitated complexes were filtered, washed first with methyl alcohol and then with ether and finally dried in vacuum on anhydrous CaCl_2 .

% Analysis, Calcd. for $[\text{Cu}(\text{HL})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$: Cu, 10.61; C, 44.10; H, 4.00; N, 18.71; Cl, 11.86; Found: Cu, 10.39; C, 43.85; H, 3.77; N, 18.47; Cl, 11.61. Calcd. for $[\text{Ni}(\text{HL})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$: Ni, 9.88; C, 44.46; H, 4.04; N, 18.86; Cl, 11.95; Found: Ni, 10.09; C, 44.18; H, 3.75; N, 18.61; Cl, 11.69. Calcd. for $[\text{Co}(\text{HL})_2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$: Co, 9.35; C, 41.90; H, 4.44; N, 17.77; Cl, 11.27; Found: Co, 9.10; C, 41.64; H, 4.17; N, 17.53; Cl, 11.02. Calcd. for $[\text{Mn}(\text{HL})\text{Cl}_2(\text{H}_2\text{O})_2]\cdot \frac{1}{4}\text{H}_2\text{O}$: Mn, 14.43; C, 34.69; H, 3.81; N, 14.72; Cl, 18.66; Found: Mn, 14.67; C, 34.41; H, 3.55; N, 14.45; Cl, 18.40.

RESULTS AND DISCUSSION

The complex combinations obtained are coloured powders, having high melting points. These complexes are stable for a longer period, insoluble in methyl alcohol, ethyl alcohol, chloroform and acetone; the Mn(II) complex is soluble in DMF.

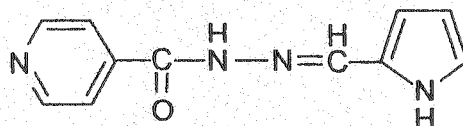


Fig. 1. Isonicotinoylhydrazone-2-aldehyde pyrrole ($C_{11}H_{10}N_4O$) (INH2AP = HL)

The analytical data of these complexes indicate a 1 : 2 (metal : ligand) stoichiometry for the Co(II), Ni(II), Cu(II) complexes and a 1 : 1 stoichiometry for the Mn(II) complex (Table-1). The low value of molar conductance in the case of the Mn(II) complex suggests a non-electrolytic nature.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES*

Compounds	m.p. (°C)	Colour	μ_{eff} (B.M.)	Λm^{\dagger} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
[Cu(HL) ₂ Cl ₂].2H ₂ O	260	Dark green	1.98	—
[Ni(HL) ₂ Cl ₂].2H ₂ O	270	Light brown	3.37	—
[Co(HL) ₂ Cl ₂].4H ₂ O	263	Dark brown	4.90	—
[Mn(HL)Cl ₂ (H ₂ O) ₂]. $\frac{1}{4}$ H ₂ O	265	Light yellow	5.91	13.54

*All complexes provide satisfactory metal, as well as C, H, N, Cl analyses.

$\dagger 10^{-3}$ M solution in DMF.

TABLE-2
CHARACTERISTIC IR (cm^{-1}) BANDS OF METAL COMPLEXES

Compounds	$\nu(\text{OH})$ lattice coord. water	$\nu(\text{NH})$ pyrrole	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$ amide	$\nu(\text{C}=\text{N})$	$\delta(\text{NH})$ amide	$\nu(\text{M}-\text{N})$
INH2AP(HL)	—	3265	3219	1645	1608	1547	—
[Cu(HL) ₂ Cl ₂].2H ₂ O	3450	3371	3110	1627	1603	1523	420
[Ni(HL) ₂ Cl ₂].2H ₂ O	3420	3372	3130	1605	1566	1520	475
[Co(HL) ₂ Cl ₂].4H ₂ O	3430	3388	3138	1604	1571	1525	438
[Mn(HL)Cl ₂ (H ₂ O) ₂]. $\frac{1}{4}$ H ₂ O	3450	3376	3218	1642	1606	1546	418

IR Spectra: The key infrared spectral bands are presented in Table-2. In the ligand spectra, the absorption band at *ca.* 3265 cm^{-1} is assignable to the $\nu(\text{NH})$ -pyrrole; this vibration appears at lower values on account of the intramolecular hydrogen links between (N—H) pyrrole and the atoms of nitrogen and oxygen in the (N=C) azomethine and the (O=C) links, respectively. The $\nu(\text{NH})$ vibration in the amide group is located at 3219 cm^{-1} . The amide I band is positioned at 1645 cm^{-1} and the band at 1608 cm^{-1} corresponds to the valency vibrations for the azomethine group⁶. The amide II (δNH) and amide III (γNH) bands are to be found at 1547 and 1357 cm^{-1} respectively. The ligand exhibits a weak band at 598 cm^{-1} , which can be associated to the deformation vibration in the plane for the pyridinic ring. The spectra in IR for the complex combinations

contain a broad band in the 3450–3420 cm^{-1} region; this absorption can be assigned to the lattice water or/and coordinated water, present in the complexes⁷. For the Mn(II) complex the coordinated water is present through the valency band $\nu(\text{Mn-OH}_2)$ (618 cm^{-1}), which is not present in the ligand spectrum. The $\nu(\text{NH})$ -pyrrole vibration appears at normal values and this aspect corresponds to the fact that the nitrogen in the pyrroleic ring does not take part in the coordination. The absorption band associated to the $\nu(\text{NH})$ frequency in the isoniazide fragment is situated within the 3218–3110 cm^{-1} interval, which demonstrates that the amide group maintains its structure during the process of coordination. The amide I band appears to have smaller wave numbers, which proves the fact that the ligand is coordinated to the metal ions through the oxygen amide ($\text{O}=\text{C}$). The valency vibration for the azomethine group shifts towards lower values, $\Delta\nu = 42 - 2 \text{ cm}^{-1}$ and suggests the coordination of the azomethinic nitrogen to metal ions. The amide II and amide III bands exhibit a negative and positive displacement, respectively, in the complexes⁸. The band corresponding to the deformation in the plane for the pyridinic ring is present at values close to the one in the free ligand and this result evinces the fact that the nitrogen in the pyridinic ring is not involved in coordination⁹. The coordination of the ligand to the metal ions through the azomethinic nitrogen is also supported by the $\nu(\text{M}-\text{N})$ vibrations, which are situated in the 475–418 cm^{-1} region.

The electronic and ESR spectra: The information concerning the geometry of the complexes is obtained from the electronic spectra (Table-3) and from the values of the magnetic moments.

TABLE-3
REFLECTION SPECTRA FOR THE LIGAND AND COMPLEXES

Compounds	Frequencies (cm^{-1})	Assigning
INH2AP(HL)	27777	$n \rightarrow \pi^*$
[Cu(HL) ₂ Cl ₂] \cdot 2H ₂ O	25641	$n \rightarrow \pi^*$
	14492	${}^2E_g \rightarrow {}^2T_{2g}$
[Ni(HL) ₂ Cl ₂] \cdot 2H ₂ O	26315	$n \rightarrow \pi^*$
	10101	${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$
	17241	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$
[Co(HL) ₂ Cl ₂] \cdot 4H ₂ O	26666	$n \rightarrow \pi^*$
	17543	${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$
	10204	${}^4T_{1g} \rightarrow {}^4T_{2g}(\text{F})$
[Mn(HL)Cl ₂ (H ₂ O) ₂] \cdot $\frac{1}{4}$ H ₂ O	26666	$n \rightarrow \pi^*$
	18181	CT

In the UV-Vis spectrum of the INH2AP ligand can be noticed an intense band at 27777 cm^{-1} (360 nm), which is assignable to the transition $n \rightarrow \pi^*$. Within the spectra of the complexes, this band is positioned at smaller wavenumbers, which indicate the coordination of the ligand to metal ions.

For the Cu(II) complex a broad band is observed at 14492 cm^{-1} (690 nm); this band is specific to the Cu(II) ion in octahedral stereochemistry and corresponds to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition¹⁰. The transition allowed by the spin is placed towards smaller wavenumbers and this result suggests a nondeformed octahedral geometry. From the electronic spectrum is obtained the Dq parameter, which has the value $Dq = 1449\text{ cm}^{-1}$. The magnetic moment determined experimentally is of 1.98 BM and it supports a monomeric octahedral structure.

In the spectrum of the Ni(II) complex, two bands of absorption at 10101 cm^{-1} (990 nm) and 17241 cm^{-1} (580 nm), are assignable to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ respectively; these transitions are characteristic of the Ni(II) ion in an octahedral coordination and this geometry is also supported by the value of the magnetic moment of 3.37 BM. The band of absorption associated to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ transition is concealed by the transition specific to the $n \rightarrow \pi^*$ ligand, which exhibits a much higher intensity. For the Ni(II) complex the parameters Dq, B, β have been calculated; $Dq = 1010\text{ cm}^{-1}$, $B = 795\text{ cm}^{-1}$, $\beta = 0.77$.

The Co(II) complex exhibits two absorption maxima at 10204 cm^{-1} (980 nm) and 17543 cm^{-1} (570 nm), which correspond to the ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_2)$ transitions respectively. These bands are specific to the Co(II) ion in octahedral stereochemistry, a geometry also confirmed by the magnetic moment of the complex, which is of 4.90 BM. 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 transitions¹⁰. The absorption band at 18181 cm^{-1} (550 nm) can be attributed to the charge transfer of ligand \rightarrow metal. The magnetic moment of 5.91 BM supports an octahedral configuration of the type high spin around the Mn(II) ion.

The ESR spectrum for the Cu(II) complex is presented in Fig. 2.

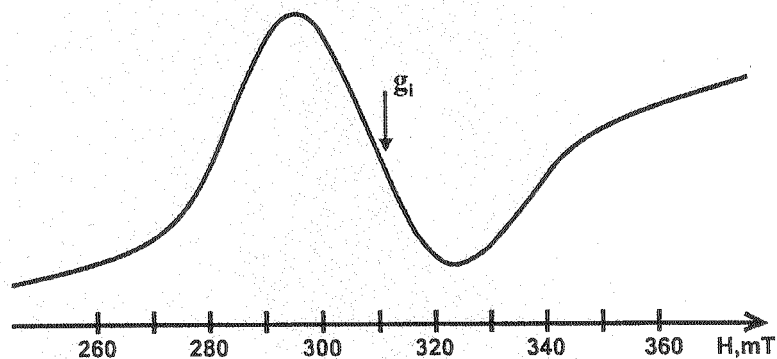


Fig. 2. ESR spectrum for the complex $[Cu(HL)_2Cl_2] \cdot 2H_2O$.

The fact that the "g" parameter has only one value ($g_{\text{isotropic}} = 2.1132$) and the shape of the signal is symmetric, entitles us to consider that the geometry of the Cu(II) complex is nondeformed and octahedral. The fact that the breadth of the

signal is of approximately 50.7 mT means that the concentration of the complex most probably was very high (no magnetic dilution was achieved)¹¹.

The thermal analyses of the complexes are presented in Table-4.

TABLE-4
THERMAL ANALYSIS FOR THE COMPLEX COMBINATIONS

Complexes	Total mass losses		Temp. (°C)	Loss (%)
	Theoretical (%)	Experimental (%)		
[Cu(HL) ₂ Cl ₂].2H ₂ O	77.52	77.58	50–75	5.19
			75–150	6.25
			150–435	24.45
			435–730	46.88
			730–1000	13.54 exp./res. 13.28 calc./res.
[Ni(HL) ₂ Cl ₂].2H ₂ O	78.15	78.61	70–140	6.19
			140–570	72.42
			570–1000	12.86 exp./res. 12.58 calc./res.
[Co(HL) ₂ Cl ₂].4H ₂ O	79.37	79.72	70–150	11.77
			150–410	17.24
			410–780	50.71
			780–1000	12.21 exp./res. 11.89calc./res.
[Mn(HL)Cl ₂ (H ₂ O) ₂].1/4H ₂ O	66.90	67.58	75–140	1.19
			140–260	9.68
			260–425	42.17
			425–600	14.54
			600–1000	20.37 exp./res. 20.04 calc./res.

Within the interval (50–75°C), for the Cu(II) complex, the solvent is eliminated that has been absorbed during the synthesis, a process shown by an endothermic peak. For all the complex combinations, the lattice water is lost within the domain 70–150°C; in the case of the Mn(II) complex, the coordination water is eliminated at higher temperatures, which corresponds to the interval 140–260°C. At high temperature values (> 260°C), the complexes decompose and the ligand is lost in a fractional manner, finally the oxides corresponding to CuO, NiO, CoO, Mn₃O₄ are obtained as stable products. The data in the thermogravimetric analysis represent an argument that supports the molecular formulae proposed.

On the basis of the experimental data obtained from the elemental analysis, the study of the IR, UV-Vis, ESR spectra and the thermic analysis, we can propose for the complex combinations the following structural formulations (Figs. 3 and 4):

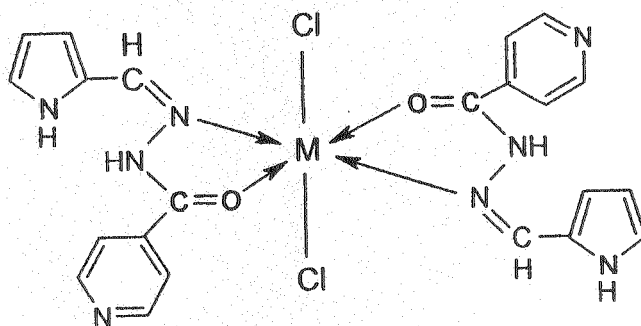


Fig. 3. The proposed structure of the complexes $[M(HL)_2Cl_2 \cdot xH_2O]$, $M = Ni(II), Cu(II)$, $x = 2$; $M = Co(II)$, $x = 4$.

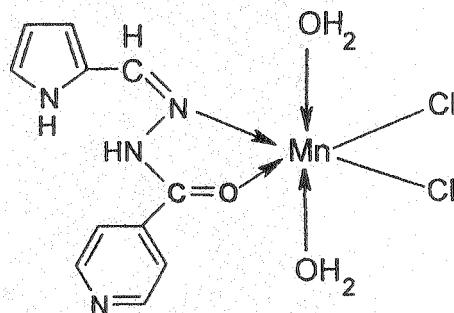


Fig. 4. The proposed structure of the complex $[Mn(HL)Cl_2(2H_2O)_2] \cdot \frac{1}{4}H_2O$.

REFERENCES

1. K.K. Narang and P. Vinod, *Synth. React. Inorg. Met-Org. Chem.*, **2**, 191 (1996).
2. R.N. Pandey and S. Sarita, *Orient. J. Chem.*, **11**, 145 (1994).
3. N. Kaur, R. Herjinder and S.K. Sangal, *Chim. Acta Turc.*, **26**, 123 (1996).
4. A. Kriza, L. Mitu and N. Stănică, *Revista. de Chimie (Chem. J.)*, **2**, 137 (2005).
5. C.Gh. Macarovici, *Analiza Chimică Cantitativă Anorganică (Inorganic Quantitative Chemical Analysis)*, Editura Academiei R.S.R., București, p. 364 (1979).
6. M. Avram and G.D. Mateescu, *Spectroscopia în Infraroșu-Aplicații în Chimia Organică, (Infrared Spectroscopy: Applications in Organic Chemistry)*, Editura Tehnică, București, p. 385 (1966).
7. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, p. 155 (1963).
8. K.K. Narang and P.V. Singh, *Transition Met. Chem.*, **21**, 507 (1996).
9. B.V. Agarwala, *Acta Chim. (Hung.)*, **102**, 269 (1990).
10. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, London, p. 355 (1968).
11. B.J. Hathaway, *Struct. Bonding*, **14**, 60 (1973).

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