COORDINATION OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) WITH THE NEW SCHIFF-BASE DERIVED FROM 4,5-DIHYDROXIPHTALALDEHIDE AND 2-AMINOTHIAZOLE

Monica Iliş[*], Angela Kriza, Veronica Pop, Anca Nicolae[**]

abstract: A series of new complexes of type $[ML_2].xH_2O$ (where x = 0 for M = Zn(II), Cd(II) and Hg(II); x = 1 for M = Co(II), Ni(II) and Cu(II); LH_2 is a Schiff-base derived from 4,5-dihydroxiphtalaldehide and 2-aminothiazole) have been prepared. The compounds were characterized by elemental analysis, IR and UV-VIS spectra, magnetic moments and thermal behaviour have been discussed.

Introduction

A great number of complexes of different transitional metallic ions with bidentate Schiff-bases, derived from 2-aminothiazole and from different type of carbonylic compounds, have been reported. Heterocyclic ligands containing nitrogen and sulf donor atoms have been extensively studied due to their biological applications, in particular as pesticides and drugs [1-4]. In order to obtain more information about the preparation conditions, the properties and the stereochemistry of the metallic chelates with Schiff-bases, derived from 2-aminothiazole, a new series of complexes of type $[ML_2].xH_2O$ (x = 0 for M = Zn(II), Cd(II) and Hg(II); x = 1 for M = Co(II), Ni(II), Cu(II); LH_2 is a Schiff-base derived to 2-aminothiazole and 4,5-dihydroxiphtalaldehide, has been prepared.

Materials and Methods

The chemicals were purchased from Aldrich and all manipulations were performed using materials as received. The IR spectra were recorded on a BIO-RAD FTIR 135 spectrophotometer using KBr pellets. Electronic spectra have been obtained by diffuse reflectance technique, using MgO as standard, with a UV-VIS Carl Zeiss Jena spectrophotometer. The magnetic moments have been measured by the Faraday method. Thermal decomposition was studied with a MOM Q-1500 D derivatograph. Metallic ions were estimated by the AA 6 DA – VARIAN TECHTRON atomic absorbtion spectrophotometer and nitrogen has been determined by the Kjeldahl method.

The Schiff-base (LH_2) was prepared by mixing the methanolic solutions of 4,5-dihydroxiphtalaldehide and 2-aminothiazole (molar ratio 1:1) and refluxing for 2 h, on a water bath, filtered, washed with methanol, dried and recrystallized from methanol, with melting point at 210^{o}C.

[*] Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest
[**] Department of Organic Chemistry, Faculty of Chemistry, University of Bucharest

Analele Universităţii din Bucureşti – Chimie, Anul XIV (serie nouă), vol. I-II, pg. 117-121

The compounds were prepared by mixing, at room temperature, with stirring the methanolic solutions of Schiff-base derived from 4,5-dihydroxiphtalaldehide and 2-aminothiazole and the salt of the appropriate metallic ion, in molar ration 2:1. The pH of the resulting solution was adjusted to about 7 by adding aqueous solution of Na_2CO_3. By changing the pH, coloured precipitates have been obtained. The precipitates were filtered, washed with methanol and were dried in vacuum.

Results and Discussion

The Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) compounds with the Schiff-base derived from 4,5-dihydroxiphtalaldehide and 2-aminothiazole, were obtained as powers with high melting points and low solubility in organic solvents. Anal. for $C_{22}H_{16}O_7N_4S_2Co$: calc. (%) N 9.80, Co 10.31, found (%) N 9.60, Co 10; for $C_{22}H_{16}O_7N_4S_2Ni$: calc. (%) N 9.81, Ni 10.28, found (%) N 9.50, Ni 9.98; for $C_{22}H_{16}O_7N_4S_2Cu$: calc. (%) N 9.73, Cu 11.04, found (%) N 9.21, Cu 10.74; for $C_{22}H_{14}O_6N_4S_2Zn$: calc. (%) N 9.73, Zn 11.35, found (%) N 9.32, Zn 11.00; for $C_{22}H_{14}O_6N_4S_2Cd$: calc. (%) N 8.99, Cd 18.05, found (%) N 8.62, Cd 17.45; for $C_{22}H_{14}O_6N_4S_2Hg$: calc. (%) N 7.88, Hg 28.21, found (%) N 7.42, Hg 27.98.
The elemental analysis for all these complexes are in agreement with the proposed formula $[ML_2].xH_2O$ (where x = 0 for Zn(II), Cd(II) and Hg(II); x = 1 for Co(II), Ni(II) and Cu(II)).
In order to get data concerning the ligand mode coordination to metallic ions, the IR spectra, on the 400-4000 cm^{-1} range, for free ligand and for complexes, have been carried out (Table 1).

Table 1. The characteristic frequencies in IR (cm^{-1}) for the ligand and complexes

Compound	$\nu_{C=N}$	ν_{C-O} phenolic	ν_{C-N} exocyclic	ν_{-CHO}	ν_{C-S}	ν_{H-OH}
LH_2: $C_{11}H_8O_3N_2S$	1595	1141	1290	1634	730	-
$[CoL_2].H_2O$	1586	1148	1272	1633	732	3415
$[NiL_2].H_2O$	1579	1154	1281	1635	733	3407
$[CuL_2].H_2O$	1589	1158	1280	1636	738	3447
$[ZnL_2]$	1588	1152	1274	1633	734	-
$[CdL_2]$	1587	1143	1273	1636	733	-
$[HgL_2]$	1578	1148	1276	1635	732	-

In the spectrum of the free ligand, the sharp band at 1595 cm^{-1} can be assigned to the $\nu_{C=N}$ vibration. In the spectrum of the complexes, this band is found at the lower values ($\Delta\nu$ = 9-17 cm^{-1}). The lowering of the $\nu_{C=N}$ frequency in the complexes, indicates the coordination of the azomethine nitrogen atom at the metallic ion [5].
The coordination through the azomethinic nitrogen atom is supported by the shift of ν_{C-N} (exocyclic) frequency to lower wave number ($\Delta\nu$ = 9-18 cm^{-1}) in the IR spectra of complexes compare to IR spectrum of the free ligand.
The infrared spectrum of the free ligand shows a band at 1141 cm^{-1} assigned to the vibration frequency of the phenolic C-O group. In the spectrum of the complexes, this band undergoes a positive shifts (with 7-17 cm^{-1}) indicating that the Schiff-base is bonded to the metallic ions through the oxygen phenolic atoms [6-8].
The ν_{C-S} and ν_{-CHO} are not affected by coordination to metallic ion.

In addition, all IR spectra belonging to the Co(II), Ni(II) and Cu(II) compounds present an absorption band at 3415, 3407 and 3417 cm^{-1}, confirming the existance of water molecules in the structure of the crystalline lattice [9]. The presence of the crystallizations water was indicated by the thermogravimetric analysis.

The information reffering to the geometry of these complexes are obtained from the electronic spectra and from the value of the magnetic moments (Table 2).

Table 2. Electronic spectra and magnetic moments of the $[ML_2].xH_2O$ complexes

Compound	ν (cm^{-1})	Assignments	μ_{eff} (MB)
LH_2	22220	$\pi\rightarrow\pi^*$	
	16660	$n\rightarrow\pi^*$	
$[CoL_2].H_2O$	21000	$\pi\rightarrow\pi^*$	2.30
	15607	$n\rightarrow\pi^*$	
	14129	$^4A_2\rightarrow{}^4T_1(P)$	
	12195	$^4A_2\rightarrow{}^4T_1(F)$	
$[NiL_2].H_2O$	22190	$\pi\rightarrow\pi^*$	dia.
	15200	$n\rightarrow\pi^*$	
	14814	$^1A_{1g}\rightarrow{}^1B_{2g}$	
	12658	$^1A_{1g}\rightarrow{}^1A_{2g}$	
$[CuL_2].H_2O$	20000	$\pi\rightarrow\pi^*$	1.82
	16100	$n\rightarrow\pi^*$	
	15873	$d_{xy}\rightarrow d_{xz}$	
	14285	$d_{xy}\rightarrow d_{z2}$	
$[ZnL_2]$	21255	$\pi\rightarrow\pi^*$	dia.
	18867	TS	
	15900	$n\rightarrow\pi^*$	
$[CdL_2]$	21390	$\pi\rightarrow\pi^*$	dia.
	18181	TS	
	16000	$n\rightarrow\pi^*$	
$[HgL_2]$	21000	$\pi\rightarrow\pi^*$	dia.
	18230	TS	
	16000	$n\rightarrow\pi^*$	

In the electronic spectrum of the ligand there are two absorption bands assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions [10, 11]. These transitions are found also in the spectra of the complexes, but they are shifted towards lower frequencies, confirming the coordination of the ligand at the metallic ions.

In the electronic spectrum of $[CoL_2].H_2O$ complex two new absorption bands at 14129 cm^{-1} and 12195 cm^{-1}, are observed. These bands are assigned to $^4A_2\rightarrow{}^4T_1(P)$ and $^4A_2\rightarrow{}^4T_1(F)$ transitions, respectively [12]. These transitions indicate a square-planar geometry of the complexes. The observed magnetic moment, 2.30 MB [13] is in agreement with this structure.

The electronic spectrum of $[NiL_2].H_2O$ complex shows two new bands at 14814 cm^{-1} and 12658 cm^{-1}, which are attributed to $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1B_{2g}$, respectively [12]. These transitions and the magnetic moments ($\mu_{eff} = 0$) suggest a square-planar stereochemistry [14].

In the electronic spectrum of the $[CuL_2].H_2O$ complex was noticed the presence of a two new bands at 15873 cm^{-1} and 14285 cm^{-1}, assigned to the $d_{xy}\rightarrow d_{xz}$, respectively $d_{xy}\rightarrow d_z2$ transitions [12]. These transitions, as well as the measured value of the magnetic moment

(1.82 MB) suggest a square-planar stereochemistry of the compound. We assumed for the Zn(II), Cd(II) and Hg(II) complexes a tetrahedral geometry [12].
The thermal behaviour of the compounds of Co(II) and Ni(II) was studied by thermogravimetric analysis. The heating rate was 10°C/min, while the temperature interval was 20-1000°C. The weight losses are presented the Table 3.

Table 3. Thermal behaviour of the prepared compounds

Compound	Decomposing stages	Temperature range (°C)	Thermal effect	Weight losses (%)	Residue (%)
$[CoL_2].H_2O$	1	50-180	exo-	3.50	3.15
	2	240-420	exo-	83	85.93 (Co_3O_4)
$[NiL_2].H_2O$	1	80-180	endo-	3.45	3.15
	2	290-540	exo-	85	86.91 (NiO)

The studied of Co(II) and Ni(II) compounds are decomposing in two successive stages. The first stage of decomposition consisted in elimination of the crystallization water; the last stage is exotherme and corresponds to the burning of the organic components. From the weight losses registered in TG and TDG of the Ni(II) compound, the following process of decomposition may be presented:

1. $NiC_{22}H_{16}O_7N_4S_2(s) \xrightarrow{80\text{-}180^oC} NiC_{22}H_{14}O_6N_4S_2(s) + H_2O(g)$

2. $NiC_{22}H_{14}O_6N_4S_2(s) + 29O_2(g) \xrightarrow{290\text{-}540^oC} NiO(s) + 22CO_2(g) + 2SO_2(g) + 4NO_2(g) + 7H_2O(g)$

The above-mentioned data suggest the following structural formula (Figure 1):

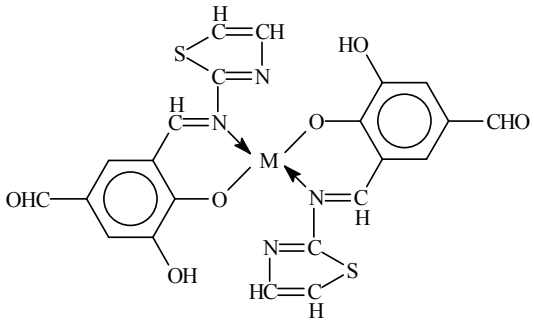

Fig 1. *The proposed structure for compounds*

Conclusions

In this article we present the results of a study of the new complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with Schiff-base derived from 4,5-dihydroxiphtalaldehide and 2-aminothiazole. The complexes were characterized as square-planar species of Co(II),

Ni(II), Cu(II), and as tetrahedral species of Zn(II), Cd(II) and Hg(II) based on the chemical analysis, thermal behaviour, spectrometric and magnetic measurements.

REFERENCES

1. Dash C., Pradhan J., (1991) Indian J,Chem. Sect.A, Inorg., Bio-Inorg.,Phys., Theor.Anal.Chem., **70**, 7601
2. Rosamma T., Parameswaran G., (1992) J.Indian Chem.Soc., **69**, 3117
3. Bhaskare C.K., Hankare P.P., (1995) J.Indian Chem.Soc., **72**, 9585
4. Zaidi A. Aftab S., Zaidi A. Rehan S., Shaher S.A., Tabrez A., (1987) Indian J.Chem Sect.A, **26**, 8715
5. Percy G.C., Thornton D.A., (1972) J.Inorg.Nucl.Chem., **34**, 3357
6. Lewis J.W., Sandorfy H., (1982) Can.J.Chem., **60**, 1737
7. Gillard R.D., McCleverts J.A., (1987) **Comprehensive Coordination Chemistry**, Eds. Wilkinson, Pergamon Press, Oxford
8. Bhardway S., Ansari M.N., Jain M.C., (1987) Indian J.Chem., **28A**, 81
9. Nakamoto K., (1978) **Infrared and Raman Spectra of Inorganic and Coordination Compounds**, 3rd Ed., John Wiley, New York
10. Ito M., Hata M., (1955) Bull.Chem.Soc.Jpn., **28**, 260
11. Friedel R.A., Orchin M.,)1958) **Ultraviolet Spectra of Aromatic Compounds**, John Wiley, New York
12. Level A.B.P., (1984) **Inorganic Electronic Spectroscopy**, Elsevier Publishing Company, Amsterdam
13. Sacconi L. et al., (1968), J.Am.Chem.Soc., **84**, 3246
14. Holm R.M., (1961) J.Am.Chem.Soc., **83**, 468