

# COORDINATION OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) WITH THE NEW SCHIFF-BASE DERIVED FROM 5-FORMYLVANILINE AND *o*-PHENYLENEDIAMINE

Angela Kriza\*, Monica Voiculescu and Anca Nicolae

A series of new complexes of type  $[ML] \cdot xH_2O$  (where  $x = 0$  for Zn(II), Cd(II) and Hg(II) and  $x = 1$  for M = Co(II), Ni(II) and Cu(II), and where  $LH_2$  is a Schiff-base derived from 5-formylvaniline and *o*-phenylenediamine) have been prepared. The compounds were characterized by elemental analysis, and 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 tetradentate Schiff-bases, derived from *o*-phenylenediamine and from different type of carbonylic compounds, have been reported [1÷8]. In order to obtain more information about the preparation conditions, the properties and the stereochemistry of the metallic chelates with Schiff-bases, derived from *o*-phenylenediamine, a new series of complexes of type  $[ML] \cdot xH_2O$ , where  $x = 1$  for M = Co(II), Ni(II) and Cu(II) and  $x = 0$  for M = Zn(II), Cd(II) and Hg(II) and where  $LH_2$  is a Schiff-base derived from *o*-phenylenediamine and 5-formylvaniline, 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 AA6DA – VARIAN TECHTRON atomic absorption spectrophotometer, and nitrogen has been determined by the Kjeldahl method.

The compounds were prepared by mixing, at room temperature, with stirring the methanolic solutions of *o*-phenylenediamine, 5-formylvaniline and the salt of the appropriate metallic ion, in molar ratio 1:2:1. 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, ethyl ether and were dried in vacuum.

---

\* Professor, chemist, Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest

The Schiff-base (LH<sub>2</sub>) was prepared by mixing the methanolic solutions of *o*-phenylenediamine and 5-formylvaniline (molar ratio 1:2) and refluxing for 2 h, on a water bath, filtered, washed with methanol, dried and recrystallized from methanol.

## Results and Discussion

The Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) compounds with the Schiff-base derived from 5-formylvaniline and *o*-phenylenediamine, were obtained as powders with high melting points and low solubility in organic solvents. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>O<sub>7</sub>N<sub>2</sub>Co: N 5.52, Co 11.63. Found: N 5.10, Co 11.10. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>O<sub>7</sub>N<sub>2</sub>Ni: N 5.52, Ni 11.58. Found: N 5.26, Ni 11.10. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>O<sub>7</sub>N<sub>2</sub>Cu: N 5.47, Cu 12.41. Found: N 5.00, Cu 12.87. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>N<sub>2</sub>Zn: N 5.45, Zn 12.73. Found: N 5.10, Zn 12.30. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>N<sub>2</sub>Cd: N 5.14, Zn 20.64. Found: N 4.70, Cd 19.80. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>N<sub>2</sub>Hg: N 4.00, Hg 30.10. Found: N 5.00, Hg 32.82.

The elemental analysis for all these complexes are in agreement with the proposed formula [ML]·xH<sub>2</sub>O (where x = 0 for Zn(II), Cd(II) and Hg(II); x = 1 for M = 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<sup>-1</sup> range, for free ligand and for complexes, have been carried out (Table 1).

**Table 1. The characteristic frequencies in IR (cm<sup>-1</sup>) for the ligand and complexes**

Compound	$\nu_{C=N}$ (cm <sup>-1</sup> )	$\nu_{C=O}$ phenolic (cm <sup>-1</sup> )	$\nu_{-CHO}$ (cm <sup>-1</sup> )	$\nu_{-OCH_3}$ (cm <sup>-1</sup> )	$\nu_{H-OH}$ (cm <sup>-1</sup> )
LH <sub>2</sub> : C <sub>24</sub> H <sub>20</sub> O <sub>6</sub> N <sub>2</sub>	1608	1151	1672	2833	–
[CoL]·H <sub>2</sub> O	1602	1154	1671	2833	3438
[NiL]·H <sub>2</sub> O	1603	1153	1675	2832	3417
[CuL]·H <sub>2</sub> O	1602	1159	1672	2832	3454
[ZnL]	1601	1159	1672	2831	–
[CdL]	1601	1158	1671	2831	–
[HgL]	1600	1159	1671	2832	–

In the spectrum of the free ligand, the sharp band at 1608 cm<sup>-1</sup> can be assigned to the  $\nu_{C=N}$  vibration. In the complexes, this band is found at the lower values ( $\Delta\nu = 8$  cm<sup>-1</sup>). The lowering of the  $\nu_{C=N}$  frequency in the complexes, indicates the coordination of the azomethine nitrogen atom at the metallic ion [9].

The infrared spectrum of the free ligand shows a band at 1151 cm<sup>-1</sup>, assigned to the vibration frequency of the phenolic C-O group. In the complexes, this band undergoes a positive shifts (with 8 cm<sup>-1</sup>), indicating that the Schiff-base is bonded to the metallic ions through the oxygen phenolic atoms [10÷12].

The absorption band characteristic to the formyl group and methoxy group observed in the ligand spectrum at 1672 cm<sup>-1</sup> and at 2833 cm<sup>-1</sup> don't undergo changes in the complexes spectra.

In addition, all IR spectra belonging to the Co(II), Ni(II) and Cu(II) compounds present an absorption band at 3438, 3417 and 3454  $\text{cm}^{-1}$ , confirming the existence of water molecules in the structure of the crystalline lattice [13]. The presence of the crystallizations water was indicated by the thermogravimetric analysis.

The information referring 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] $\cdot$ xH<sub>2</sub>O complexes**

Compound	$\nu(\text{cm}^{-1})$	Assignments	$\mu_{\text{eff}}(\text{MB})$	Colour
LH <sub>2</sub>	25 641	$\pi \rightarrow \pi^*$	2.40	orange
	19 230	$n \rightarrow \pi^*$		
	22 727	$\pi \rightarrow \pi^*$		
[CoL]·H <sub>2</sub> O	17 857	$n \rightarrow \pi^*$	2.40	dark-brown
	14 925	${}^4A_2 \rightarrow {}^4T_1(\text{P})$		
	20 408	$\pi \rightarrow \pi^*$		
[NiL]·H <sub>2</sub> O	17 857	$n \rightarrow \pi^*$	diamagnetic	dark-orange
	14 084	${}^1A_{1g} \rightarrow {}^1A_{2g}$		
		$\pi \rightarrow \pi^*$		
[CuL]·H <sub>2</sub> O	24 390	$n \rightarrow \pi^*$	1.84	light-green
	17 857	$n \rightarrow \pi^*$		
	12 658	$d_{xy} \rightarrow d_{z^2}$		
[ZnL]	23 500	$\pi \rightarrow \pi^*$	diamagnetic	yellow
	17 800	CT		
	16 128	$n \rightarrow \pi^*$		
[CdL]	22 200	$\pi \rightarrow \pi^*$	diamagnetic	yellow
	17 000	CT		
	16 000	$n \rightarrow \pi^*$		
[HgL]	23 200	$\pi \rightarrow \pi^*$	diamagnetic	light-brown
	17 200	CT		
	16 620	$n \rightarrow \pi^*$		

In the electronic spectrum of the ligand there are two absorption bands assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions [14,15]. 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]·H<sub>2</sub>O complex, two new absorption bands are observed at 14 925  $\text{cm}^{-1}$  and 12 363  $\text{cm}^{-1}$ . These bands are assigned to  ${}^4A_2 \rightarrow {}^4T_1(\text{P})$  and  ${}^4A_2 \rightarrow {}^4T_1(\text{F})$  transitions, respectively [16]. These transitions indicate a square-planar geometry of the complexes. The observed magnetic moment, 2.40 MB, [17] is in agreement with this structure.

The electronic spectrum of [NiL]·H<sub>2</sub>O complex shows two new bands at 14 084  $\text{cm}^{-1}$  and 12 195  $\text{cm}^{-1}$ , which are attributed to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1B_{2g}$  transitions, respectively.

These transitions [16] and the magnetic moments ( $\mu_{\text{eff}} = 0$ ) suggest a square-planar stereochemistry [18].

In the electronic spectrum of the [CuL]·H<sub>2</sub>O complex was noticed the presence of a new band at 12 658  $\text{cm}^{-1}$ , assigned to the  $d_{xy} \rightarrow d_{z^2}$  transition [16]. These transitions, as well as the measured value of the magnetic moment (1.84 MB) suggest a square-planar

stereochemistry of the compound. We assumed for the Zn, Cd and Hg complexes a tetrahedral geometry [16].

The thermal behaviour of the compounds was studied by thermogravimetric analysis. The heating rate was  $10^0 \text{ C}\cdot\text{min}^{-1}$ , while the temperature interval was  $20\div 1000 \text{ }^\circ\text{C}$ . The weight losses are presented the Table 3.

**Table 3. Thermal behaviour of the prepared compounds**

Compound	Decomposing stages	Temperature range ( $^\circ\text{C}$ )	Thermal effect	Weight losses (%)	Residue (%)
[CoL] $\cdot$ H <sub>2</sub> O	1	70-160	exo-	3.24	3.55
	2	320-490	exo-	82.40	82.18 (Co <sub>3</sub> O <sub>4</sub> )
[NiL] $\cdot$ H <sub>2</sub> O	1	70-155	endo-	3.75	3.76
	2	410-620	exo-	82.25 (NiO)	80.63 (NiO)
[CuL] $\cdot$ H <sub>2</sub> O	1	65-185	exo-	3.85	3.51
	2	250-335	exo-	82.25	84.45 (CuO)
[CdL]	1	260-480	exo-	76.44	76.32 (CdO)

The studied of Co(II), Ni(II) and Cu(II) compounds are decomposing in two successive stages, and the Cd(II) complex in only one stage. For the Co(II), Ni(II) and Cu(II) compounds, 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 Cu(II) compound, the following process of decomposition may be presented:

- $$\text{CuC}_{24}\text{H}_{20}\text{O}_7\text{N}_2(\text{s}) \xrightarrow{65-185^\circ\text{C}} \text{CuC}_{24}\text{H}_{18}\text{O}_7\text{N}_2(\text{s}) + \text{H}_2\text{O}(\text{g})$$
- $$\text{CuC}_{24}\text{H}_{18}\text{O}_6\text{N}_2(\text{s}) + 28 \text{O}_2(\text{g}) \xrightarrow{250-335^\circ\text{C}} \text{CuO}(\text{s}) + 24 \text{CO}_2(\text{g}) + 2 \text{NO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{g})$$

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

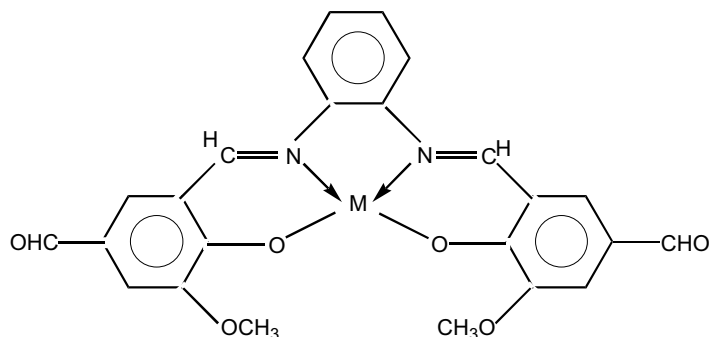


Fig. 1: The proposed structure for compounds

## 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 5-formylvaniline and o-phenylenediamine.

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. Dziembowska T., Guskos N., Typek J., Grech E., Likodimos V., Wabia M., Fuks H., Ramos J., Palios G., Kawecka J. (1996) *Polish. J. Chem.*, **70**, 1425-1434.
2. Guskos N., Dziembowska T., Palios G., Paraskevas S. M., Likodimos V., Grech E., Typek J., Wabia M., Jagodzinska E. (1995) *Polish. J. Chem.*, **69**, 1630.
3. Hassaan A. M. (1997) *Bull. Soc. Chim. Belg.*, **106**, 73.
4. Hassaan A. M., Khalifa M. A. (1993) *Monatsh. Chem.*, **124**, 803-808.
5. Hassaan A. M., Khalifa M. A., Sehata A. K. (1995) *Bull. Soc. Chim. Belg.*, **104**, 121.
6. Sreenivasulu I., Reddy K.H. (1994) *J. Indian. Chem. Soc.*, **71**, 41-43
7. Sreenivasulu I., Reddy K.H. (1993) *J. Indian. Chem. Soc.*, **70**, 1
8. Reddy K.H., Krishnaiah G., Sreenivasulu I. (1991) *Polyhedron*, **10**, 2785
9. Percy G. C., Thornton D. A. (1972) *J. Inorg.Nucl. Chem.*, **34**, 3357
10. Lewis J. W., Sandorfy C. (1982) *Can. J. Chem.*, **60**, 1737
11. Gillard R. D., McCleverty J. A. (1987) **Comprehensive Coordination Chemistry**, Eds. Wilkinson, Pergamon Press, Oxford
12. Bhardway S., Ansari M. N., Jain M. C. (1989) *Indian J. Chem.*, **28A**, 81
13. Nakamoto K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3<sup>rd</sup> ed., John Wiley, New York, 231.
14. Ito M., Hata M. (1955) *Bull. Chem. Soc. Jpn.*, **28**, 260
15. Friedel R. A., Orchin M. (1958) **Ultraviolet Spectra of Aromatic Compounds**, John Wiley, New York
16. Level A. B. P. (1984) **Inorganic Electronic Spectroscopy**, Elsevier Publishing Company, Amsterdam, 498, 535, 587
17. Sacconi L. *et al* (1968) *J. Am. Chem. Soc.*, **84**, 3246
18. Holm R. M. (1961) *J. Am. Chem. Soc.*, **83**, 468