

# Preparation, Spectroscopic Studies of (Z)-2-(2-methoxybenzylideneamino)-3-methylbutanoic acid Mixed Ligand Chelates

Halima F. Salem<sup>1</sup>, Marei M. El-ajaily<sup>1\*</sup> and Hanan, M. Eghreibeel<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Benghazi University, Benghazi, Lbya

<sup>3</sup>Department of Chemistry, Faculty of Science, Benghazi University, Al-Kufra, Libya

\* [melajaily@gmail.com](mailto:melajaily@gmail.com)

## Abstract

Two mixed ligand chelates of divalent transition metal ions (Co and Ni) with (E)-2-(2-methoxybenzylideneamino)-3-methylbutanoic acid Schiff base resulted from the condensation of 2-methoxybenzaldehyde with L-valine represents as primary ligand HL<sup>1</sup>, whereas, anthranilic acid (HL<sup>2</sup>) as secondary ligand were prepared and characterized by using several physiochemical techniques such as; elemental analysis, molar conductance, magnetic susceptibility measurements, IR, UV-Vis and mass spectra. Based on the obtained data, the mixed ligand chelates were formed in 1:1:1 [L<sup>1</sup>:M:L<sup>2</sup>] ratio and an octahedral geometry was proposed.

**Keywords:** Schiff bases; Schiff base chelates ; l-valine; 2-methoxybenzaldehyde.

## Introduction

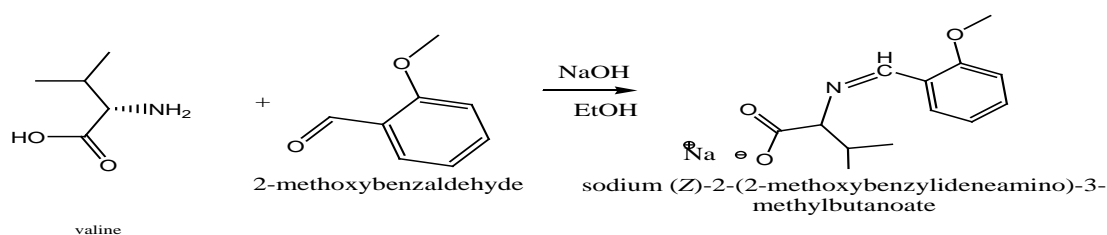
The Schiff bases are types of the ligands most broadly used as chelating ligands in coordination chemistry<sup>1,2</sup>. They revealed suitable biological activity agents and catalysts in polymer and dyes industry.<sup>3-8</sup> They are resulted from the refluxing reactions of carbonyl compounds and primary amines and particularly suited for binding to metal ions via the nitrogen atom lone pair (-N:) and when contain one or more donor atoms in addition to (-C=N-) group they act as polydentate ligands.<sup>9</sup> Transition metal complexes containing oxygen and nitrogen donor Schiff bases have been of research interest for previous years<sup>10</sup> and acted as active sites and thereby catalyze chemical reactions.<sup>11</sup> Antimicrobial diseases are now more common than during the first half of the century and still difficult to detect clinically.<sup>12</sup> Schiff bases derived from 4-methoxybenzaldehyde and amino acids with Pb(II) complexes have been reported.<sup>13</sup>

The present study aims to prepare and characterize the geometrical structures two mixed ligand chelates of Co(II) and Ni(II) ions with a Schiff base formed by the condensation of 2-methoxybenzaldehyde and L-valine amino acid as main ligand and anthranilic acid as secondary ligand.

## Materials and Methods

All materials used in this study were of reagent grade and purchased commercially from British Drug House (BDH). They include; amino acid (L-valine), 2-methoxybenzaldehyde, anthranilic acid, NaOH,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , absolute  $\text{CH}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$ , double distilled water was used during the experimental process. The prepared Schiff base and its mixed ligand chelates were provided by elemental analysis using 2400 elemental analyzer. Molar conductance measurements of  $10^{-3}$  M solutions of the mixed ligand chelates in DMF solvent were measured on the conductivity meter ORION model 150 of 0.6 cell constant. The magnetic susceptibility measurements for the mixed ligand chelates were determined by the Gouy balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibration. The IR spectra of the Schiff base and its mixed ligand chelates were recorded on as 8001-PC FTIR Shimadzu spectrophotometer using KBr pellets. Mass spectra of the Schiff base and its Ni(II) mixed ligand chelate were performed using GC-2010 Shimadzu. All previous analysis were done at micro-analytical centre, Cairo University, Giza, Egypt.

**Preparation of polar amino acid Schiff base:** The Schiff base was prepared according to the procedure previously described in the literature<sup>14</sup> polar amino acid L-valine (1.17 g, 0.01mol) was add to ethanolic solution(20 mL) containing 0.4 gram of NaOH, then 2-methoxybenzaldehyde ( 1.36g, 0.01mol) in the same amount of the same solvent was added. The mixture was refluxed for 2 hrs, the white product was filtered off, washed with ethanol and recrystallized from the same solvent. The purity of the prepared compounds was checked by chemical analysis.



**Figure 1: Formation of the Schiff base HL<sup>1</sup>**

### Preparation of Co(II) and Ni(II) Mixed ligand chelates

A general procedure has been adopted for the preparation of the mixed ligand chelates in presence of a basic media. Ethanolic solutions (25 ml) of 0.01 moles of the salts [CoCl<sub>2</sub>.6H<sub>2</sub>O; 2.38 g and NiCl<sub>2</sub>.6H<sub>2</sub>O; 2.37 g] were added to the same amount of the solution containing 0.01 moles of each of Schiff base 2.57 g and L<sup>2</sup> 1.37 g of anthranlic acid. Few drops of NaOH solution (10%) were added to bring the mixture up to pH 7-8 which the precipitates will start to appear. Then, the mixtures were refluxed with stirred for three hours. The formed precipitates were filtered and washed several times with hot ethanol until the filtrates become clear. The obtained chelates were dried in desiccator under calcium chloride.

### Results and Discussion

The reaction between the carbonyl group (C=O) of 2-methoxybenzaldehyde and amine group(-NH<sub>2</sub>) of L-Valin amino acid in ethanolic solution containing sodium hydroxide produces the required compound which is the Schiff base as shown in fig.1.

#### Microanalysis and molar conductivity

The CHN elemental analyses of the Schiff base and its mixed ligand chelates are listed in table 1. The obtained elemental analysis data were in a good a agreement with the calculated values and display the formation of 1:1:1 [M:L<sup>1</sup>:L<sup>2</sup>] ratio. The molar conductance values revealed that the prepared chelates are electrolyte in nature.<sup>15</sup> This is due to the presence of sodium ion out of the coordination sphere.

#### Infrared spectra

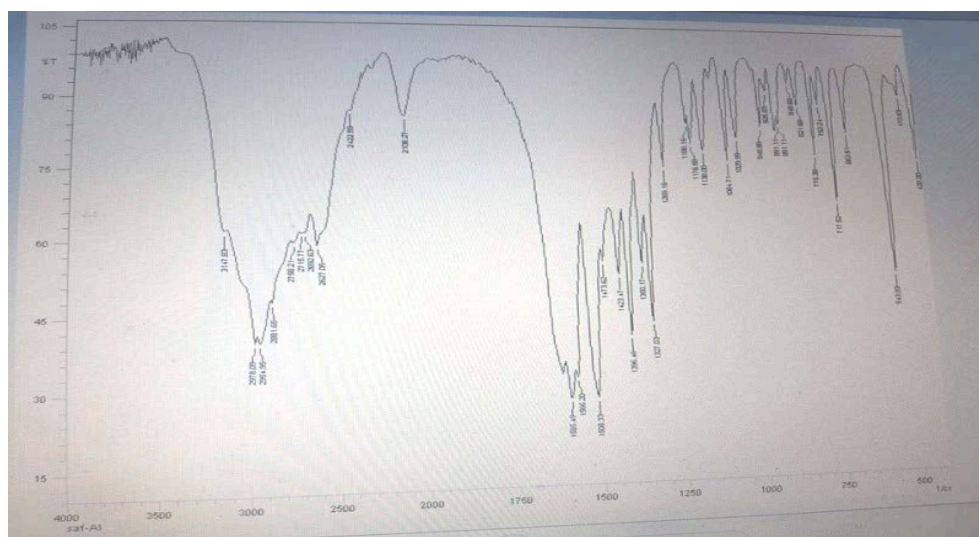
The infrared spectrum of the Schiff base ligand HL<sup>1</sup> shows a band at 1585 cm<sup>-1</sup> is characteristic of the azomethine (HC=N) bound formation<sup>16,17</sup>, the shifting of this band to a higher frequency compared with the free Schiff base suggesting a coordination of metal ions through nitrogen atom of azomethine group<sup>18</sup>. The spectra of the Schiff base and Anthranlic acid contain a broad absorption band appeared in the region 3147–2627 cm<sup>-1</sup> which is assigned to hydrogen bonded ν(COOH).<sup>19</sup> The Infrared spectra of the chelates exhibit a broad bands in the range of 3100-3400 attributed to the presence of water molecules as hydrated and coordinated<sup>20</sup>. The new bands appeared at 796 cm<sup>-1</sup> and 813cm<sup>-1</sup> assigned to ν (M–N) and ν (M–O) stretching vibrations, respectively. which described the complexation behavior between the used

metals towards to nitrogen atom of the azomethane group and oxygen atom of the carboxylate anions group of the studied amino acids.<sup>21- 23</sup> The spectral data of the Schiff base, anthranilic acid and their chelates were given in Table-2.

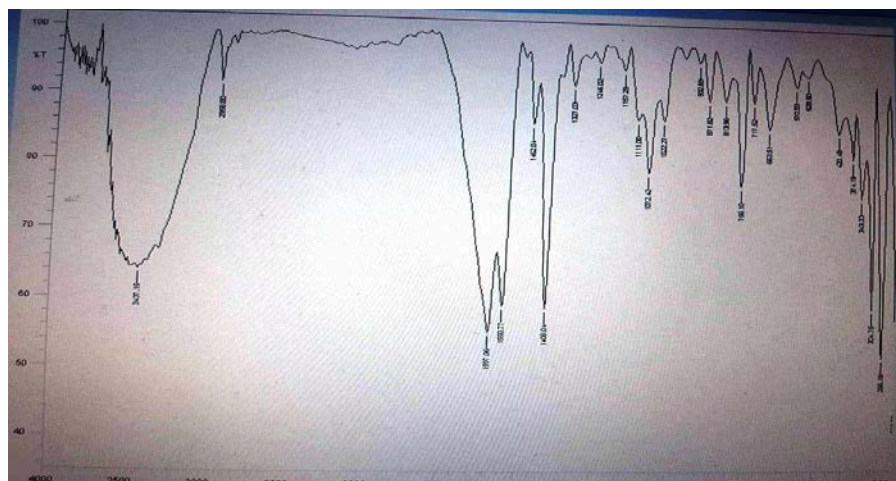
**Table-1: Elemental analysis and some physical properties of Schiff base and its mixed ligand chelates**

Schiff base HL <sup>1</sup> / Chelates	M.wt. (gm/mol)	m.p (°C)	color	Elemental analysis			μsB M	Λ* max
				C%	H%	N%		
Na(C <sub>13</sub> H <sub>16</sub> NO <sub>3</sub> ) ; HL <sup>1</sup>	257	223	white	60.70 (61.00)	6.22 (6.16)	5.44 (5.40)	-	-
Na [Co (L <sup>1</sup> )(L <sup>2</sup> ) 2H <sub>2</sub> O] 3H <sub>2</sub> O	543	322	Brown	44.19 (44.10)	4.20 (4.18)	5.43 (5.06)	4.3	33
Na [Ni (L <sup>1</sup> )(L <sup>2</sup> ) 2H <sub>2</sub> O] 3H <sub>2</sub> O	544	267	Pale blue				3.1	38

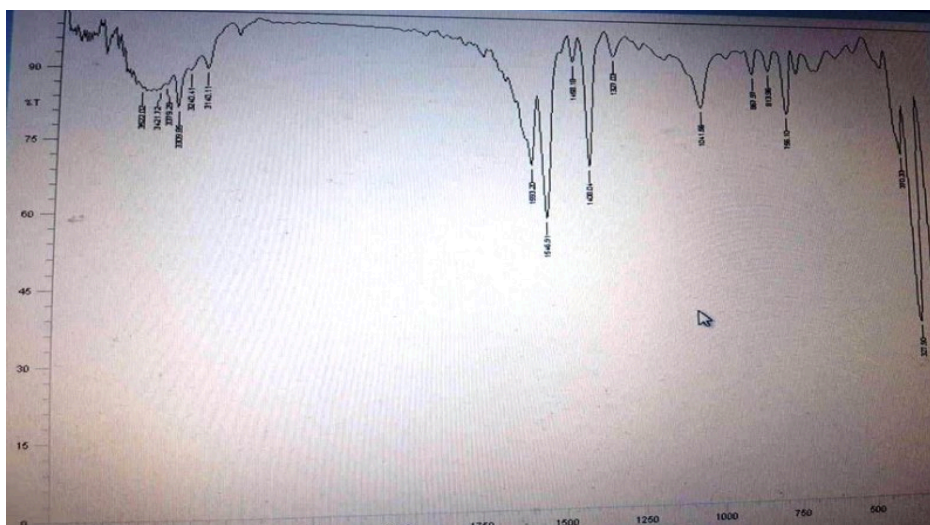
\*= Ω Ohm<sup>-1</sup> cm<sup>-1</sup>



**Figure 2: Infrared spectrum of Schiff base**



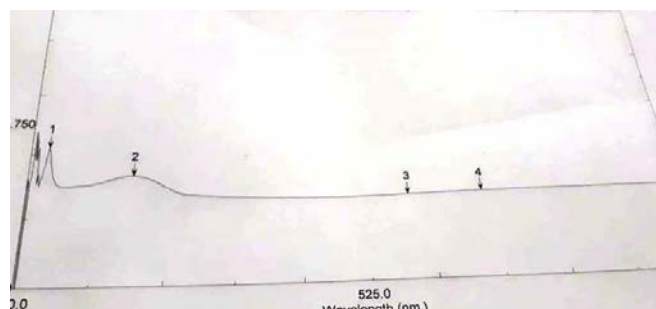
**Figure 3:** Infrared spectrum of Ni (II) chelate



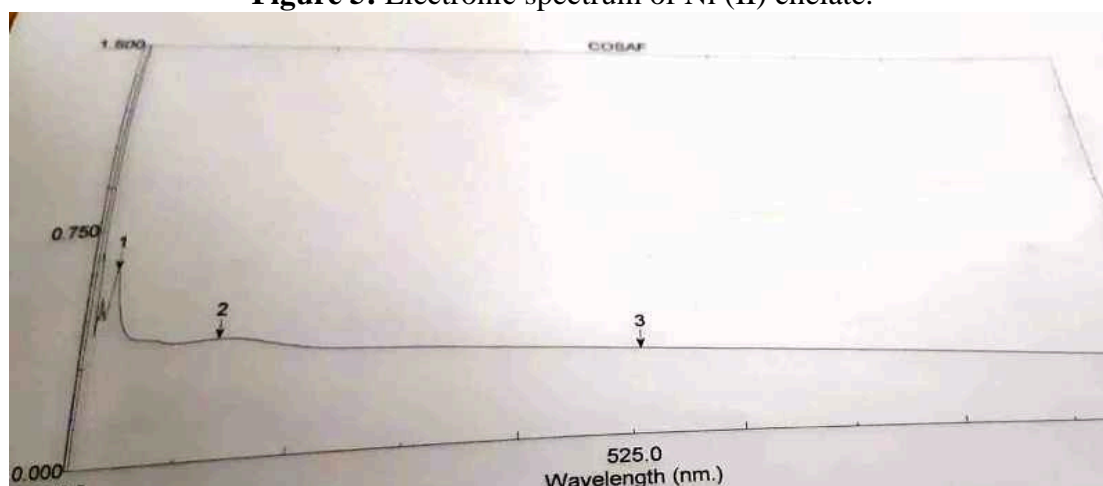
**Figure 4:** Infrared spectrum of Co (II) chelate

### Electronic spectra and magnetic moments

The electronic spectral studies of the Schiff base (HL<sup>1</sup>) and the mixed ligand chelates are shown in Table 2 and their spectra are shown in figures 5-6. The spectrum of the Schiff base exhibits  $\pi-\pi^*$  (phenyl ring) and  $n-\pi^*$  (H-C=N, COO<sup>-</sup>) transition.<sup>24-27</sup> Whereas, The electronic absorption spectral data of Ni(II) chelate shows three bands in the range of 561nm 625 nm and 332nm (30.1200- 16.000 and 12.2562  $\text{cm}^{-1}$ ) corresponding to the  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  transitions, of octahedral structure and the presence of a paramagnetic character supporting the suggested structure.<sup>27</sup> and the magnetic moment of the chelate (3.1 BM). Electronic spectra of Co (II) chelate shows three bands at 530 nm (18867  $\text{cm}^{-1}$ ), 321nm (31.152  $\text{cm}^{-1}$ ) and at 264nm (37789  $\text{cm}^{-1}$ ) which may be assigned to  ${}^4T_{1g}(F) \rightarrow A_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$  which indicated the octahedral geometry of co(II) and supported by  $\mu_{\text{eff}}$  value 4.3 B.M<sup>28</sup>.



**Figure 5:** Electronic spectrum of Ni (II) chelate.



**Figure 6:** Electronic spectrum of Co (II) chelate

**Table 2: Infrared spectral data (cm<sup>-1</sup>) and the electronic spectral results (nm,cm<sup>-1</sup>) of the ligands and its chelates.**

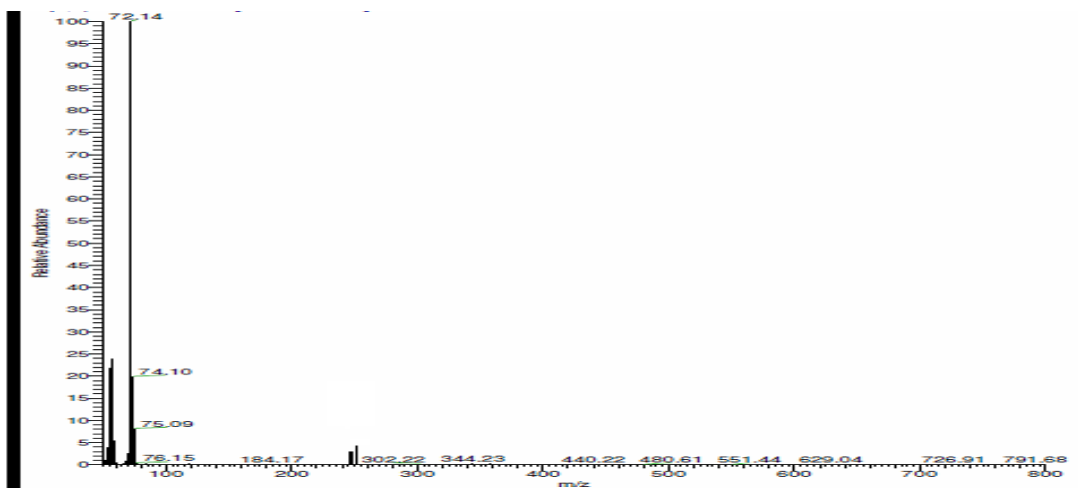
Schiff base / chelates	$\gamma$ (OH)water OH-Phenolic	$\gamma$ (C=O)	HC=N)	$\gamma$ (M-O)	$\gamma$ (M-N)	$\Lambda$ max nm (cm <sup>-1</sup> )
Na( C <sub>13</sub> H <sub>16</sub> NO <sub>3</sub> ) (HL <sup>1</sup> )	-	1685	1585	-	-	<b>300</b> (33333), <b>701</b> (14265)
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub> (HL <sup>2</sup> )	-	-	-	-	-	<b>337</b> (29673), <b>360</b> (27777)
Na[Co(L <sup>1</sup> L <sup>2</sup> ) 2H <sub>2</sub> O] 3H <sub>2</sub> O	3421	1593 1546	1593	813	756	<b>264</b> (37789), <b>321</b> (31152), <b>530</b> (18867)
Na[Ni(L <sup>1</sup> L <sup>2</sup> 2H <sub>2</sub> O) ] 3H <sub>2</sub> O	3437	1597 1550	1597	813	756	<b>332</b> (30120) <b>561</b> (17835) <b>625</b> (16.000) <b>796</b> (12.562)

**Mass spectra Study:** Mass spectral fragmentations of the Schiff base and Ni(II) mixed ligand chelate are shown in table-3, Schiff base is represented by the peak at  $m/e+ = 234$  analogous to structure [C<sub>13</sub>H<sub>16</sub>NO<sub>3</sub>]. The peak at  $m/e+=191$  is equal to the formula [C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>], the peak at  $m/e+=147$  is attributing to [C<sub>9</sub>H<sub>9</sub>NO ], where the last peak at  $m/e+=121$  is attributing to [C<sub>8</sub>H<sub>9</sub>O]. The peak at  $m/e+ = 121$  is attributing to [C<sub>8</sub>H<sub>9</sub>O]. The structure C<sub>6</sub>H<sub>3</sub> is analogous to peak at  $m/e+ = 75$ . The peak at  $m/e+ = 74$  is analogues to loss of hydrogen atom. Meanwhile, the last peak at  $m/e+ = 72$  due to loss of two hydrogen atoms. The mass spectrum of the nickel mixed ligand

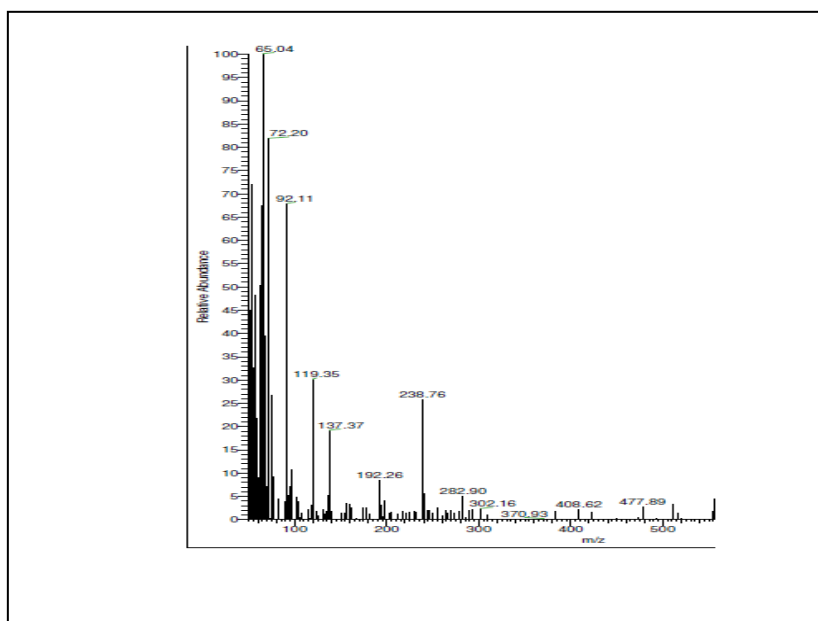
chelate shows a peak at  $m/e+=489$  analogues to  $\text{Na}[\text{Ni}(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_5(\text{H}_2\text{O})_2)]$ , The peak at  $m/e+=466$  related to  $[\text{Ni}(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_5(\text{H}_2\text{O})_2)]$ . The same spectrum shows a peak at  $m/e+=387$  corresponding to  $[\text{Ni}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5)]$ , The final peak appeared at  $m/e+=330$  due to  $[\text{Ni}(\text{C}_{13}\text{H}_7\text{N}_2\text{O}_5)]$ . Meanwhile, the peak at  $m/e+=137$  analogous to anthranilic acid  $\text{C}_7\text{H}_7\text{NO}_2$ . The structure  $\text{C}_7\text{H}_6\text{NO}^+$  is analogous to peak at  $m/e+=120$ . Meanwhile, the peak at  $m/e+=92$  are due to  $\text{C}_6\text{H}_6\text{N}^+$ . The final peak appeared at  $m/e+=66$  due to  $\text{C}_4\text{H}_4\text{N}^+$ .

**Table- 3:** Mass spectral fragmentation of Schiff base and their Ni(II) mixed ligand chelate.

Compound	fragmented ion	m/e+ values
Schiff base	$\text{C}_{13}\text{H}_{16}\text{NO}_3\text{Na}$	257
- Na	$\text{C}_{13}\text{H}_{16}\text{NO}_3$	234
$-\text{C}_3\text{H}_7$	$\text{C}_{10}\text{H}_9\text{NO}_3$	191
$-\text{COO}$	$\text{C}_9\text{H}_9\text{NO}$	147
$-\text{CN}$	$\text{C}_8\text{H}_9\text{O}$	121
$-\text{C}_2\text{H}_5\text{O}$	$\text{C}_6\text{H}_3$	75
$-\text{H}^+$	$\text{C}_6\text{H}_2$	74
$-\text{2H}^+$	$\text{C}_6$	72
Mixed ligand chelate of Ni	$\text{Na}[\text{Ni}(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_5)(\text{H}_2\text{O})_3]$	543
$-\text{3H}_2\text{O}$	$\text{Na}[\text{Ni}(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2]$	489
-Na	$[\text{Ni}(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2]$	466
$-\text{C}_3\text{H}_7.2\text{H}_2\text{O}$	$[\text{Ni}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5)]$	387
$-\text{C}_4\text{H}_9$	$[\text{Ni}(\text{C}_{13}\text{H}_7\text{N}_2\text{O}_5)]$	330
$-\text{NiC}_5\text{H}_2\text{O}_3\text{N}$	$\text{C}_7\text{H}_7\text{NO}_2$	137
$-\text{OH}$	$\text{C}_7\text{H}_6\text{NO}^+$	120
$-\text{CO}$	$\text{C}_6\text{H}_6\text{N}^+$	92
$-\text{C}_2\text{H}_2$	$\text{C}_4\text{H}_4\text{N}^+$	66



**Figure 7:** Mass spectrum of Schiff base

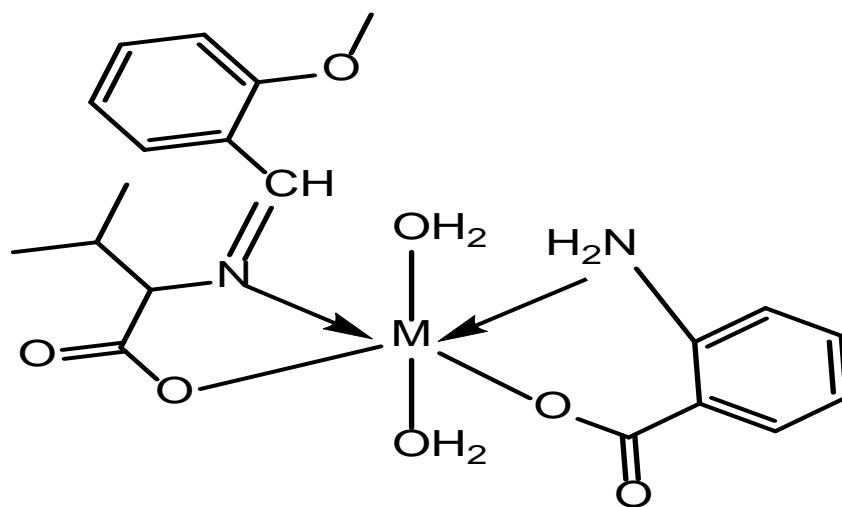


**Figure 8:** Mass spectrum of Ni(II) chelate



## Conclusion

The idea of the preparation and characterization of mixed ligand chelates of two boarder acids; cobalt(II) and nickel(II) ions with Schiff base formed from the refluxing of 2-methoxybenzaldehyde and L-valine as main ligand and anthranilic acid as secondary ligand is to establish the geometrical structures of the chelates. These compounds were subjected to some physiochemical tools. Based on the obtained data, an octahedral geometry was suggested for all chelates and their suggested structures are shown below:



M(II) = Co, Ni

Suggested chemical structure of the mixed ligand chelates

## REFERENCES:

- 1-D. Sadhukhan, A. Ray, G. Rosair, L. Charbonnière, S. Mitra, *Bull. Chem. Soc. Jpn*, **84**,(2011) 211.
- 2- A. T. Chaviara, P. J. Cox, R. M. Papi, K. T. Papazisis, D. Zam- bouli, A. H Kortsaris, D. A. Kyriakidis, C. A. Bolos, *J. Inorg. Chem*, **98**,(2004) 1271.
- 3- A. Prakash, D. Adhikari, *International J. Chem Tech Research*, **3**, (2011)1891.
- 4- G. Nizami, R. Sayyed, *IOSR J. of Applied Chem*, **10** ,(2017)40.
- 5- W. Al Zoubi, *International J. of Organic Chem*, **3**, (2013)73.
- 6-S. K. Tobriya, *International J. of Science and Research*, **3**, (2014)1254.

- 7- M. F. A. Ahamed, V M. Yunus, *International J. of Pharma Research and Health Sciences*, **2**, (2014)361.
- 8- G. Kumar, D. Kumar, C. P. Singh, A. Kumar, V. B. Rana, *J. of The Serbian Society*, **75**, (2010)629.
- 9- A. Prakash, S. Kabir, M. Agrawal, R. Sharma, A. K. Gupta, *International, J. Chem. Tech Research*, **6**, (2014)1276.
- 10- Yamada S, *Coord Chem. Rev.*, **537** ( 1999):190-192.
- 11- S.M. Krishnaraj ,M.P Viswanathamurthi, S. Sivakumar, *Trans. Met.Chem.*; **33**(2008) 643.
- 12- M. A. Ashraf, K. Mahmood, A. Wajid, *International Conference on Chem. and Chemical Process*,**10**, (2011) 1.
- 13- S. Bhanuka, H. L. Singh, *Rasayan J. of Chem*, **9**,(2016)614-626.
- 14- R. N. Fl-daghare, M. M. El-ajaily, *Asian J. Adv. Basic Sci*, **6**, (2018) 86.
- 15- Geary, W. J, *Coord. Rev*, **7**, (1971) 81.
- 16- N. Raman, Y.P. Raja and A. Kulandaisary, *Proc. Indian Acad. Sci.*, 113, 183 (2001).
- 17- W. RM, H. C.J, Wang YP, Benli S. *J MolCatal A Chem.*, , **147**,173-179(1999)
- 18- M.M. El-ajaily and A.A. Maihub, *Jerash for Res. Studies*, **8**, (2004)7
- 19- K. R., Choudhury, C. R., Mitra, S., Dahlenburg, L, *Structural Chem*, 16, **6**(2005) 611-616.
- 20- G.W, Watt , D.S, Klett. *Inorg. Chem.*, **5**, (1966)1278.
- 21- M. S. Suresh, V. Prakash, *International J. of the Physical Sciences*, **5**, (2010)1443.
- 22- R. Pradhan, S. k. Sinha, P. Verma, S. Kumar, S. Sharma, *Asian J. of Chem*, **30**, (2018)1989
- 23- H. Yu, W, Zhang , Q. Yu. F.P. Huang, H. Bian , H. Liang, *Molecules* 2017.
- 24- S. Gaur and B. Sharma, *J. Indian Chem. Society*, **8**, (2003)841.

- 25- K. M. Abuamer, A. A. Maihub, M.M. El-ajaily, A. M. Etorki, M. M. Abou-Krishna, M. A. Almagani, *International J. of Organic Chem*, **4**, (2014)7.
- 26- R. L. Prasad, A. Kushwaha, B.S. Gautam, *J. of Coordination Chem.*, **62**, (2009) 2983.
- 27- A. A. Maihub, M. M. El-ajaily, N. A. El-hassy, *International J. of ChemTech Research*, **4**, (2012) 63.
- 28- S. Neeraj & S. Neelam . *J. Chem.* **2** 277-287 (2010 )