



## Preparation, Spectroscopic Studies of (E)-2((2-hydroxybenzylidene) amino)-3-mercaptopropanoic acid Chelates

R. N. Fl-daghare<sup>1</sup> and M. M. El-ajaily<sup>2\*</sup>

<sup>1&2</sup> Department of Chemistry, Faculty of Science, Benghazi University, Benghazi, LIBYA

\* Correspondence: E-mail: [melajaily@gmail.com](mailto:melajaily@gmail.com)

(Received 08 May, 2018; Accepted 31 May, 2018; Published 02 June, 2018)

**ABSTRACT:** Three chelates of divalent transition metal ions [Co, Ni and Cu] with (E)-2((2-hydroxybenzylidene)amino)-3-mercaptopropanoic acid (HL1) formed from the condensation reaction of 2-hydroxybenzaldehyde (salicylaldehyde) and L-cysteine have been prepared and studied by using several physicochemical tools, such as; CHNS elemental analyses, molar conductivity, magnetic moment measurements and spectroscopic techniques [IR, <sup>1</sup>HNMR, UV-Vis]. The CHNS elemental analysis data show the formation of the chelates in 1:2[M:L] ratio. Whereas, the IR spectral data exhibit the chelation sites of the active groups in the Schiff base towards to the metal ions. The electronic spectral results display the presence of the electronic transitions in the free Schiff base and its chelates. An octahedral geometrical structure was suggested for all chelates.

**Keywords:** Schiff Base; 3-hydroxybenzaldehyde; L-Cysteine; Chelates and Physicochemical Tools.

**INTRODUCTION:** Several studies showed that the Schiff bases derived from carbonyl groups with polar amino acids have been prepared and characterized.<sup>1</sup> Both cysteine and salicylaldehyde are bidentate ligands have a good ability to form many chelates with non transition and transition metal ions, also this type of the ligands are using to prepare metal chelates due to their active groups as shown in the preparation of uranium (VI) Schiff base chelate which formed from the refluxing of salicylaldehyde and L-cysteine. The chelate has been studied by using some physical techniques and the obtained physical data showed the expected geometrical structure for the chelate.<sup>2</sup> Three chelates of Mn(II), Co(III) La(III) with a Schiff base formed from salicylaldehyde and amino acid (methionine) have been synthesized and characterized by using several techniques such as [elemental analysis, magnetic measurement, thermogravimetric analysis and X-ray powder diffraction method, IR, electronic spectroscopy] from spectral studies, it was found that the synthesized Schiff base acted as a tetradentate molecule, coordinates metal via phenolic oxygen, sulfur, azomethine nitrogen and carboxylate oxygen. The electronic spectral data exhibited bands attributing to a square planar geometry for La(III) and Mn(II) metal chelates and tetrahedral geometry for Co(III) complex. The XRD data revealed that the Mn(II) and cobalt complexes were crystalline, but the La(III) complex was amorphous in nature.<sup>3</sup> The preparation of Schiff base chelate which formed from condensation of salicylaldehyde and amino acids [

glycine, alanine, phenylalanine, methionine and cysteine] acted as tridentate ligand towards divalent metal ions (cobalt, copper, nickel and zinc) through the azomethine, deprotonated carboxyl group of the respective amino acid and deprotonated oxygen atom of salicylaldehyde.<sup>4</sup>

**MATERIALS AND METHODS:** All chemicals used in this work are of pure grade (BDH or Aldrich). include; salicylaldehyde, L-Cysteine, DMF, DMSO, NaOH, C<sub>2</sub>H<sub>5</sub>OH, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O and distilled water. The Schiff base and its chelates were analyzed by CHNS elemental analysis using 2400-CHN elemental analyzer. The molar conductivity of the chelates was measured in DMF solvent using digital conductivity meter CMD-650, at chemistry department, Benghazi University, Benghazi, Libya. The infrared spectra were carried out applying KBr disc technique using IFS-25 DPUS/IR spectrometer. Proton nuclear magnetic resonance spectrum of the Schiff base was recorded on Varian Gemini200-200MHz spectrometer using TMS as internal standard and d<sub>6</sub>-DMSO as a solvent. The UV-Vis spectra of the Schiff base and its chelates were measured in DMF solvent by using a Perkin-Elmer lambda-4β spectrophotometer. All previous analysis were done at micro-analytical centre, Cairo University, Giza, Egypt.

**Preparation of polar amino acid Schiff base (HL1):** The present Schiff base was prepared as follows: NaOH (0.01 mol; 0.4 gm) was dissolved in 20 mL

ethanol and a polar amino acid ( L-Cysteine) (0.01 mol; 1.81gm) was added to it. The mixture reaction was stirred magnetically at room temperature. When the mixture becomes homogeneous, salicylaldehyde (0.01 mole; 1.22 gm) in the same amount of the same solvent was added. The mixture was refluxed for two hours. A yellow product was formed, filtered, washed and dried in excellent yield of 80 %, Figure 1.

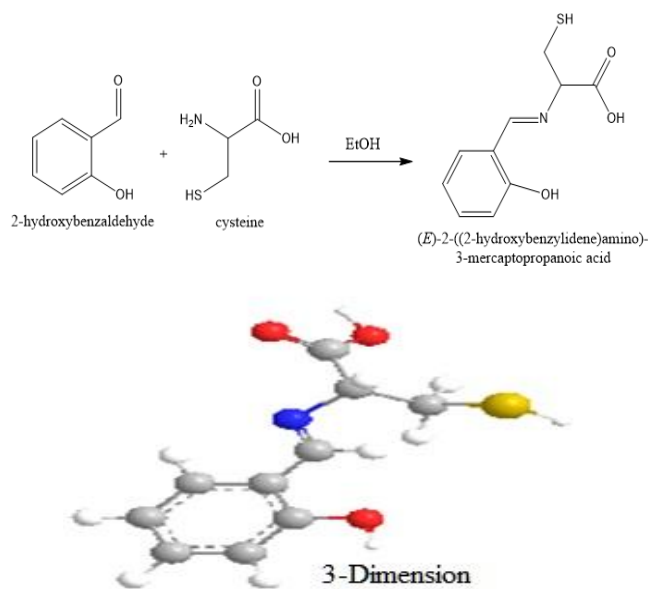


Figure 1: Formation of the Schiff base (HL1).

**Preparation of polar amino acid Schiff base chelate:** The prepared Schiff base was used to form Co(II), Ni(II) and Cu(II) chelates by adding 0.01 mole, 2.25 gm of the Schiff base (HL1) in 20mL of the absolute ethanol to 0.01mole; 2.38, 2.37 and 1.70 gms) of the desired metal salts, respectively. Few drops of sodium hydroxide solution were added slowly to adjust the pH value at 8 until the chelates separated, and then the mixtures were stirred and refluxed for three hours. The formed precipitates were filtered and washed several time with hot ethanol until the filtrates become clear. The obtained chelates were dried in desecrator under calcium chloride.

Table 1: Elemental analyses and some physical properties of the Schiff base and its chelates .

Schiff base / Chelates	M.wt. (gm/mole)	M.P (°C)	Color	Elemental analysis (Found)				$\mu\text{s (BM)}$	$\Lambda^*_{\text{max}}$
				C%	H%	N%	S%		
(C <sub>10</sub> H <sub>13</sub> NO <sub>4</sub> S) L1	(225)	103	Yellow	53.95 (53.33)	4.80 (5.77)	5.45 (6.22)	15.03 (14.22)	-----	-----
Na <sub>2</sub> [Co(L1) <sub>2</sub> ].2H <sub>2</sub> O	(587)	241	Brown	40.07 (40.88)	4.68 (4.43)	4.72 (4.77)	11.28 (10.90)	3.25	43.4
Na <sub>2</sub> [Ni(L1) <sub>2</sub> ].2H <sub>2</sub> O	(586.7)	224.7	Gray green	39.89 (40.90)	4.58 (4.43)	4.10 (4.77)	11.27 (10.90)	2.25	63.4
Na <sub>2</sub> [Cu(L1) <sub>2</sub> ].2H <sub>2</sub> O	(591.5)	214	Green	39.58 (40.57)	4.50 (4.39)	3.93 (4.73)	11.09 (10.82)	1.23	61.2

\*=  $\Omega \text{ Ohm}^{-1} \text{ cm}^{-1}$

## RESULTS AND DISCUSSION:

**CHNS Elemental Analyses and Molar Conductivity:** Table (1) comprises the elemental analyses and some physical properties of the Schiff base and its chelates, the analytical data show a good agreement between the theoretical and experimental values, indicating the formation of the Schiff base and the chelates in 1:2[M:L] ratio. The obtained molar conductance values revealed that the prepared chelates are electrolyte in nature.<sup>5</sup> This is due to the presence of sodium ion out of the coordination sphere.

**Infrared spectra of amino acid Schiff base and its chelates:** The infrared spectral data of the Schiff base and its chelates are listed in table 2 and their spectra are shown in figures 2-5. The infrared spectral data of the Schiff base show a broad band at 3402 cm<sup>-1</sup> due the presence of hydrogen bond that formed between –OH and –COOH groups.<sup>6</sup> The same spectrum of displays a band at 1601 cm<sup>-1</sup> attributed to the existence of  $\nu(\text{HC}=\text{N})$  vibration.<sup>7</sup> In the chelates (Table 2), 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. Meanwhile, the band at 1392 cm<sup>-1</sup> due to  $\nu(\text{COO}^-)$  stretching frequency is shifted to a higher frequency in the spectra of the chelates (1408-1546 cm<sup>-1</sup>) indicating the participation of this group via oxygen atom of hydroxyl group of –COOH group in chelation.<sup>8</sup> The spectra of the chelates exhibit bands in the range of 3360-3452 cm<sup>-1</sup>) assigned to the presence of water molecules as hydrated and coordinated.<sup>9, 10</sup> New bands which are not present in the spectrum of free Schiff base appeared at 451-525 cm<sup>-1</sup> and 675-833 cm<sup>-1</sup> are attributed to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations, respectively. The appearance of  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations support the involvement of nitrogen and oxygen atoms in chelation with the metal ions under investigation.<sup>11, 12</sup>

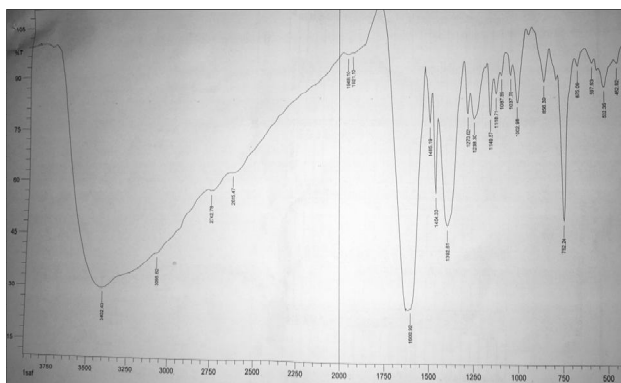


Figure 2: Infrared spectrum of Schiff base.

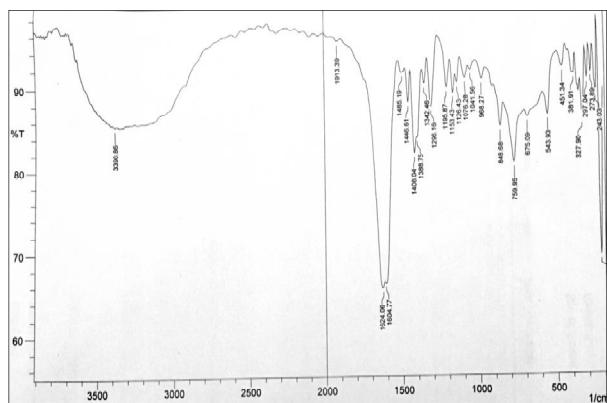


Figure 3: Infrared spectrum of Co (II) chelate.

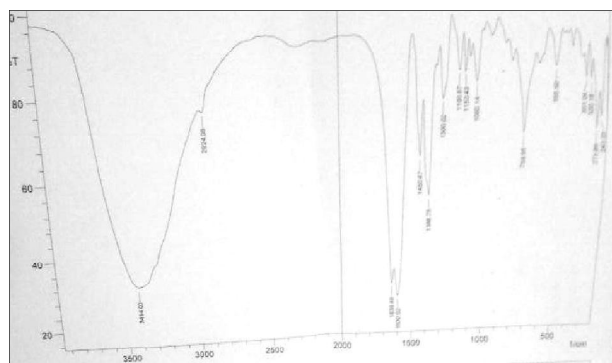


Figure 4: Infrared spectrum of Ni (II) chelate.

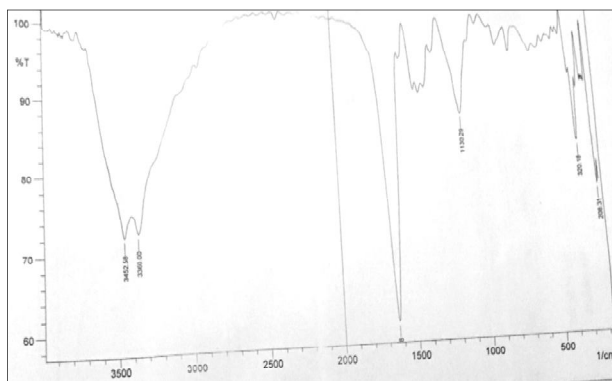


Figure 5: Infrared spectrum of Cu (II) chelate.

**<sup>1</sup>HNMR spectrum of the Schiff base:** The <sup>1</sup>HNMR spectrum of the free Schiff base (Figure 6) was measured in d<sup>6</sup>-DMSO solvent and shows two signals at 6.84 and 4.34 ppm, the first one is attributed to phenyl ring and the second signal is due to the formation of hydrogen bond between –OH group of the salicylaldehyde and –COOH group of the amino acid (L-cystein).<sup>13</sup> The same spectrum exhibits another signals at 2.45 and 9.2 ppm which are refer to (–HC=N) and methyl groups.<sup>14</sup>

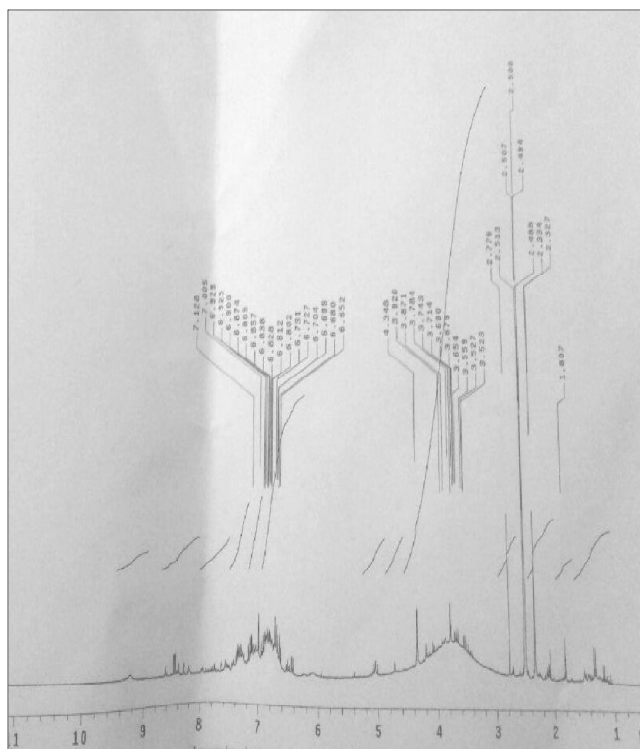


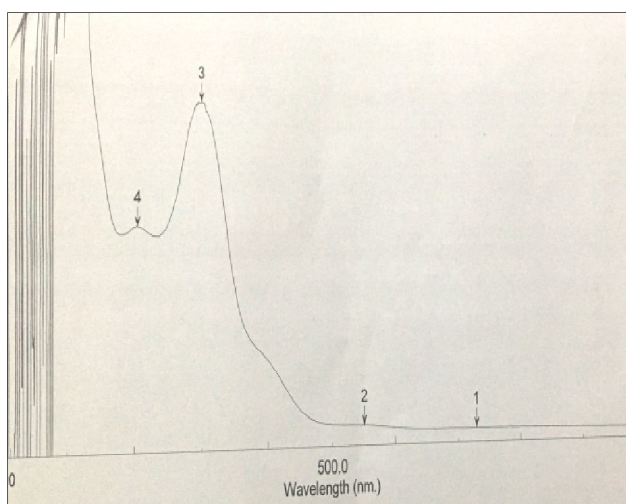
Figure 6: <sup>1</sup>HNMR spectrum of Schiff base.

**Electronic spectra and magnetic moment:** The electronic absorption spectra of Schiff base and its chelates are shown in Table 2 and their spectra are shown in figures 7-10. All spectra exhibit important data to interpret the transitions occurred. The absorption bands at 322nm (31056 cm<sup>-1</sup>) and 380 (26315cm<sup>-1</sup>) are observed in the spectrum of the free Schiff base suggesting the presence of π-π\* and n- π\* (HC=N) transitions.<sup>15</sup> The Co(II) chelate spectrum exhibits two bands at 781nm (12804 cm<sup>-1</sup>) and 364nm (27397 cm<sup>-1</sup>), The first band is due to <sup>4</sup>T<sub>2g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F) transition and the second one is assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transition.<sup>16</sup> The intensity of the bands and the magnetic moment value (3.25 BM) suggest the presence of an octahedral geometry.<sup>17, 18</sup> The electronic absorption spectral data of Ni (II) chelate shows bands in the range of 379-638 nm (26385-15673 cm<sup>-1</sup>), attributed to <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transitions, of an octahedral structure and the presence of a paramagnetic character supporting the suggested structure.<sup>19</sup> The Cu(II) amino acid

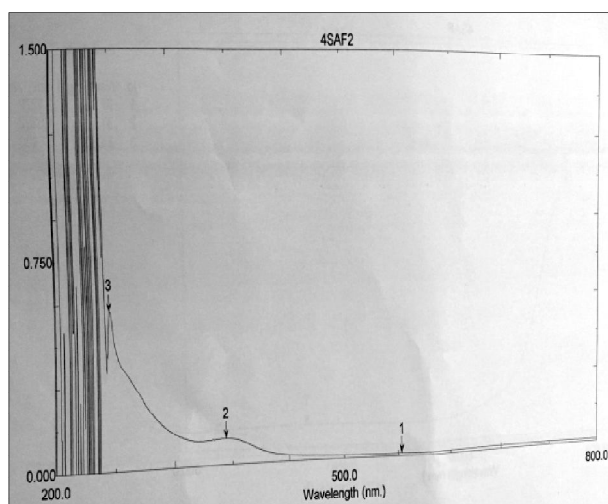
Schiff base chelate exhibits one odd electron and (17730 cm<sup>-1</sup>) due to charge transfer and <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> transition. An octahedral geometry was proposed.<sup>20</sup> shows bands at 373nm (26810cm<sup>-1</sup>) and 564 nm transition.

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

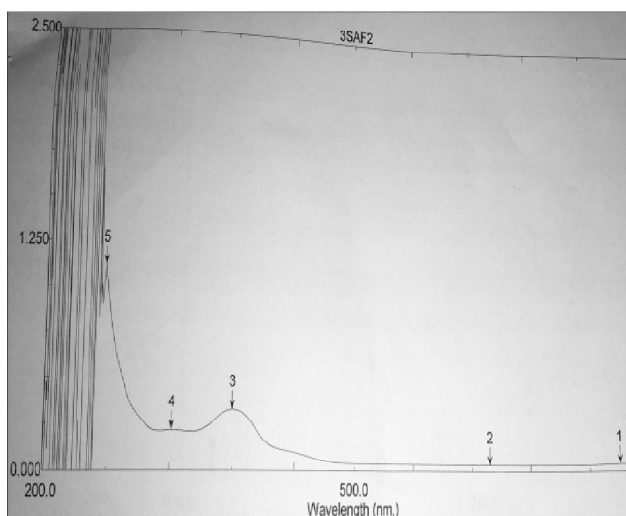
Schiff base / Chelates	IR bands cm <sup>-1</sup>					λ <sub>max</sub> nm (cm <sup>-1</sup> )
	γ (OH) Water	γ (COO <sup>-</sup> )	γ (HC=N)	γ (M-O)	γ (M-N)	
(C <sub>10</sub> H <sub>13</sub> NO <sub>4</sub> S) L1	3402	1392	1601	--	--	322 (31056) , 380 (26315)
Na <sub>2</sub> [Co(L1) <sub>2</sub> ].2H <sub>2</sub> O	3390	1408	1624	675	451	781 (12804), 365 (27397)
Na <sub>2</sub> [Ni (L1) <sub>2</sub> ].2H <sub>2</sub> O	3414	1512	1624	760	525	770 (12987), 638 (15673), 379 (26385), 321 (31152)
Na <sub>2</sub> [Cu(L1) <sub>2</sub> ].2H <sub>2</sub> O	(3452- 3360)	1546	1631	833	454	564 (17730), 373 (26810)



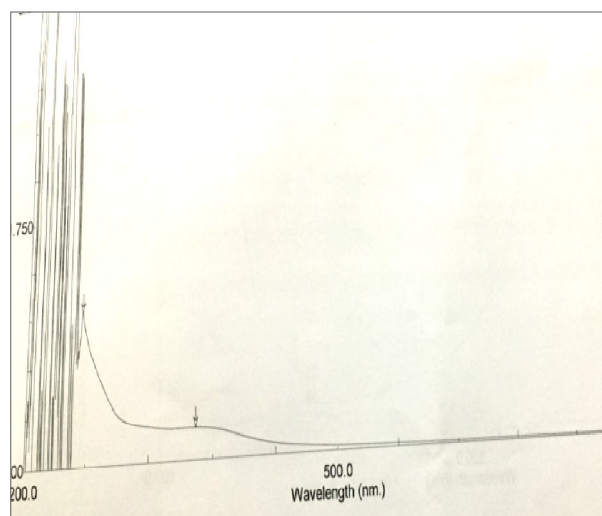
**Figure7: UV spectrum of Schiff base.**



**Figure 9: Electronic spectrum of Ni (II) chelate.**



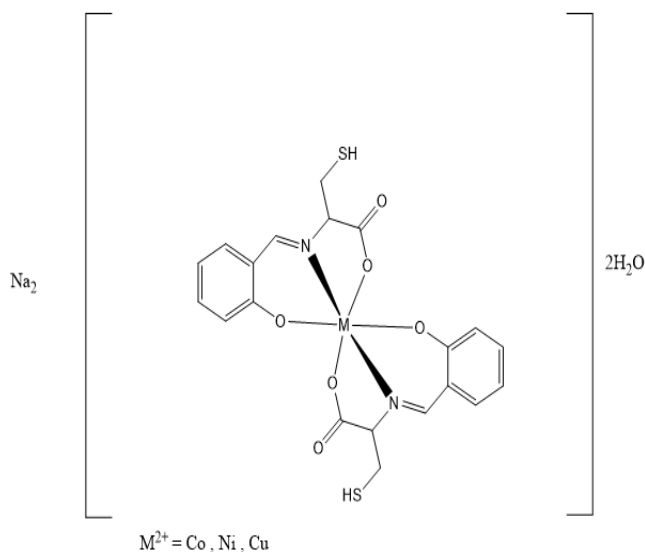
**Figure 8: Electronic spectrum of Co (II) chelate.**



**Figure 10: Electronic spectrum of Cu (II) chelate.**



**CONCLUSION:** From the physiochemical data, we concluded that the prepared chelates have an octahedral structure as shown in figure 11.



**Figure 11: Suggested geometrical structure of the chelates.**

#### REFERENCES:

1. El-ajaily, M. M., Maihub, A. A., El-meshety, F. I. and Boshala, H. A., (2011) *Egypt. J. Anal. Chem.*, 20, 16-23.
2. Morad, F. M., El-ajaily, M. M. and Maihub, A. A., (2006) *Egypt. J. Anal. Chem.*, 15, 98-103.
3. Shariful Islam, A. K. M. Nur Alam Siddiki, Shahida Begum, Md. Abdus Salam., (2018) *Open Journal of Inorganic Chemistry.*, 8, 55-69.
4. Chohan, Z. H., Arif, M. and Sarfraz, M., (2007) *Applied Organic Chemistry*, 21, 294.
5. Geary, W. J., (1971) *Coord. Rev.*, 7, 81.
6. Ossonicz, P., Janus, E., Schoerder, G. and Rozwadowski, Z., (2013) *Molecules*, 18, 4986-5004.
7. Azzouz, A. S. P., Ali, R. T., (2010) *National Journal of Chemistry*, 37, 158- 168.
8. El-Ferjani, R. M., Ahmad, M., Harun, F. W., Bulgasem, B. Y., (2017) *Journal of Applied Chemistry (IOSR-JAC)*, 10, 06-13
9. Maihub, A. A., El-ajaily, M. M., Azzouz, A. H., El-Barasi, N. B., AL-Ferjani, R. M., (2006) *Journal of science and its application*, 1, 275-283.
10. Karmakar, R., Choudhury, C. R., Mitra, S., Dahlenburg, L., (2005) *Structural Chemistry*, 16 (6), 611-616.
11. El-ajaily, M. M., Ben-Gweirif, S., Maihub, A. A., El-tajoury A. N., (2006) *New Trends in Science and their applications (Symposium, Garyounis University)*, 1, 196-210.
12. El-ajaily, M. M., Hamil, A. M., Abdalkarem, M. and Himmet. M. (2016) *J. Biol. Chem. Chron.*, 2(2), 01-07.
13. El-ajaily, M. M., Bomoraiwaha H. F., and Maihub, A. A., (2007) *Egypt. J. Anal. Chem.*, 16, 36-46.
14. El-ajaily, M. M., Alassbaly, F. S., Etorki, A. M., and Maihub, A. A., (2015) *International Research Journal of Pure & Applied Chemistry*, 5, 229-237
15. Baiu, S. H., El-ajaily, M. M., and El-Barasi, N. M., (2009) *Asian Journal of Chemistry*, 21, 5-10
16. Maihub, A., Alassbaly, F., El-ajaily, M. and Etorki, A. (2014) *Green and Sustainable Chemistry*, 4, 103-110.
17. Shayma, A. S. (2011) *E. J. Chem.*, 8(1), 153.
18. El-ajaily, M. M., Abdullah, F. I., Suliman, M. S. and Akasha, R. A. (2014) *Asian J. of Adv. Basic Sci.*: 2(2), 17-30.
19. El-ajaily, M. M., Abdlseed, F. A. and Ben-Gweirif, S., (2007) *E-Journal of Chemistry*, 4, 461- 466.
20. Suresh, M. S. and V. Prakash, V., (2010) *International Journal of the Physical Sciences*, 5, 1443-1449.