



# Synthesis, Characterization and Biological Evaluation of Cr(III), Fe(III), Co(II), Ni(II), Zn(II) and Cd(II) Complexes Using an Azo Dye as Ligand

RANA ABDULILAH ABBAS<sup>1</sup>, AFNAN E. ABD-ALMONUIM<sup>2</sup>, AMER J. JARAD<sup>3</sup>, SZIDONIA-KATALIN TANCZOS<sup>4\*</sup>, PAUL CONSTANTIN<sup>5</sup>

<sup>1</sup>Department of Chemical Industrial, Institute of Technology/ Baghdad, Middle Technical University, Iraq

<sup>2</sup>Pharmacy Department, Al-Rasheed University College, Baghdad, Iraq

<sup>3</sup>Department of Chemistry, College of Education for Pure Science /Ibn-Al-Haitham, University of Baghdad, Iraq

<sup>4</sup>Sapientia Hungarian University of Transylvania, Faculty of Economics, Socio - Human Sciences and Engineering, 1 Libertății Sq., 530104, Miercurea Ciuc, Romania

<sup>5</sup>IFIN Horia Hulubei, Radioisotopes & Radiat. Metrol. Dept. DRMR, 30 Reactorului Str, 023465, Magurele, Romania

**Abstract:** Azo ligand 11-(4-methoxyphenyl azo)-6-oxo-5,6-dihydro-benzo[4,5] imidazo[1,2-c]quinazoline-9-carboxylic acid was derived from 4-methoxyaniline and 6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid. The presence of azo dye was identified by elemental analysis and spectroscopic methods (FT-IR and UV-Vis). The compounds formed have been identified by using atomic absorption in flame, FT-IR, UV-Vis spectrometry magnetic susceptibility and conductivity. In order to evaluate the antibacterial efficiency of ligand and its complexes used in this study three species of bacteria were also examined. Ligand and its complexes showed good bacterial efficiencies. From the obtained data, an octahedral geometry was proposed for all prepared complexes.

**Keywords:** - 4-methoxyaniline, azo dyes, complexes, dyeing

## 1. Introduction

Azo dyes which contain O, N-donor atoms react as chelating agents for many elements and present bioactive properties [1, 2]. Because of their low price and color fastness, the produced azo dyes have been investigated for industrial applications mainly, such as clothes, leather, plastics, food, cosmetics and toys [3, 4]. Azo compounds have been widely used as analytical reagents in spectrophotometric and extraction-photometric analysis for metals determination [5]. Metal chelates for heterocyclic azo compounds which were more interesting in inorganic and organometallic chemistry, and also have been granted for application in bioactive systems, catalysis and materials science [6]. These metal chelates were used for industrial applications, synthesis, leather dyeing, vinyl polymers, for pharmaceuticals, inhibition of DNA, RNA, protein synthesis, nitrogen fixation [7, 8].

In this work synthesis of azo dye by reaction of 4-methoxyaniline with 6-oxo-5,6-dihydro-benzo[4,5] imidazo[1,2-c]quinazoline-9-carboxylic acid, the metal chelates of azo dye have been produced and identified using different spectral analyses.

## 2. Materials and methods

### 2.1. Equipment

UV-Vis spectra were recorded using a Shimadzu UV-160 A Ultra Violet-Visible Spectrophotometer. IR-spectrum have been recorded using a Shimadzu, FTIR-8400 S Fourier Transformed. Spectrophotometer (4000-400)  $\text{cm}^{-1}$  patterns were obtained using KBr discs. Atomic absorption results have been acquired by means of a Shimadzu A.A-160A Atomic Absorption / Flame Emission Spectrophotometer. The conductors with  $10^{-3}\text{M}$  concentration from DMSO complexes measured at  $25^\circ\text{C}$  with a Philips PW - Digital Conductometer. Magnetic characteristics were obtained

\*email: [tczszidonia@yahoo.com](mailto:tczszidonia@yahoo.com)

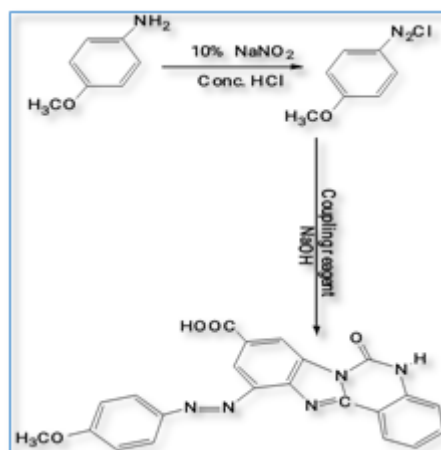
using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. Moreover, melting points were established by means of a Melting Point Apparatus.

## 2.2. Materials and reagents

The following chemical substances  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (Merck), 4-methoxyaniline and 6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid (Fluka) have been used as received from providers.

## 2.3. Azo ligand preparation

4-methoxyaniline (0.307 gm, 1mmole) melted in a mixture of 10mL ethanol including 2mL conc. HCl and 10mL distilled water and diazotized at 5°C with 10% solution of  $\text{NaNO}_2$ . The diazotized solution was gradually added under stirring into a cooling ethyl alcohol solution at 0.697 gm, 1mmole of 6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid. After that, 25 mL of NaOH 1M solution was added into the dark color mix, and the deposition of azo ligand was also observed. This precipitate was filtrated, several times washed with ethyl alcohol, then allowed to dry. The interaction are presented in Figure 1.



**Figure 1.** The azo ligand synthesis

## 2.4. The preparation of metal complexes

Aqueous solution of metal salts containing 0.118, 0.118, 0.068 and 0.100 gm (1mmole) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  were added dropwise to (0.413 gm, 2mmol) of azo ligand melted in ethyl alcohol for molar ratio (1:2 M:L) and aqueous solution of metal salts containing 0.088 and 0.054 gm (1mmol) of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_3$  were added gradually under stirring to ethyl alcohol (0.413 gm, 3mmol) of azo ligand by using stoichiometric amount (1:3 M:L) molar ratio. The mix has been refluxed for continuous stirring about an hour. Then, the same mix has been cooled in room temperature and subsequently dark deposit has been created, filtered also recrystallized of  $\text{C}_2\text{H}_5\text{OH}$  and dried in room temperature. The reactions involved in the results are depicted in Figure 2 and Figure 3.

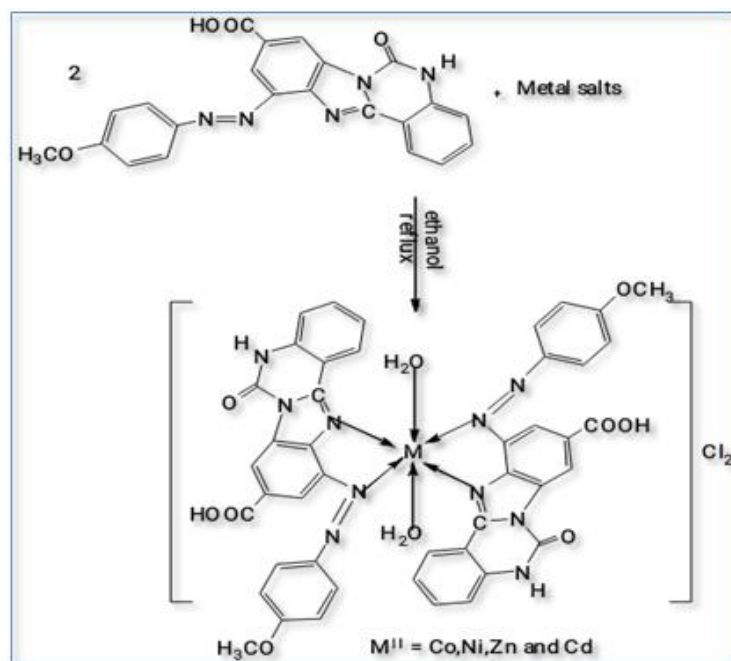


Figure 2. The expected geometry of metal (II) complexes

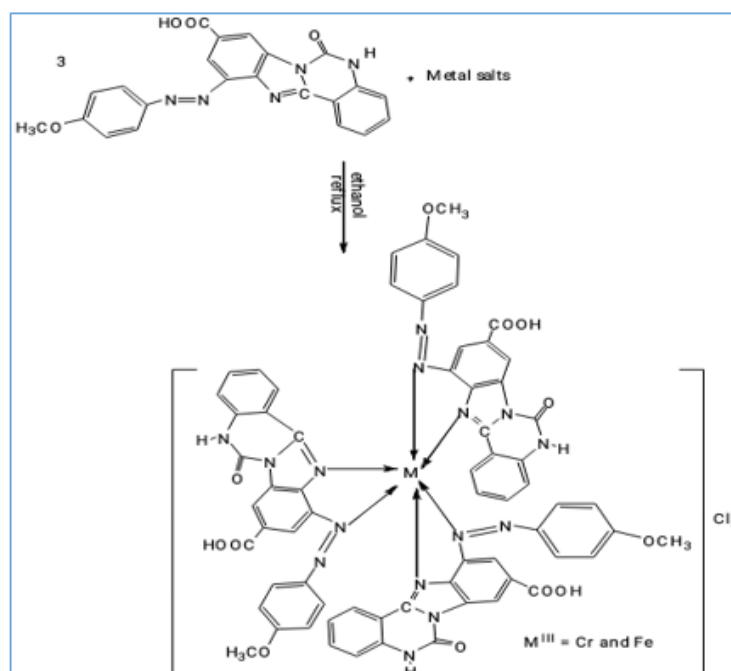


Figure 3. The expected geometry of the metal (III) complexes

## 2.5 Study of biological properties

Three bacterial species have been used during this study: Escherichia Coli (E.Coli) as Gram Negative Bacteria, Staphylococcus Aureus (Staph. Aurous) as Gram Positive Bacteria, and Morganelia Marganii in Nutrient Agar medium. DMSO was used as solvent and also as control, focus from compounds has been  $10^{-3}\text{M}$ , using disc sensitivity evaluation. That path includes exposition from zone for inhibition towards spread from micro-organism at agar dish. Dishes have been brood into 24 h at  $37^\circ\text{C}$ .

### 3. Results and discussions

Azo ligand (L) was characterized using FTIR and UV-Vis spectra. The solid compounds were generated through reaction from ethyl alcohol solution from ligand for aqueous solution from metal ions at (1:2) and (1:3) ratio. Metal compounds from complexes have been into good correspondence for calculated values (Table 1) considering physical characteristics. Molar conductance for the compounds at a concentration  $10^{-3}$  M on ethyl alcohol consist electrolytic style [9], the data being presented in Table 2.

**Table 1.** Physical characteristics of the ligand as well its complexes

Compounds	Color	M.P (°C)	Yield (%)	Analysis Calc./ (Found)			
				M%	C%	H%	N%
Ligand(L)	Brown	185-187	82	-	63.92 (62.88)	3.63 (3.11)	16.94 (15.76)
[Cr(L) <sub>3</sub> ]Cl <sub>3</sub>	Deep brown	210-212	80	3.72 (2.85)	56.67 (55.93)	3.22 (3.01)	15.02 (14.88)
[Fe(L) <sub>3</sub> ]Cl <sub>3</sub>	Reddish brown	225-227	88	3.99 (2.72)	56.51 (55.90)	3.21 (2.85)	14.98 (13.94)
[Co(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	Deep brown	253-255	82	5.94 (4.84)	53.22 (52.77)	3.02 (2.98)	14.11 (13.76)
[Ni(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	Orange	216-218	87	5.85 (4.91)	53.27 (52.66)	3.02 (2.97)	14.12 (13.78)
[Zn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	Yellow	193-195	83	6.51 (5.86)	52.90 (51.93)	3.00 (2.78)	14.02 (13.65)
[Cd(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	Yellow	220-222	81	10.71 (9.82)	50.52 (49.94)	2.87 (2.23)	13.39 (12.57)

### Electronic spectra

The UV-Vis spectrum of azo ligand (L) and their compounds are presented in Table 2. UV-Vis spectroscopy into ligand (L) presents three peaks. The first and second appear for 247 and 287 nm due to ( $\pi-\pi^*$ ) electronic transitions, while the third peak is present at 370 nm as consequence to ( $n-\pi^*$ ) electronic transitions [10]. The spectrum of Cr<sup>III</sup> displays peaks for 251, 328 and 383 nm whom was qualified into ligand field and charge transfer. Other two peaks can be observed at 460 and 584 nm due to the continuity electronic transitions type  $^4A_{2g} \rightarrow ^4T_{1g(P)}$   $^4A_{2g} \rightarrow ^4T_{1g(F)}$  continuity. The magnetic moment of the complex was found at 3.86 B.M, which was much closer to the octahedral perimeter [11].

**Table 2.** UV-Vis, conductance and magnetic data of the ligands and their compounds

Compounds	( $\lambda_{max}$ ) nm	ABS	$\epsilon_{max}$ (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\Lambda_m$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) In ethyl alcohol	$\mu_{eff}$ (B.M)
Ligand(L)	247 287 370	2.056 0.878 1.363	2056 878 1363	-	-
[Cr(L) <sub>3</sub> ]Cl <sub>3</sub>	251 328 383	2.037 1.197 0.885	2037 1197 885	125.32	3.86



	460	0.003	3		
	584	0.001	1		
[Fe(L) <sub>3</sub> ]Cl <sub>3</sub>	271	2.366	2366	130.65	5.90
	329	1.664	1664		
	391	0.872	872		
	438	0.004	4		
[Co(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	283	1.307	1307	74.42	4.62
	333	1.271	1271		
	380	1.042	1042		
	440	0.002	2		
	561	0.001	1		
[Ni(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	276	1.285	1285	77.81	2.91
	352	1.071	1071		
	397	0.788	788		
	437	0.002	2		
[Zn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	274	0.899	899	80.44	Dia
	342	1.187	1187		
	381	1.017	1017		
[Cd(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	250	2.491	2491	78.93	Dia
	319	1.243	1243		
	388	1.136	1136		

Fe<sup>III</sup> spectrum displays peaks at 271, 329 and 391 nm due to ligand field and charge transfer. Other peak shows at 438 nm due to the electronic transition type  ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$ . The magnetic moment of the complex was found at 5.90 B.M which was much close to the octahedral perimeter [12]. The spectrum for Co<sup>II</sup> complex displays peaks in 283, 333 and 380 nm 236 nm whom were qualified into ligand field and charge transfer. Else two peaks at 440 and 561 nm whom were referred into electronic transition type  ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$  and  ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ , also the value for magnetic moment on 4.62 B.M may be considered as an extra confirmation to octahedral geometry [13]. Electronic spectrum for Ni<sup>II</sup> complex showed peaks in 276 and 352 nm consequent into ligand field. Peak in 397 whom was appointed into charge transfer and electronic transition style  ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$  and peak in 437 nm whom was into  ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$  continuity. The magnetic moment for complex has been discovered in 2.91 B.M whom was much close to the octahedral perimeter [14]. Electronic spectral from Zn<sup>II</sup> and Cd<sup>II</sup> complexes do offer charge transfer, and magnetic susceptibility seemed the complex has diamagnetic moments, result to (d-d) transition are not likely hence electronic spectrum did not confer any productive datum, on fact outcome is a good agreement for former work from geometry of octahedral [15].

#### Fourier transformed infrared spectra

Pertinent vibration bands for free ligands as well their compounds have been registered into KBr at area 4000-400 cm<sup>-1</sup>. Assignments into distinctive bands for FT IR spectra to free azo ligand (L) and compounds are abbreviated in Table 3.

**Table 3.** Fundamental frequencies to the ligand and its compounds ( $\text{cm}^{-1}$ )

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{N})$
Ligand(L)	-	3364 br. <sup>*)</sup>	1682 sh. <sup>*)</sup>	1622 sho. <sup>*)</sup>	1483 sh. <sup>*)</sup>	-
$[\text{Cr}(\text{L})_3]\text{Cl}_3$	-	3364 br.	1680 s. <sup>*)</sup>	1596 s	1466 sh.	473 w. <sup>*)</sup>
$[\text{Fe}(\text{L})_3]\text{Cl}_3$	-	3362 br.	1682 sh.	1594 s.	1470 s.	487 w.
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	437/3	3364 br.	1682 s.	1585 s.	1458 s.	466 w.
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	4385	3364 br.	1681 sh.	1590 s.	1460 sh.	430 w.
$[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	4365	3365 br.	1680 s.	1581 s.	1455 sh.	458 w.
$[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	4380	3362 br.	1682 sh.	1587 s.	1460 s.	445 w.

<sup>\*)</sup> br = broad, sh = sharp, s = strong, w = weak, sho = shoulder

**Table 4.** Diameters (mm) to suppression of compounds by bacteria

Compounds	<i>Morganella</i> <i>Morganii</i>	<i>Staphylococcus</i> <i>Aureus</i>	<i>Escherichia</i> <i>Coli</i>
Ligand(L)	22	30	25
$[\text{Cr}(\text{L})_3]\text{Cl}_3$	27	32	33
$[\text{Fe}(\text{L})_3]\text{Cl}_3$	18	21	32
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	16	23	30
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	20	30	25
$[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	21	28	22
$[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	28	32	30

The IR spectrum for the azo ligand offer bands in 3364 and 1682  $\text{cm}^{-1}$ , whom were qualified into stretching vibration for  $\nu(\text{OH})$  carboxyl and  $\nu(\text{C}=\text{O})$ . Since no significant change in these bands was observed, we can conclude that is no coordination through these group [16,17]. The band on 1622  $\text{cm}^{-1}$  has been attributed to  $\nu(\text{C}=\text{N})$  stretching frequency [18], ion complexation a shifting for alteration into form was noticed for this band, whereas growing into density was observed, specifically being an outcome from coordination for metal ion. IR spectra band for ligand at 1483  $\text{cm}^{-1}$  is consequently due to stretching vibration for  $\nu(\text{N}=\text{N})$  [19]. For complexation process a shifting of this band was noticed, whereas growing into density was observed, which can be an outcome of metal ion coordination. The new bands that were registered at 487-430  $\text{cm}^{-1}$  are temporarily attributed to  $\nu(\text{M}-\text{N})$  (Metal-Ligand) stretching bands [20-22]. The presence of coordination water [23] in the spectra of  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  complexes have been observed at (453-433) $\text{cm}^{-1}$ .

Finally, the antibacterial activities of the ligand and their compounds have as well been examined using the bacteria species chosen for this study. In Table 4 are shown the suppression capability of various bacteria pattern for the generated compounds during this study.

#### 4. Conclusions

Complexes can be a synthetic challenge to improve the properties of metal complexes and have been shown to exhibit a broad range of possible geometry for synthesized complexes. The studies revealed octahedral and six coordinated metal complexes formation. Azo dye prepared was identified



by elemental analysis and spectroscopic methods (FT-IR and UV-Vis). Attended compounds have been identified by means of atomic absorption flame, FT-IR also UV-Vis spectra, magnetic susceptibility and conductivity measurements. For the study regarding antibacterial efficiency of ligand and its compounds three species of bacteria were as well examined.

## References

1. ANITHA, C., SHEELA, C.D., YHARMARAJ, P., SHANMUGAKALA, R., Studies on synthesis and spectral characterization of some transition metal complexes of azo-azomethine derivative of diaminomaleonitrile, *Int. J. Inorg. Chem.*, 13, 2013, p. 1.
2. SYHOOD, A.A., MOHAMED, H.J., Thermal analysis of different pyrazolone azo derivative and their complexes with Pd(II), Ni(II) and Ag(I), *Int. J. Sci. Res.*, 4, no. 6, 2015, p. 504.
3. AHLSTROM, L., ESKILSSON, C.S., BJORKLUNED, E., Determination of banned azo dyes in consumer goods, *Trends Anal. Chem.*, 24, 2005, p. 49.
4. TUPYS, A., KALEMBKIEWICS, J., OSTAPIUK, Y., MATIICHUK, V., TYMOSHUK, O., WOZNICKA, E., BYCZYNSKI, L., Synthesis, structural characterization and thermal studies of a novel reagent 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol, *J. Them. Anal. Calorim.*, 127, 2017, p. 2233.
5. ZAMANI, H.A., NEKOEI, M., MOHAMMADHOSSEINI, M., GANJALI, M.R., Construction of Tm<sup>3+</sup>. PVC membrane sensor based on 1-(2-thiazolylazo)-2-naphthol as sensing materials, *Mater Sci. Eng C.*, 30, 2010, p. 480.
6. SAAD, F.A., KHEDR, A.M., Azo-azomethine ligands with N<sub>2</sub>O<sub>2</sub> donor atom sets and their binuclear UO<sub>2</sub>(II) complexes: synthesis, characterization and biological activity, *Bulgarian Chem. Commun.*, 47, no. 2, 2015, p. 654.
7. ASIRI, A.M., KHAN, S.A., Palladium (II) complexes of NS donor ligands derived from steroidal thiosemicarbazones as antibacterial agents, *Molecules*, 15, no. 7, 2010, p. 4784.
8. MASOUD, M.S., HAGAGG, S.S., ALI, A.E., NASR, N.M., Synthesis and spectroscopic characterization of gallic acid and some of its azo complexes, *J. Mol. Struct.*, 1014, 2012, p. 17.
9. GEARY, W.J., Characterization of coordination compounds, *Coord. Chem. Rev.*, 7, 1971, p. 81.
10. MOHAMED, G.G., OMAR, M.M., A.N. HINDY, A.N., Metal complexes of Schiff bases: preparation, characterization and biological activity, *Turk. J. Chem.*, 30, 2006, p. 61.
11. MALDHURE, A.K., AZWAR, A.S., Synthesis, characterization and antimicrobial studies of some transition metal complexes of N-(5-chloro-2-hydroxyacetophenone)-N-(2-hydroxyacetophenone)-ethylenediamine, *Am. J. Pharm. Techn. Res.*, 3, no. 6, 2013, p. 462.
12. GAFER, H.E., ZAKY, R.R., Synthesis and characterization of 3-hydroxy-4-(2-hydroxyphenyl) diazenyl-2-naphthoic acid and its Fe(III) and Cr(III) complexes and their application on nylon 6 and wool, *Egypt. J. Chem.*, 53, no. 5, 2010, p. 719.
13. AL-JIBOURI, M.N., Synthesis and characterization of transition metal complexes with azo ligand derived from 4-hydroxy-6-methyl-2-pyranone, *Eur. Chem. Bull.*, 3, no. 5, 2014, p. 447.
14. RAVANASIDDAPPA, M., SURESHG, T., SYED, K., RADHAVENDRAY, S.C., BASAVARAJA, C., ANGADI, S.D., Transition metal complexes of 1,4-(2-hydroxyphenyl)di-iminoazine: synthesis, characterization and antimicrobial studies, *E-J. Chem.*, 5, no. 2, 2008, p. 395.
15. AL-NOOR, T.H., JARAD, A.J., ABO, S.B., Synthesis, spectral and antimicrobial activity of mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 4-aminoantipyrine and tributylphosphine, *Inter. J. Curr. Res.*, 7, no. 05, 2015, p. 15605.
16. KUMARAND, H., CHANDHARY, R., Biological studies novel azo based heterocyclic Schiff base and its transition metal complexes, *Der. Chem. Sin.*, 1, 2010, p. 55.
17. YAHYAZZDEH, A., AZIMI, V., Synthesis of some unsymmetrical new Schiff bases from azo dyes, *Eur. Chem. Bull.*, 2, 2013, p. 453.
18. JARAD, A.J., JAAFAR, Z.N., ABOUD, N.A., Synthesis and characterization of benzoic acid-2-salicylidene complexes with selected metal ions, *Int. J. Sci. Res.*, 2, no. 6, 2013, p. 64.



- 19.JARAD, A.J., TAWFIQ, M.T., SHAKIR, S., Synthesis and characterization of some new metal complexes 2-(4-nitrophenyl azo)-2,4-dimethylphenol, *Int. J. Engin. Sci. Res. Techn.*, 3, no. 8, 2014, p. 401.
- 20.KHALIL, M.M.H., ISMAIL, E.H., MOHAMED, G.G., ZAYED, E.M., BADR, A., Synthesis and characterization of novel Schiff base metal complexes and their application in determination of iron in different types of natural water, *Open. J. Inorg. Chem.*, 2, 2012, p. 31.
- 21.JARAD, A.J., Synthesis and characterization of 6-(4-nitrobenzene azo)-3-amino benzoic acid complexes with Y(III) and La(III) ions, *Eur. Chem. Bull.*, 2, no. 6, 2013, p. 383.
- 22.ABBAS, R.A., JARAD, A.J., NAFLIU, I.M., NECHIFOR, A.C., Synthesis, characterization and antibacterial activity from mixed ligand complexes of 8-hydroxyquinoline and tributylphosphine for some metal ions, *Rev. Chim.*, **70**(1), 2019, 36.
- 23.MOUSTATA, I.M.I., ABDELLATTIF, M.H., Synthesis, spectroscopic studies and biological evaluation of Co(II), Ni(II), Cu(II) and Zr(IV) complexes of azo dyes and thiamine hydrochloride as antimicrobial agents, *Mod. Chem. Appl.*, 5, no. 1, 2017, p. 1.

Manuscript received: 18.12.2019