Research Journal of Chemistry and Environment Vol. **27 (5)** May **(2023)**
Res. J. Chem. Environ.

Synthesis and Characterization of New Azo dye and applications in colorimetric analysis of trace metal ions in Aqueous Medium

Alsouz Mohammed A.K.[1] and Al-jibouri Mahmoud Najim[2*]
1. Department of Medical Lab. Techniques, College of Medical Technology, Al- Farahidi University, Baghdad, IRAQ
2. Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, IRAQ
*mahmoud_inor71@uomustansiriyah.edu.iq

Abstract

The chelation behavior of azo dye HL derived from coupling 4-nitrophenyl diazonium salt with 7-hydroxycoumarin with Cd (II), Hg(II) and Fe (III) metal ions has been studied. Reaction of the azo dye with Cd (II) and Hg(II) ions at different pH gave new two complexes. At pH=8, complex of the formula $[Cd(L)_2]Cl_2$ *was formed while at pH=4.5, the complex* $[Cd(L)\ Cl_2].\ 2H_2O$ *was obtained. Another two new complexes of the formula* $[Fe(L)_2Cl_2]Cl.2H_2O$ *have been obtained from the reaction of aqueous solution of the azo dye with* $FeCl_3.6H_2O$*. All the above preparations were performed after fixing the optimum pH and molar concentration. Wide range of molar concentrations was investigated and the concentration which obeyed the Lambert-Beer's Law, was chosen.*

The effects of time on the stability of these complexes were checked. The stoichiometry of the above prepared complexes was determined using mole ratio and Job methods. A great bathochromic shift was observed in the UV–Vis absorption spectra of (10^{-6}-10^{-8} mole/lit.) of an aqueous solution of the solid complexes. The vibration spectra of these complexes gave different changes compared to that of the free ligand. The ^1H NMR spectra for one of the complexes were also performed.

Keywords: Colorimetric determination of iron(III) and cadmium(II), reagent of coumarin azo, spectroscopic determination of iron(III) and mercury(II) ions.

Introduction

Azo compounds are characterized by the presence of azo group (-N=N-), which links two sp^2 hybridized carbon atoms, especially ones possessing chromene and heterocyclic rings[1-3]. Azo compounds are highly colored that enjoy widespread use as dyes and pigments in a variety of applications that include textile dyeing as well as non-linear and photo electronics, especially in optical information storage[4]. These compounds are very important molecules and have attracted much attention in both academic and applied research[5]. For example, azo derivatives and their metal complexes are very important pigments for synthetic leather and vinyl polymers. Synthetic azo compounds were widely used in different application fields such as medicines, cosmetics, food, paints, plastics, shipbuilding, automobile industry, cable manufacture etc.[6,7]

However, the traditional application field of the synthetic azo dyes still remains the textile industry and the finishing of fibrous material in order to impart simultaneously with coloration[8-10]. Azo derivatives of transition metal complexes have attracted much attention in recent years due to their potential applications in catalytic processes which may have an industrial dimension. The synthesis of novel metal chelating systems , based upon azo scaffolds, has also been extensively investigated[11]. For example, systems based upon dye metal complexes which possess ortho-metallated aromatics such as compound a and b are relatively common[12,13].

In the present study, we have presented the preparation soluble azo dye in water via coupling the active 7-hydroxycoumarin with diazonium salt of 4-nitro aniline in alkaline medium and their stochiometric structures on the basis of NMR, MS, FT-IR and elemental analyses. Beside that, the colorimetric analysis of trace metal ions of Fe^{3+} , Cd^{2+} and Hg^{2+} has been performed after optimization of the time of reaction and P_H of complexation.

Material and Methods

Chemicals: Table 1 shows the chemicals used along with their percentage purity.

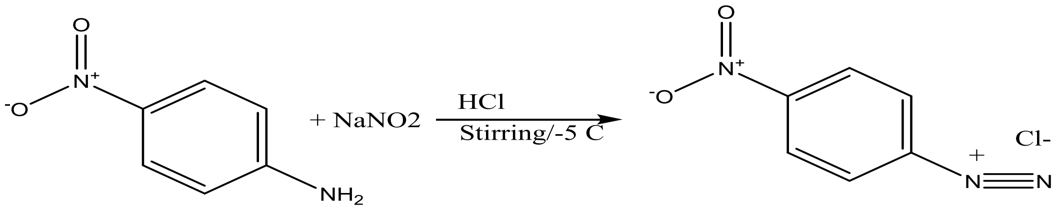
Instrumentation: The UV–Vis spectra were recorded using UV-1800 Shimadzu UV-Vis Spectrophotometer. The NMR spectra were performed by using Bruker Ultra Shield 500 MH_Z NMR in Kashan University, Iran.The IR Spectra were measured using Bruker FTIR Fourier Transform Infrared Spectrophotometer in the range (4000-400) cm^{-1}. The percentage of metal in complexes was measured by using GBC 933 Flame Atomic Absorption Spectrophotometer. The elemental microanalyses of the prepared azo dye and their metal complexes were performed using Euro EA 3000 analyzer. The electrolytic properties of complex ions were measured on HANA-conductivity meter model HI 9811-5 with cell constant K_{cell}= 1 cm^{-1}. The pH of the solution was measured by using "JENWAY 3020" pH Meter.

Preparation of the Azo dye: The azo dye; (E)-7-hydroxy-6-(4-nitrostyryl)-2H-chromen-2-one was prepared according to the modified procedure established in literature[12].

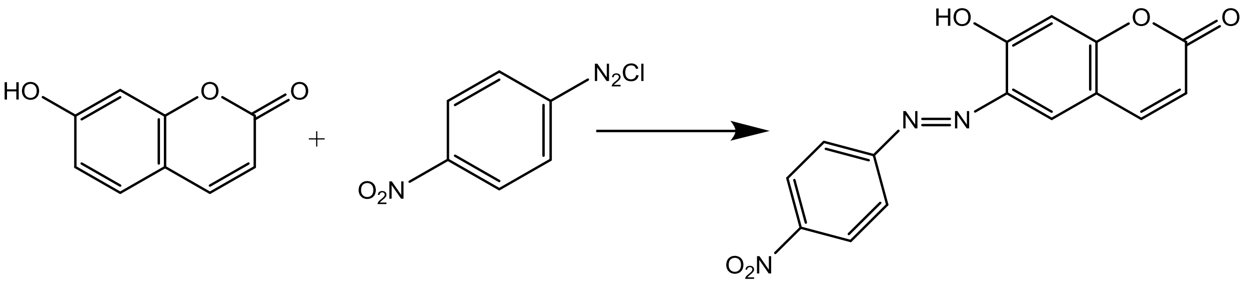
https://doi.org/10.25303/2705rjce022026

Table 1
Chemical Substances Used in the present work

S.N.	Substance	Formula	Company	%Purity
1	7-hydroxycoumarin	$C_9H_6O_3$	Fluka AG	98
2	P-Nitro Aniline	$C_6H_6N_2O_2$	Sigma Aldrich	99
3	Potassium hydroxide	KOH	Merck	99
4	Iron(III) chloride hexahydrate	$FeCl_3.6H_2O$	BDH	95
5	Cadmium chloride	$CdCl_2$	Fluka AG	94
6	Sodium Nitrite	$NaNO_2$	Sigma Aldrich	99
7	Sodium Hydroxide	NaOH	Fluka	96
8	Mercury chloride	$HgCl_2$	Merck	98
10	Acetic Acid	CH_3COOH	BDH	99.9
11	Sulphuric Acid	H_2SO_4	BDH	18N
12	Hydrochloric Acid	HCl	BDH	12N
13	Methanol	CH_3OH	BDH	99
14	Ethanol	C_2H_5OH	BDH	99



Scheme 1: Preparation of diazonum salt



Scheme 2: Preparation of Azo dye, HL

A solution of 4-nitobenzenediazonium chloride was prepared by the dissolution of 4-nitroaniline (1.38 g ,0.01 mole) in hot distilled water (5ml) followed by addition of conc. HCl (3ml). On cooling this solution to -3 ˚C, a solid white precipitate was formed which was dissolved by addition of 5 ml distilled water. To this solution, a cooled aqueous solution of sodium nitrite 0.370 g (0.005mole) in 2 mL of distilled water was added slowly with constant stirring maintaining the temperature of the reaction mixture around 0˚C. The resulting diazonium salt solution was added drop wise to a solution of 7-hydroxycoumarin (1.62 g, 0.01 mole) in 0.6 N sodium hydroxide (40 ml) around 0˚C while stirring.

The stirring was further continued for 15 min. The solution was neutralized to pH 6.5 by dropwise addition of 1.0N HCl. The resulting brown colored precipitate was filtered, washed thoroughly with chloroform, water and finally dried. M.P. 230-232 °C, %yield =90, 2.6963g. % Found C: 65.11, H: 2.99, N: 4.01, % Calculated C: 66.03, H: 3.60, N: 4.55, Chemical Formula: $C_{17}H_{11}NO_3$.

Preparation of Buffer Solutions: The buffer solutions covering the pH values from 3.5 to 8.5 of ammonium acetate (0.01M) were prepared by dissolving 0.770g of CH_3COONH_4 in one liter of doubly distilled deionized water. The required pH was obtained by the addition of either ammonium hydroxide solution or acetic acid.

Preparation of Metal Salts Solutions: The metal salts solutions were prepared by dissolving the appropriate weight of each of the following salts $CdCl_2$, $HgCl_2$ and hydrated $FeCl_3$ in the buffer solutions. These solutions were prepared in concentrations ranging between (10^{-2}-10^{-4}) M.

Preparation of the complexes: A solution of 0.2075g (0.001mole) of $CdCl_2$ in 150 ml buffer solution (pH=6.5) was added to 0.311g (0.001mole) of the azo dye dissolved in 20 ml ethanol. The metal solution was added gradually with stirring to the ligand solution. The mixture was stirred for one hour until deep colored precipitate appeared. The solution mixture was filtered off and the precipitate was washed several times with (1:1) water: ethanol mixture and then left to dry. The complexes of Fe(III) and Hg(II) were prepared in the same manner with formation of olive colored complex of FeL and red precipitate of [HgLCl].

Results and Discussion

The azo dyes are considered to be one of the most common compounds used as ligands. The azo dye characterization by elemental analyses and NMR confirmed the suggested chemical structure. The ^{1}H NMR spectrum of the azo dye shows a singlet signal at δ (12.50) ppm corresponding to the –OH at C-7 of coumarine ring. This signal appeared in the complex spectrum as a singlet. The mass spectrum of the azo dye exhibits molecular ion at $M^+=312$ assigning the molecular weight of azo dye with chemical formula $C_{17}H_{11}NO_3$.

Study of the UV-Visible spectrum: The UV-Vis spectrum of the azo dye) in ethanol within the range 250-1100 nm displayed mainly two peaks as in fig. 1. The first peak at (274 nm) was assigned to the moderate energy $\pi\rightarrow\pi^*$ transition of the aromatic rings. The broad (λ_{max}) peak at 498 nm was related to the $\pi\rightarrow\pi^*$ transition of intermolecular charge-transfer taking place through the –N=N- and –C=O groups[13,14]. Aqueous-EtOH solutions of Cd(II), Hg(II) and Fe(III) ions with azo dye were studied spectrophotometrically over a wide molar concentrations and pH ranges 4 to 8. The interaction between the metal ion and the ligand manifests itself by the change in color from brown to reddish-violet.

Reaction of metal ions of Fe^{3+}, Hg^{2+} and Cd^{2+} with aqueous solution of azo dye has shown remarkable changes in the intensity and energies of the bands of the free azo ligand. As soon as Cd(II) ,Fe(III) and Hg(II) solutions were added, the brown solution rapidly changed to reddish-violet. Figure 3 showed a comparison between the spectra of the free azo dye and Fe (III)-L mixed solutions in DMSO at pH 6.5[13,14].

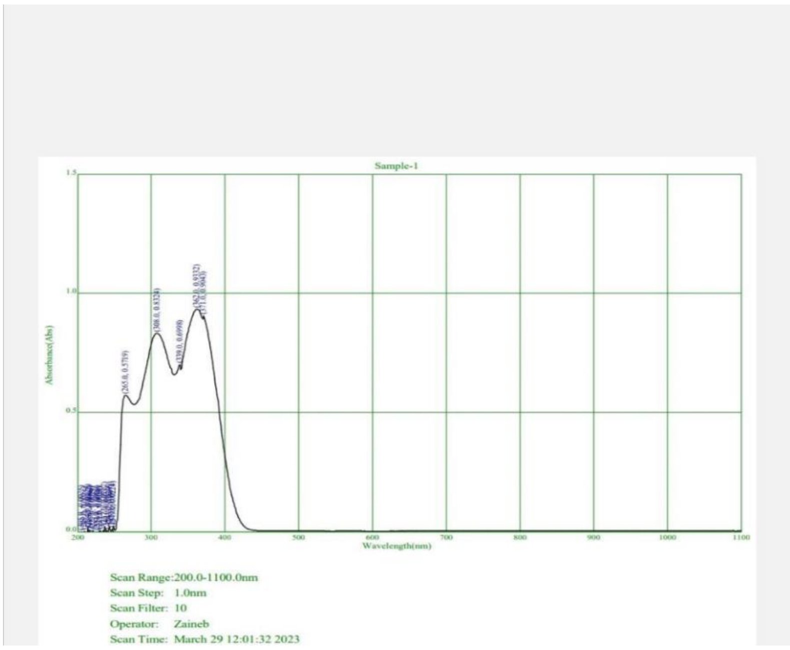


Fig. 1: Electronic spectrum of azo dye in ethanol (10^{-3} M) concentration

Table 2
Absorbance at different pH and concentration of Fe(III)-L

	Absorbance (λ_{max}) at pH									
Molar Conc. 10^{-3}	**3.5**	**4**	**4.5**	**5**	**5.5**	**6**	**6.5**	**7**	**7.5**	**8**
0.25	553 0.175	553 0.422	547 0.569	553 0.227	545 0.17	546 0.13	545 0.133	545 0.140	547 0.260	553 0.232
0.50	553 0.284	549 0.495	545 0.563	552 0.286	549 0.289	545 0.271	545 0.244	547 0.276	548 0.415	549 0.443
0.75	553 0.430	551 0.583	547 0.634	557 0.384	551 0.385	551 0.361	551 0.357	552 0.394	551 0.583	557 0.695
1.00	553 0.491	553 0.623	547 0.682	556 0.561	551 0.528	551 0.513	552 0.529	551 0.512	553 0.616	557 0.940
1.25	553 0.605	552 0.757	546 0.795	557 0.644	552 0.62	552 0.576	550 0.571	552 0.590	554 0.882	557 1.150

https://doi.org/10.25303/2705rjce022026

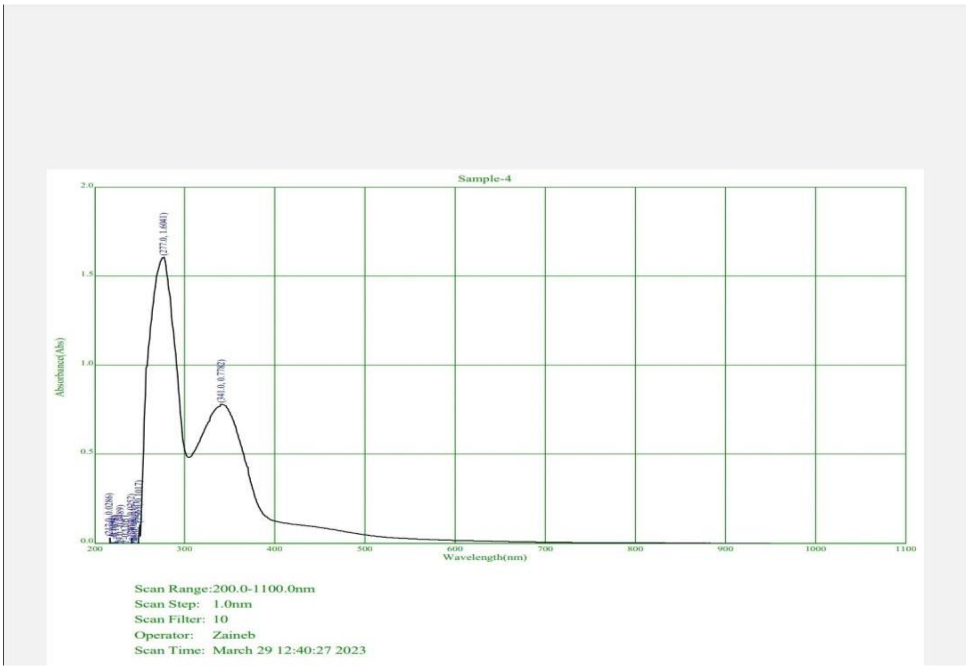


Fig. 2: Electronic spectrum of (a) free azo and (b) Fe(III)-L in EtOH dashed.

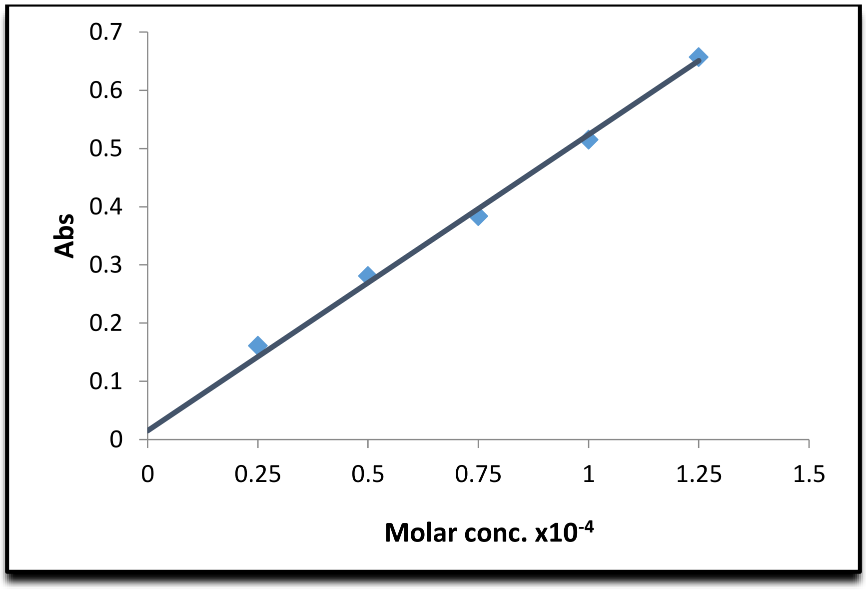
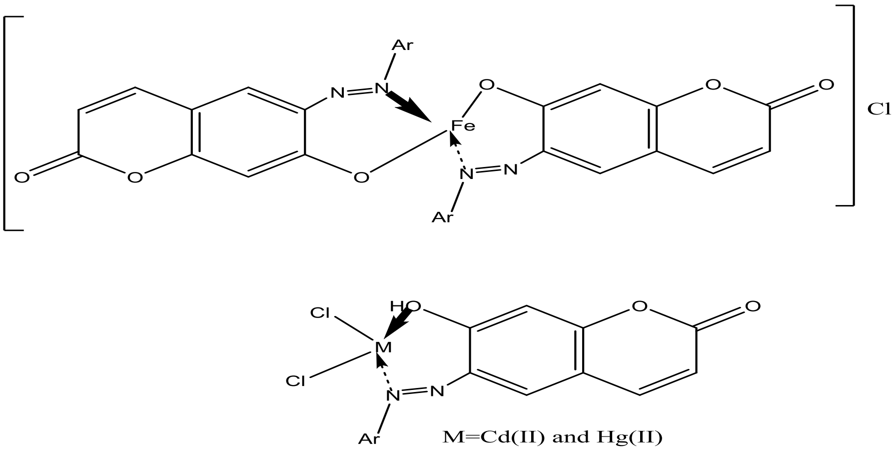


Fig. 3: Linear relationship between molar concentration and absorbance for Fe(III)-L solution at pH = 6.5.



Scheme 3: Octahedral and tetrahedral structures of complex ions

Molar Conductance Measurements: The molar conductance values for Cd(II) pH= 6, Hg(II) pH= 6.5 an Fe (III) pH= 7.5 were measured at 25°C. The data in Table (2) reveals that all complex ions are electrolytes in 2:1 and 1:1 ratio due to the presence of counter ions of chlorides in the structure of metal chelates as in table 2. These results suggested the following chemical formula for the prepared complexes: $[Cd^{II}(L)_2]Cl_2.H_2O$, $[Hg^{II}(L)_2]Cl_2$ and $[Fe^{III}(L)_2Cl_2]Cl.2H_2O$[17,18].

Conclusion

According to the results, the geometry of Fe^{3+}, Cd^{2+} and Hg^{2+} is octahedral and tetrahedral respectively as in scheme 3.

Acknowledgement

The authors would like to express their gratitude to the members of laboratory service at Chemistry Department, College of Science, Mustansiriyah University for carrying out FT-IR, UV-Visible spectra and molar conductance measurements.

References

1. Al-jibouri M.N., Synthesis and characterization of transition metal complexes with Azop ligand derived from 4-hydroxy-6-methyl-2-pyranone, *Europ. Chem. Bull.*, **3(5)**, 447-451 **(2014)**

2. Andriani Yuli, Iskandar, Herawati Titin, Zidni Irfan and Detrik Sudarsa, Effect of Chromium Addition in Lemna sp. on Feed Conversion and Chromium Retention in Gourami (Osphronemus goramy) Flesh, *Res. J. Chem. Environ.*, **24(1)**, 34-37 **(2020)**

3. Bailar J.C., Emeleus H.J., Nyholm R. and Trotman-Dickenson A.F., Comprehensive Inorganic Chemistry, Pergamon Press, **3**, 1156 **(1975)**

4. Carceller E., Salas J., Merlos M., Giiral M., Ferrando R., Escamilla I., Ramis J., Garciia Rafanell J. and Forn J., Novel azo derivatives as prodrugs of 5-aminosalicylic acid and amino derivatives with potent platelet activating factor antagonist activity, *J Med Chem.*, **44(18)**, 3001-3013 **(2001)**

5. Chate Asha V., Redlawar Ankita A., Bondle Giribala M., Sarkate Aniket P., Tiwari Shailee V. and Lokwani Deepak K., A new efficient domino approach for the synthesis of coumarinpyrazolines as antimicrobial agent stargeting bacterial D-alanine D-alanine ligase, *New J. Chem.*, **43**, 9002—9011 **(2019)**

6. Donia Bensalah, Mnasri Aziza, Chakchouk-Mtibaa A., Mansour Lamjed, Mellouli L. and Hamdi N., Synthesis and antioxidant properties of some new thiazolyl coumarin derivatives, *Green Chemistry Letters and Reviews*, **13(2)**, 155-163 **(2020)**

7. Emara A.A., Novel asymmetric tetradentate Schiff base ligands derived from 6-metwia-formyl4-hydroxy-2-(1H)-quinolone and their metal complexes, *Synth React Inorg Met Org Chem.*, **29(1)**, 87 **(1999)**

8. Erdem E., Sari E.Y., Kilinçarslan R. and Kabay N., Synthesis and characterization of azo-linked Schiff bases and their nickel (II), copper (II) and zinc (II) complexes, *Transit Metal Chem.*, **34(2)**, 167 **(2009)**

9. Mahmoud N. et al, Synthesis ans Structural Investigation of some Transition Metal Complexes Derived from Assembled NO Donor Lewis Base of 6,7-Dimethyl-Quinoxaline-2,3-dion, IOP Conference series: Materials Science and Engineering, 571 **(2021)**

10. Masoud M.S., Amira M.F., Ramadan A.M. and El-Ashry G.M., Synthesis and characterization of some pyrimidine, purine, amino acid and mixed ligand complexes, *Spectrochim Acta A.*, **69(1)**, 230 **(2008)**

11. Sengan M. et al, N-myristoyltaurine capped copper nanoparticles for selective colorimetric detection of Hg^{2+} in wastewater and as effective chemo catalyst for organic dye degradation, *Michrochem. Journal*, https://doi.org/10.1016/j.microc.2019.04.049 **(2019)**

12. Oberhausen K.J., Richardson J.F., Buchanan R.M., McCusker J.K., Hendrickson D.N. and Latour J.M., Synthesis and characterization of dinuclear copper (II) complexes of the dinucleating ligand 2, 6-bis [(bis ((1-methylimidazol-2-yl) methyl) amino) methyl]-4-methylphenol, *Inorg. Chem.*, **30(6)**, 1357 **(1991)**

13. Ran Liu et al, Colorimetric determination of lead (II) or mercury (II) based on target induced switching of the enzyme-like activity of metallothionein-stabilized copper nanoclusters, *Microchimica Acta*, DOI:10.1007/s00604-019-3360-6 **(2019)**

14. Sönmez M., Bayram M.R. and Çelebi M., Synthesis and characterization of heterocyclic Schiff base and its complexes with Cu (II), Ni (II), Co (II), Zn (II) and Cd (II), *J Coord Chem.*, **62(16)**, 2728 **(2009)**

15. Sahoo J. and Paidesetty S.K., Antimicrobial activity of novel synthesized coumarin based transitional metal complexes, *J Taibah Univ Med Sci.*, **12(2)**, 115-124 **(2016)**

16. Shu Min Lin et al, D-penicillamine-templated copper nanoparticles via ascorbic acid reduction as a mercury ion sensor, *Talanta*, DOI: 10.1016/j.talanta.2016.01.028 **(2016)**

17. Sung Y.M. et al, Colorimetric detection of Cd (II) ions based on di-(1H-pyrrol-2-yl) methanethione functionalized gold nanoparticles, Sensor. Actuator, B Chem. **(2014)**

18. Yunus K.A.Y.A., Mutlu H. and Gazi İ.R.E.Z., Uv-Vis Spectra and Fluorescence Properties of Two Iminooxime Ligands and Their Metal Complexes: Optical Band Gaps, *Gazi University Journal of Science*, **23(1)**, 13 **(2010)**.

(Received 09th December 2021, revised 18th July 2022, accepted 20th August 2022)