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# Synthesis and characterization of azo dyes ligand complexes with some metal ions.

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**Abstract :** Azo ligand 10-(2-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-imidazol-4-ylazo)-6-oxo-5,6-dihydro-benzo[4,5] imidazo[1,2-c]quinazoline-9-carboixylic acid was prepared by combination the diazonium salt of amine with 2-methyl-3-phenyl-3,5-dihydro-imidazol-4-one. The structure of azo dye was identified on the basis of elemental analysis, FT-IR and UV-Vis spectroscopic methods. Transition metal complexes with azo dye have been synthesized and characterized by flame atomic absorption, elemental analysis, FT-IR and UV-Vis spectroscopic process as well as conductivity measurements. Analytical data revealed that all produce complexes exhibited 1:2 and 1:3 metal:ligand ratios due to octahedral geometry.
**Keywords** : spectral studies, azo dyes, biological activity, dyeing.

## Introduction

Azo dyes have been formed the azo functional group (R-N=N-R$^-$) in which R and R$^-$ can be either alkyl or aryl[1]. Azo dyes are known for large applications in several fields and have been attracting the attention of synthetic and theoretical chemists. They have been used many application as textile dyes, pharmaceuticals and indicators[2]. Many azo compounds have been applied as chromogenic reagents for the determination of several metal ions[3]. Azo complexes have also attracted an increasing attention described to their interesting electronic and geometrical teatures in connection with their application for molecular memory storage and optical elements[4]. In recent year, reported synthesis and characterization of most metal complexes containing azo compounds and their biological properties[5,6]. In this present paper the synthesis of azo dye by coupling of 10-amino-6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid with 2-methyl-3-phenyl-3,5-dihydro-imidazol-4-one, the metal chelates of azo dye were prepeared and identified using different spectral studies.

## Experimental

### Instrumentation

Metal contain was recorded by using a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. (C, H, N) analysis were done at Al- al- Bayt University, Jordan, using Euro vector EA



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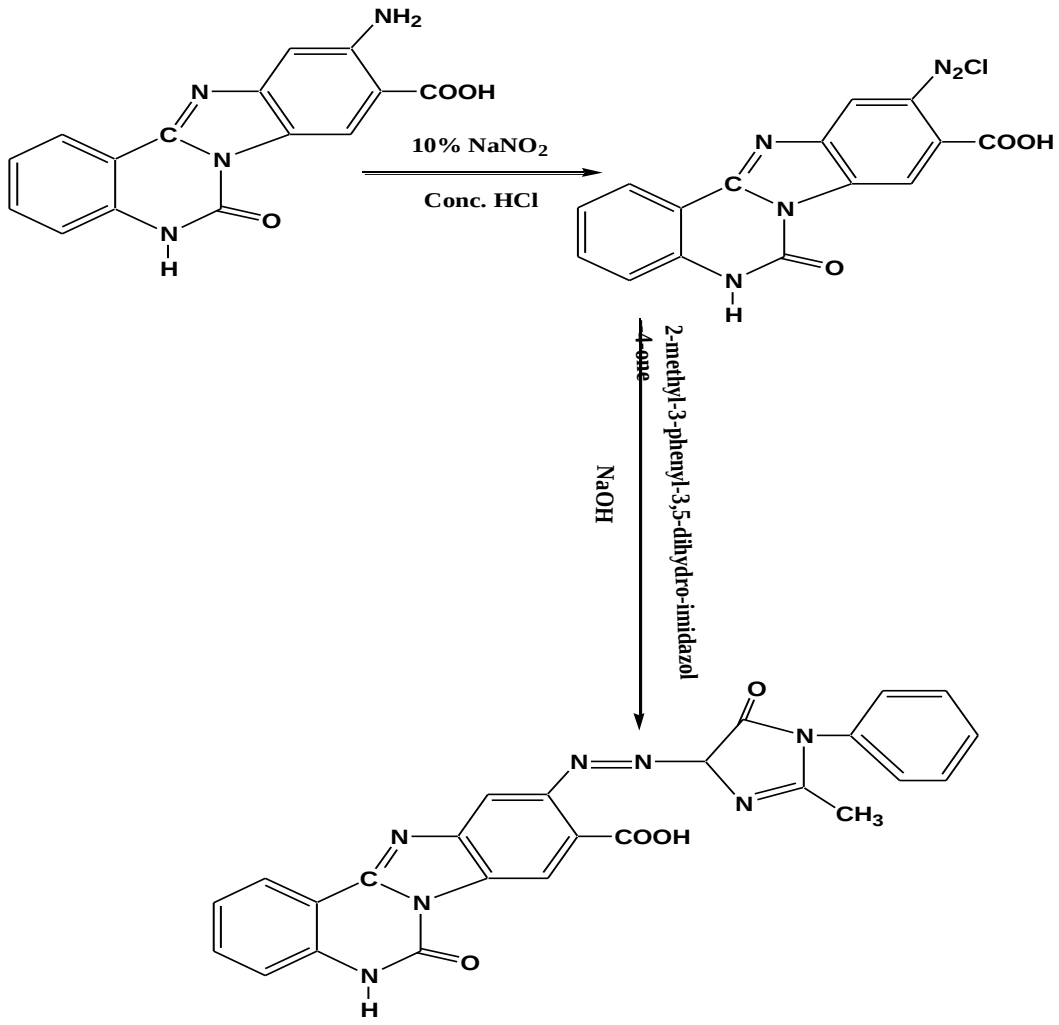
3000A Elemental Analyser. Conductivity of the complexes dissolved in ethanol ($10^{-3}$ M) was recorded at 25°C using Philips PW- Digital Conductimeter. UV- Vis spectra were registered on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer in the 4000- 400 $cm^{-1}$ spectral regions with samples produced as KBr discs. Other than, melting points were performed using Stuart Melting Point Apparatus.

## Materials and reagents

The following chemicals were used as collected from suppliers: $ZnCl_2$, $CdCl_2.H_2O$, $SmCl_3.6H_2O$ and $Eu(NO_3)_3.6H_2O$ (Fluka), 2-methyl-3-phenyl-3,5-dihydro-imidazol-4-one and 10-amino-6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid (B.D.H.).

### Preparation of the ligand

A solution was prepared[7], of 10-amino-6-oxo-5,6-dihydro-benzo[4,5]imidazo[1,2-c]quinazoline-9-carboxylic acid (0.735 g, 1mmole) in (10ml) of EtOH containing (2ml) conc. HCl which was diluted with 10 ml $H_2O$, and diazotized at 5°C with 10% solution of $NaNO_2$. The diazotized solution was added drop wise with stirring to a cooled ethanolic solution of (0.435 g, 1mmole) of 2-methyl-3-phenyl-3,5-dihydro-imidazol-4-one . Then 25 ml of 1M sodium hydroxide solution was added to the dark colored mixture and precipitation of the azo ligand was observed. This precipitate was filtered, washed several times with (1:1) ethanol: water, mixture then left to dry. The reaction is shown in scheme 1.




**Scheme 1. Synthesis of the azo ligand.**

**Preparation of metal complexes**

An aqueous solution of the metal salts containing 0.068g and 0.100g (1mmole) of $ZnCl_2$ and $CdCl_2.H_2O$ was added drop wise to 0.479g,2mmol of ethanlic NaOH solution in molar ratio 1:2 Metal:ligand and aqueous solution of the metal salts containing 0.121g and 0.148g (1mmol) of $SmCl_3.6H_2O$ and $Eu(NO_3)_3.6H_2O$ respectively was added gradually with stirring to ethanolic NaOH solution (0.479g,3mmol) of azo ligand by using stichiometric amount 1:3 Metal to Ligand molar ratio. The mixture was refluxed with constant stirring for an hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from ethanol.

## Results and Discussion

The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions in a (M:L) of (1:2) and (1:3). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-1) includes some physical properties and elemental analysis. The molar conductance of the complexes as ($10^{-3}$ M) in ethanol indicating their non-electrolytic nature[8], the data were recorded in (Table- 2).

**Table 1:- Physical properties of the ligands and its complexes.**

| Compounds | Color | M.P°C | Yield % | Analysis Calc (Found) | | | |
|---|---|---|---|---|---|---|---|
| | | | | M% | C% | H% | N% |
| Ligand(L) | Orange | 180 | 74 | - | 62.63 (61.86) | 3.55 (4.85) | 20.46 (19.89) |
| $[Zn(L)_2]$ | Yellow | 212 | 71 | 6.36 (5.85) | 58.76 (57.86) | 3.13 (3.01) | 19.19 (18.88) |
| $[Cd(L)_2]$ | Brown | 241 | 75 | 10.48 (9.64) | 56.18 (55.98) | 2.99 (2.84) | 18.35 (17.93) |
| $[Sm(L)_3]$ | Reddish brown | 206 | 77 | 9.46 (8.92) | 56.81 (55.77) | 3.03 (2.88) | 18.56 (17.92) |
| $[Eu(L)_3]$ | Brown | 210 | 70 | 9.58 (9.78) | 56.74 (55.63) | 3.02 (2.97) | 18.53 (17.78) |

**Table 2:- UV-Vis and conductance measurements Data.**

| Compounds | ($\lambda_{max}$) nm | ABS | $\epsilon_{max}$ ($L.mol^{-1}.cm^{-1}$) | $\Lambda_m$($S.cm^2.mol^{-1}$) In Absolute ethanol |
|---|---|---|---|---|
| Ligand(L) | 237<br>330<br>392 | 1.370<br>1.107<br>0.313 | 1370<br>1107<br>313 | - |
| $[Zn(L)_2]$ | 241<br>337<br>470 | 1.135<br>1.063<br>0.426 | 1135<br>1063<br>426 | 1135<br>1063<br>426 |
| $[Cd(L)_2]$ | 250<br>341<br>463 | 1.053<br>0.968<br>0.389 | 1053<br>968<br>389 | 1053<br>968<br>389 |
| $[Sm(L)_3]$ | 370<br>723<br>881 | 1.067<br>0.133<br>0.072 | 1067<br>133<br>72 | 5.861 |
| $[Eu(L)_3]$ | 360<br>680<br>831 | 1.117<br>0.246<br>0.062 | 1117<br>246<br>62 | 13.38 |

**Electronic spectra**

The UV-Vis spectra of the produced compounds in ethanolic solution ($10^{-3}$ M) have been formed and the data recorded in Table 2. The UV- Vis spectrum of the ligand shows peaks at 237 and 330 nm due to moderate energy ($\pi$- $\pi^*$) and the peak at 392 nm related to (n- $\pi^*$) transition[9]. The electronic spectra of Zn(II) and Cd(II) complexes do show the charge transfer, because d-d transition are not possible hence electronic spectra did not give any fruitful information, in fact this result is a good agreement with previous work of octahedral geometry[10] . The UV-Vis spectra of the Sm(III) and Eu(III) complexes display peaks at 370 and 360 nm related to ligand felid, other peaks at the range (680-881 nm) due to (f-f) electronic transition[11].

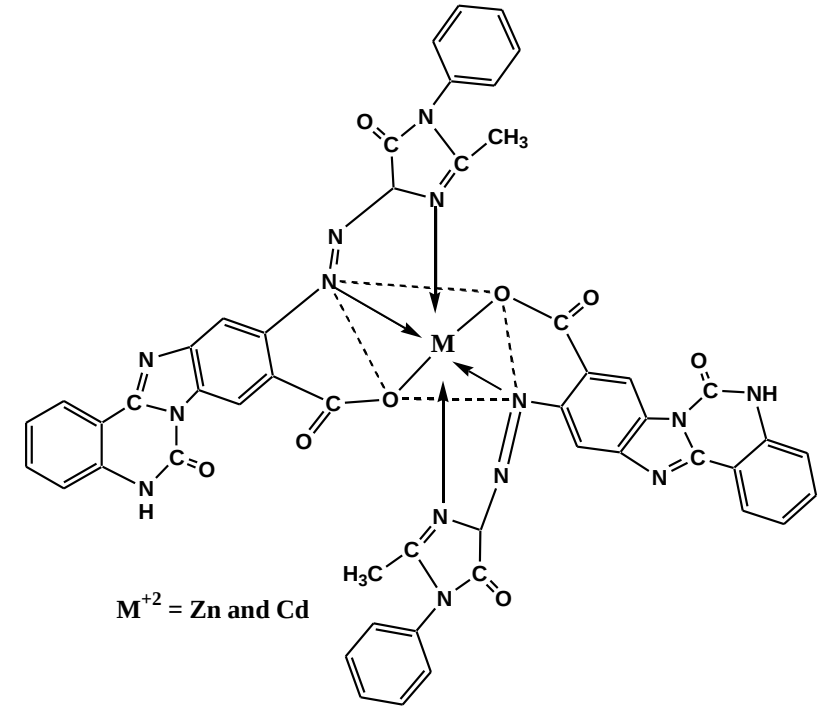
**Table 3:- The main frequencies of the ligands and their complexes ($cm^{-1}$).**

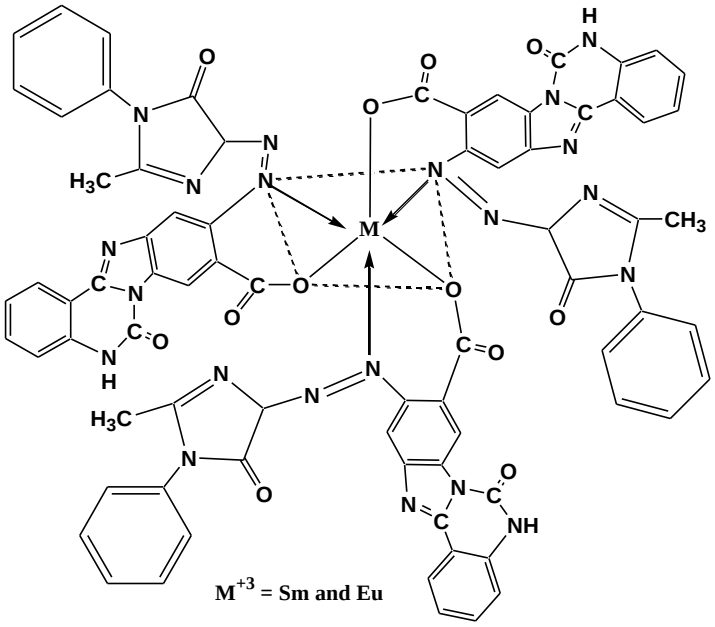
| **Compounds** | **)OHυ(** | **υ(C=O) + υ(C=N)** | **υas,s (COO)** | **υ (N=N)** | **υ (M-N ) + υ (M-O )** |
|---|---|---|---|---|---|
| Ligand(L) | 3432 br. | 1692 sh.<br>1640 s. | 1570 sho.<br>1383 s. | 1471 sh. | - |
| $[Zn(L)_2]$ | - | 1693 sh.<br>1610 sho. | 1550 sh.<br>1352 sho. | 1452 sho. | 570 w.<br>480 w. |
| $[Cd(L)_2]$ | - | 1695 sh.<br>1623 s. | 1557 sh.<br>1360 sh. | 1455 sh. | 581 w.<br>520 w. |
| $[Sm(L)_3]$ | - | 1690 sh.<br>1641 sho. | 1551 sh.<br>1371 sho. | 1447 sh. | 490 w.<br>430 w. |
| $[Eu(L)_3]$ | - | 1692 sho.<br>1642 sh. | 1538 sh.<br>1351 s. | 1440 sh. | 521 w.<br>490 w. |

As = asymmetry, s = symmetry, br = broad, sh = sharp, s = strong, w = weak, sho =shoulder

**Fourier transforms infrared spectra**

The FT-IR spectra of the produced compounds have been measured and the data was recorded in Table 3. The spectrum of azo ligand show broad band at 3432 $cm^{-1}$ related to υ(OH) phenol, the disappearance of this band in the spectra of all produced complexes indicated the deprotonation of phenol group to coordination with metal ion[12]. The band at 1692 $cm^{-1}$due to υ(C=O) vibration, Since no significant change in this band was noticed, the indicating no coordination through this group[13]. Azomethine group at 1640 $cm^{-1}$ shifted to lower frequency of Zn(II) and Cd(II) complexes but no change of Sm(III) and Eu(III) complexes related to no coordination from this group[14]. The bands at 1570 $cm^{-1}$ and 1383 $cm^{-1}$ were assigned to stretching vibration of ν($COO^-$) asymmetric and symmetric respectively, on complexation these bands have been shifted to lower frequencies at 1550,1557,1551 and 1538 $cm^{-1}$ for $\nu_{as}(COO^-)$, and 1352,1360,1371 and 1351 $cm^{-1}$ for $\nu_s(COO^-)$ respectively, that the coordination with metal ion. Moreover, $\Delta[\nu_{as}(COO^-)- \nu_s(COO^-)]$ values of complexes below 200 $cm^{-1}$ would be expected for bridging or chelating carboxylates anions[15] .The band at 1471 $cm^{-1}$ related to azo group, this band shifted to lower frequency for all produced complexes[16].The new bands for metal-nitrogen and metal-oxygen[17,18] at the range 430-5581 $cm^{-1}$. According to the results an octahedral geometry have been offered for the produced complexes.




## Conclusion

In this work, the complexes have been prepared with the ligands. The produced compounds are related by melting point, flame atomic absorption, FT.IR and UV-Vis spectral, as well as conductivity method. According the result data an octahedral structure suggested for prepared complexes.

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