Synthesis, Characterization, DFT and Antibacterial, Azo Ligand Derived From 2-Amino pyrimidine With Antipyrine Mixed ligand Complexes involving 1,10-phenanthroline

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Abstract

A new heterocyclic ligand (1,5-dimethyl-2-phenyl-4-(pyrimidin-2-yldiazenyl)-1,2-dihydro-3H-pyrazol-3-one, was synthesized by the diazotization of 2-(chlorodiazenyl)pyrimidine, and coupling with antipyrine to produce a new azo dye in an alkaline alcoholic solution under optimized experimental conditions (Azo-pyrm-Ap) (pyrimidin-2-yldiazenyl) ligand. and react with 1,10-phenanthroline, Ferric(II), Cobalt(II), Nickel(II), Copper(II), Zink(II), and Mercury(II) ions were used to build the structure of mixed-ligand Tetradentate complexes. They confirmed all that by 1H-NMR, UV-Vis, ES, XRD (DSC-TG) thermal analysis, Inferred- IR Magnetic susceptibility, The(C,H and N) analysis, molar conductance, and atomic absorption are all examples of spectroscopic techniques. The isolated solid complexes have been to have identified the formula in general [M (L)(phen) Cl] and [M (L)(phen)(H2O)] Cl. For prepared complexes, conductivity measurements revealed a [1:1] electrolyte. for Fe(II) and non-electrolyte for the Ni(II), Co(II), Zn(II), Cu(II), and, Hg(II) complexes. assemblages According to the spectral and analytical results, this ligand acts as a Bidentate chelating agent, with all metal ions having a coordination number of six. Finally, biological activity of the synthesized ligand and metal complexes against bacterial species was evaluated, Staphylococcus aureus is a Gram positive bacteria, and Escherichia coli, Pseudomonas aereuguinosa, and Klebsiella pneumoniaea are Gram negative bacteria. and it was found that these compounds have different inhibitory activity on bacteria growth.

Key Words: Azo2-amino pyrimidine, Mixed ligand, 1,10-phenanthroline antipyrine.

1. Introduction

The presence of an azo group (-N=N-) that connects two sp2 hybridized carbon atoms separates azo compounds. These carbons are often part of a chromophore, which is an extended delocalized electron system involving the aromatic ring. [1,2]. They're brightly colored and widely used as dyes and pigments in a variety of applications, including textile dyeing[3,4] and nonlinear and photo electronics[5] Especially in the field of optical data storage[6, 7] These compounds are very important molecules, especially in optical information storage, and have attracted a lot of attention in both academic and applied research[8,9]. azo compounds, on the other hand, are considered to play a role in DNA, RNA, and protein synthesis in a variety of species. inhibition, nitrogen fixation, and
carcinogenesis [10]. They're also used as an anti-inflammatory, antifungal, and antimicrobial activity. Indicators [13], anticancer [11], pharmaceuticals [12], and anticancer [11]. The nitrogen 1, 2 positions are found in A five-membered unsaturated heterocyclic loop is classified as pyrazole. It occupies a prominent position in medicinal chemistry, and its derivatives are thought to have a wide variety of biological effects, including antimicrobial [1,3], anticancer [14], anti-inflammatory [15,16], and antidepressant [17], position of the pyrazole ring, some derivatives have anticonvulsant [18] and antiptyretic [19] properties; some derivatives have inhibitory effects on specific enzymes [20] Pyrazole-based ligands have been discovered to have complex and coordinating activity with transitional metals based on computational analysis [21]. The main target of the present work is to synthesize new Azo Ligand Mixed With 1,10-phenanthroline complexes of Co(II), Fe(II), Cu(II), Zn(II) Ni(II), and Hg(II) with the ligand (1,5-dimethyl-2-phenyl-4-(pyrimidin-2-yldiazenyl)-1,2-dihydro-3H-pyrazol-3-one). The preparation conditions were examined spectroscopically. Different physicochemical methods were used to characterize the complexes. The dyeing demonstration of the ligand and its complexes' antibacterial activities were also studied.

2. Experimental

2.1. Materials
All chemicals used in this study were of the highest purity available. 2-Amino pyrimidine, Antipyrine, 1,10-phenanthroline, hydrochloride Sodium hydroxide, Sodium Nitrite, were purchased from Sigma Aldrich The C.H.N. EA 300 was used to analyze the elements of the ligand (Azo-pyrm-Ap) and its complexes. (element Analyses system GmbH). Absorption spectra in absolute ethanol (10⁻³ M) solution were recorded using U,V-visb. Shimadzu UV-1800 UV Spectrophotometers). 1H- NMR spectra of ligand recorded in DMSO-d⁶ The internal reference standard was TMS, (Varian Agillent 500 MHz) spectrometer. FT-IR alpha was used to record infrared spectra.FT-IR-ATR platinum reflective) (Bruker 4000-400 cm⁻¹ is the range. Analytic Jena Model Nova AA-350 used the atomic absorption technique to calculate the metal percentages. At room temperature, On a balance magnetic MSB, magnetic susceptibility measurements of metal complexes were performed-MK (That's the Gouy method.) Electrical conductivity was measured in DMF at room temperature and use a digital conductivity meter (Conductivity Meter-Model-Eutech pc700) with a solute concentration of (10 -3M). Electro thermal 9300 was used to determine the melting point in an open capillary tube. A Philips pw 9421 pH meter has been used to start taking the measurements. Diffractogram X,pert Phillips Holland. has been used to scan XRD patterns.. TGA analysis was recorded with Matluer Touldo. Micrograph was used to capture FESEM photographs. ZEISS GmbH.

2.2. Formulation of azo dye ligand (Azo-pyrim-Ap)
By using the flowing methods, the Pyrimidzolyl azo dye ligand (Azo-pyrm-Ap) has been synthesized by the diazotization coupling reaction. Khalid J. AL-Adilee et al. [22] . with some modi-fications (Scheme 1) by dissolving 1.635gm, (0.0172mol) of 2-amino Pyrimidine in a mixture of 5.5 ml distilled water and 5 mL concentrated hydrochloric acid, cooled and stirred continuously until the temperature was reached (0-5) C, and then added a solution of sodium nitrite made from the dissolved sodium nitrite 1.18gm (0.0172mol) in 5 ml distilled water was added drop by drop to a solution of 2-amino Pyrimidin in an ice bath at 0°C. The resulting diazonium chloride solution was added drop by drop to a solution consisting of 3.237gm (0.0172mol) Antipyrine,( solved in 18 ml ethanol and 18 ml 6% After adding the entire amount of NaOH, leaving the mixture to stabilize for 2 hours, followed by adding By changing the pH of the solution to pH = 6, leaving the precipitate overnight, and then filtering and washing it several times with distilled water, 200 ml of distilled water and cold was stable precipitate was formed. and a 10ml ethanol solution to clear any unreacted products The result was 80 % Green crystals with a melting point of 150-153 degrees Celsius. IR, 1H-NMR, C,H and N, UV-Visb are used to transform the structure of the azo dye ligand (Azo-pyrm-Ap).
Scheme 1. A heterocyclic azo dye ligand was synthesized. 1,5-dimethyl-2-phenyl-4-(pyrimidin-2-yl)diazene)-1,2-dihydro-3H-pyrazol-3-one (Azo-pyrn-Ap)

2.3. Formulated of metal complexes

The metal transition complexes were made by dissolving 0.882gm (0.003mol) in 30 ml ethanol and then adding a stoichiometric volume of [1M:1 L] mole ratio to metal chloride (0.003 mol) drop wise with stirring at pH =7.0 in buffer solution (ammonium acetate). M= Co(II), Ni(II), Fe(II), Cu (II), Zn(II), and Hg (II) ligand dissolved in 25 ml buffer solution. The reaction mixture was held at a constant temperature for 45-50 minutes.[22]. After a period of refluxing 1 h, (0.003 mol) of 1,10-phenanthroline was added to the solution. The reaction was heated for an additional 2 h. The metal transition complexes are filtered out and distilled water is used to wash the solution. becomes colorless, after which they are coated with glossy stratum and left over night. For those ligands and their metal chelate complexes, (Table 1) shows a a set of physical and analytical properties results [23,24].

\[
\text{MCl}_2.\text{nH}_2\text{O} + \text{Azo-pyrn-Ap} \xrightarrow{\text{reflux, 1,10-phenanthroline}} [\text{M (Azo-pyrn-Ap) (phen)Cl}_2] \\
\text{ammonium acetate, ethanol, pH =7.0} \\
M= \text{Co (II), Ni(II), Cu (II), Zn(II), and Hg (II)}
\]

\[
\text{MCl}_2.\text{nH}_2\text{O} + \text{Azo-pyrn-Ap} \xrightarrow{\text{reflux, 1,10-phenanthroline}} [\text{M (Azo-pyrn-Ap) (phen)(H}_2\text{O)Cl}_2\text{]} \\
\text{ammonium acetate, ethanol, pH =7.0} \\
M= \text{Fe(II)}
\]
Fig. 1. Molecular structure of Complexes

3. Results and discussion

3.1. Characterization of azo dye ligand and its metal complexes.

The heterocyclic azo dye ligand (Azo-pyrm-Ap) developed green crystals, but the Depending on the metal ion, the metal chelate complexes obtained were of different colors. The ligand and its complexes are stable in air at room temperature. Some organic solvents, such as ethanol, methanol, acetone, CHCl3, DMF, DMSO, alkaline solutions, and strongly acidic solutions, are soluble in it.

3.2. Molar conductivity measurements

The molar conductivity of the prepared metal complexes was measured at room temperature in DMF as a solvent with a concentration of (10^-3M). The conductivity values are described in the table below (Table 3). The molar conductivity of the Fe(II) complex indicates that it was an electrolyte with a [1: 1] ratio. The ionic nature of the Ni(II), Cu(II), Zn(II), and Hg (II) complexes was demonstrated Used a silver nitrate (AgNO3) solution, which resulted in a white silver chloride precipitate (AgCl) [25], However, because of the low molar conductivity of these complexes indicated their nonionic structure and nonelectrolyte nature [26,27].

Table 1. For the ligand (Azo-pyrim-Ap) and its chealte, elemental analysis and some physical properties were performed.

| compound          | Color       | M.p  (°C) | Yield % | Mol. formula (mol. Wt) | Found (calc) % |
|-------------------|-------------|-----------|---------|------------------------|----------------|
| L=Azo-pyrim-Ap    | Green       | 153       | 81      | C12H11N9O             | 61.21 (4.79)   |
| [Fe (L)(pheon)(H2O)Cl]Cl | Dark brown | 208       | 75      | C27H22ClFeN8O         | 61.48 (3.93)   |
| [Co (L)(pheon)Cl]2 | Blue greenish | 298      | 70      | C27H22ClCoN8O         | 18.54 (9.75)   |
| [Ni (L) (pheon)Cl]2 | Green       | 218       | 67      | C27H22ClNiO           | 18.55 (9.90)   |
| [Cu (L) (pheon)Cl]2 | Green       | 298       | 70      | C27H22ClCuN8O         | 18.54 (9.75)   |
| [Zn (L) (pheon)Cl]2 | Light Green | 223       | 71      | C27H22ClZnO2NiO5     | 18.55 (9.72)   |
| [Hg (L) (pheon)Cl]2 | Light Green | 204       | 78      | C27H22ClHgN8O         | 18.55 (9.90)   |
3.3. Infrared spectra

Table 3. shows the infrared spectra of the azo dye ligand (Azo-pyrim-Ap) and The metal transition complexes with Co(II), Ni (II), Fe(II), Zn(II), Cu(II), and Hg(II). ions using a KBr disc in the range (4000-400) cm$^{-1}$.

Table 2 : The azo dye ligand's main IR absorption bands (cm$^{-1}$) and its complexes.

| Group         | Ligand | Fe(II)  | Co(II)  | Ni(II) | Cu(II)  | Zn(II)  | Hg(II)  |
|---------------|--------|---------|---------|--------|---------|---------|---------|
| $\nu$(O–H)   | ----   | 3386m.br| --      | --     | --      | --      | --      |
| $\nu$(C=O)   | 1677s. | 1638s.  | 1637s.  | 1652s. | 1641s.  | 1652s.  | 1648s.  |
| $\nu$(N=N)   | 1582s. | 1567    | 1522s.  | 1538s. | 1518s.  | 1557s.  | 1559s.  |
| $\nu$(C =C) Ph | 1318s. | 1339s.  | 1321s.  | 1335s. | 1352s.  | 1330s.  | 1317s.  |
| $\nu$(C-N = N- C) |1236m.  |1294s.   |1236s.  |1270s.  |1228s.  |1281s.  |1278s.  |
| $\nu$(M – O) | ----   | 504w.   | 589w.   | 544w.  | 510w.   | 563w.   | 533w.   |
| $\nu$(M- N)  | ----   | 431w.   | 492w.   | 486w.  | 434w.   | 456w.   | 459w.   |

Fig. 2. IR Spectrum of the free ligand (Azo-pyrim-Ap) and its Complexes.
3.4. $^1$H-NMR spectra
The $^1$HNMR spectrum of ligand (Azo-pyrim-Ap) was recorded in (DMSO-d$_6$) and spectrum was shown in (Fig.3). $^1$HNMR spectrum of the Azo dye ligand shows peak at (7.34 – 7.57 δ ppm, multiplet 6H) aromatic. The ligand also shows the following signals: (2.08 δppm C-CH$_3$), (3.37 δppm -N-CH$_3$) of Antipyrene group[12,15]. (8.28 δ ppm - 1H duplet N-CH=CH) of Pyrimidine group respectively. and, All of the protons were found to be in the correct location. The results of these studies add to the support for the mode of bonding discussed in the (C.H. and N) and IR spectra.

Fig. 3. $^1$H- NMR spectrum of azo dye ligand (Azo-pyrim-Ap).

3.5. Magnetic measurements
The Fe(II), complex has a magnetic moment of 5.21 which corresponds to the stated value for octahedral, Co (II). The magnetic moment of the complex is 4.32BM (Table 3), which is consistent with previous reports for octahedral Co(II) complexes. The magnetic moment value of the current Ni(II) complex is 3.08BM, which is within the range of 2.9–3.3 BM [28,29,30], indicating an octahedral environment. The magnetic moment of the Cu(II) complex is 1.93BM, which is higher than the spin-only value of 1.73BM for one unpaired electron, monomeric, and compatible with a distorted octahedral geometry. The Zn(II) and Hg(II) complexes were diamagnetic and had an octahedral geometry, according to their empirical formulae [30].

3.6. Electronic spectra
spectrums of ligand (Azo-pyrim-Ap) and its complexes. Fe(II),Co(II),Ni(II) Zn(II) and Hg(II) in DMF [10$^{-3}$M] The geometric structures of the complexes are determined using electronic spectra and magnetic measurements. (Table 3). The electronic spectrum of Fe(II) complex displays weak absorption band at 12822cm$^{-1}$ corresponding to $^5$T$_2g$ $\rightarrow$ $^5$Eg, Co(II) complex. The electronic spectrum of Co(II) complex displays weak absorption bands at 12985 cm$^{-1}$, 14925 cm$^{-1}$ and 22728 cm$^{-1}$ characteristic of octahedral geometry corresponding to $^4$T$_1g$ $\rightarrow$ $^2$T$_2g$(F) (ν$_4$), $^4$T$_1g$(F) $\rightarrow$ $^4$A$_2g$ (F) (ν$_2$), $^4$T$_1g$ $\rightarrow$ $^4$T$_1g$ (P) (ν$_1$) transitions respectively. The
Co(II) complex which supports octahedral geometry for the complex. The Ni(II) complex also exhibits three weak absorption bands at 13157 cm\(^{-1}\), 16528 cm\(^{-1}\) and 23255 cm\(^{-1}\) assignable to 3\(A_2g \rightarrow 3T_2g(F)\), 3\(A_2g(F) \rightarrow 3T_1g(F)\), 3\(A_2g(F) \rightarrow 3T_1g(P)\) which are characteristic of octahedral geometry. The Cu(II) complex depicts a broad band in the region 13560 cm\(^{-1}\) to 17760 cm\(^{-1}\) with maximum at 15650 cm\(^{-1}\) assignable to 2\(E_g \rightarrow 2T_2g\) in its spectrum, the broadness of the band may be due to octahedral geometry.

Table 3. The electronic spectrums of ligand and its chelate complexes, magnetic susceptibility and values of molar conductance of complexes

| Compounds                  | Band position, cm\(^{-1}\) | Transition          | \(\Omega^{-1}\) cm\(^2\) mol\(^{-1}\) | Suggested geometry | \(\mu_{eff}\) (BM) |
|----------------------------|-----------------------------|--------------------|---------------------------------|------------------|-----------------|
| L=Azo-pyrim-Ap             |                             | \(\pi \rightarrow \pi^*\) | --                              | --               | --              |
|                            |                             | n \rightarrow \pi^* | 30485                           |                  | 23202           |
|                            |                             | Center ligand       | 33063                           |                  | 28670           |
|                            |                             | Center ligand       | 12822                           |                  | 12985           |
| Fe (L)(pheon)(H\(_2\)O)Cl|                             | \(5T_2g \rightarrow 5E_g\) | 32048                           |                  | 23202           |
| Fe (L)(pheon)(H\(_2\)O)Cl|                             | \(4T_1g \rightarrow 4T_2g(F)\) | 33063                           |                  | 28670           |
| Fe (L)(pheon)(H\(_2\)O)Cl|                             | \(4T_1g(F) \rightarrow 4A_2g(F)\) | 13025                           |                  | 12822           |
| Ni(L) (pheon) Cl\(_2\)    | 11266                       | 3\(A_2g \rightarrow 3T_2g(F)\) | 19925                           | 4T_1g \rightarrow 4T_2g(P) | 13157           |
| Ni(L) (pheon) Cl\(_2\)    | 13378                       | 3\(A_2g \rightarrow 3T_2g(P)\) | 22728                           | 4T_1g \rightarrow 4T_2g(P) | 12822           |
| Ni(L) (pheon) Cl\(_2\)    | 21786                       | 3\(A_2g \rightarrow 3T_2g(P)\) |                                |                  | 12822           |
| Cu (L) (pheon) Cl\(_2\)   | 15650                       | \(2E_g \rightarrow 2T_2g\) | 26088                           | 4T_1g \rightarrow 4T_2g(P) | 15650           |
| Zn (L) (pheon) Cl\(_2\)   | 26088                       | \(d\pi(Zn)^{2} \rightarrow \pi*(L)\) | 31273                           | 4T_1g \rightarrow 4T_2g(P) | 15650           |
| Hg (L) (pheon)Cl\(_2\)    |                             | \(d\pi(Hg)^{2} \rightarrow \pi*(L)\) | 31273                           | 4T_1g \rightarrow 4T_2g(P) | 15650           |

3.7. XRD analysis

In the X’pert high score software kit, the XRD powder pattern is processed (Fig.5). The PXRD pattern for the Fe(II) complex was subjected to a check matching procedure, which revealed a match with a copper compound JCPDS powder diffraction file, PDF No 991218. (Table 4) The pattern is a tetragonal crystal system with \(a = b = 10.19\), \(c = 5.468\), \(\alpha = \beta = \gamma = 90\), lattice = body centred, and space group is 14/mmm(139), \(K\) is a constant (0.94 for Cu grid), is the Bragg diffraction angle, is the X-ray wavelength (1.5406 A), and is the full-width at half-maximum (FWHM) of prominent intensity peak, intensity (percentage), and integrated intensity [30,31].
Fig. 4. X-RD patterns of Fe(II)-Complex,

Table 4. XRD analysis data of the Fe(II) complex

| Strongest peak no | 2θ (deg) | Height [cts] | FWHM [°2Θ.] | d (Å)   | Intensity (counts) |
|-------------------|----------|--------------|--------------|--------|-------------------|
| 1                 | 8.4443   | 3974.33      | 0.1968       | 10.46259 | 100.00            |
| 4                 | 12.0576  | 2765.97      | 0.2460       | 7.33418  | 69.60             |
| 5                 | 13.1128  | 2741.65      | 0.2460       | 6.74627  | 68.98             |
| 7                 | 16.0801  | 2720.05      | 0.2952       | 5.50743  | 68.44             |
| 8                 | 16.8057  | 776.03       | 0.2460       | 5.27124  | 19.53             |
| 9                 | 18.2207  | 1787.76      | 0.2460       | 4.86495  | 44.98             |
| 10                | 18.9593  | 2564.71      | 0.2460       | 4.67706  | 64.53             |
| 14                | 26.2719  | 739.19       | 0.1968       | 3.38948  | 18.60             |
| 15                | 27.4727  | 1955.52      | 0.2460       | 3.24398  | 49.20             |
| 16                | 28.7608  | 2198.36      | 0.2460       | 3.10156  | 55.31             |

3.8. SEM analysis

The ligand and its complexes had different morphologies, as shown in (Fig.6). The FESEM of the ligand (a) appeared to be a particle form with an average size (200-100nm). FESEM images of -(b) Fe (II) complex segments of column crystals of average size (200-100nm). The SEM of the -(c) Co (II) complex showed a number of small crystals of average size (100-50 nm). FESEM image of -(d) Cu (II)- Glass sheets crystals of average size seemed to be complex (200-100 nm). The -(e) Zn (II)- complex appeared on FESEM to be a type of crystal with irregularly perpendicular walls and average size (100-50 nm). (additional)EDX of the Fe (II) complex.
Fig. 5. SEM images of (a) ligand-binding proteins (b) Fe (II) complex (c) Complex of cobalt (II) - (d) Complex Cu (II) (e) Complex Zn (II) - (f) Fe (II) complex EDX

3.9. Thermal studies

The (Azo-pyrim-Ap) Ligand and Its Complexes. \([\text{Fe (L)(pheon)}(\text{H}_2\text{O})\text{Cl}]\text{Cl} \) and \([\text{Co (L)(pheon)}\text{Cl}_2]\). The decomposition occurs in at least six major detectable steps; each step does not refer to a single process in general, but rather to three data obtained that support the proposed structure and indicate the Ligand and its complexes Fe(II) and Co(II) go through. [30.31,22]
Table 5. Date (DSC- T.G) of the Ligand and its complex Fe(II), Co(II).

| Compound          | TG Range (°C) | Mass loss% | Assignment                                      | Residue   | DSC (°C) |
|-------------------|---------------|------------|-------------------------------------------------|-----------|----------|
| Azo-pyrim-Ap      | 28-150        | 1.55       | Evolution of Co2 and moisture                    | --        | 235(+)   |
|                   | 150-270       | 10.15      | - Loss Azo group -N=N-                           |           |          |
|                   | 275-330       | 26.50      | - Loss -CH3 -CH2 group                           |           |          |
|                   | 330-418       | 35.80      | - Loss -CH3 -C6H5 group                          |           |          |
|                   | 418-540       | 74.0       | - Loss -C6H5, C=O group                          |           |          |
|                   | 540-600       | 81.9       | - Loss of a part of the ligand                   |           |          |
| [Fe (L)(phen)(H2O)Cl] | 31-105       | 1.50       | Evolution of CO2 and moisture                    | Fe2O3 +2C | 290(+)   |
|                   | 107-250       | 9.36       | - Loss -H2O Coordination                         |           |          |
|                   | 300-340       | 19.5       | - Loss -CH3 -CH2 group                           |           |          |
|                   | 360-385       | 30.4       | - Loss -CH3 -C6H5 group                          |           |          |
|                   | 385-500       | 69.42      | - Loss -C6H5, C=O group                          |           |          |
|                   | 500-600       | 88.92      | - Loss of a part of the ligand                   |           |          |
| [Co (L)(phen)Cl2] | 32-125        | 1.50       | Evolution of CO2 and moisture                    | CoO +2C   | 255(+)   |
|                   | 123-170       | 9.30       | - Loss Azo group -N=N-                           |           |          |
|                   | 170-300       | 19.5       | - Loss -CH3 -CH2 group                           |           |          |
|                   | 300-450       | 69.45      | - Loss -CH3 -C6H5 group                          |           |          |
|                   | 450-600       | 88.95      | - Loss -C6H5, C=O group                          |           |          |
|                   |               |            | - Loss of a part of the ligand                   |           |          |

L = ligand (Azo-pyrm-Ap)

3.10. Computational study

The studied compounds are subjected to a computational analysis to determine their reactivities and geometrical parameters. The perspective of Gauss The structures are described using 4,1[31]. The structures of the ligand and all of its metal complexes are optimized using the 6-311++G(d,p) basis set at the B3LYP[32] level of theory. 6-311++G(d,p) is a broad basis collection that includes diffused and polarized wave functions to account for the properties of ionic species with heavy atoms such as N. Chemcraft software[33], is used to visualize the studied compounds’ optimized geometry. To ensure that the structures are real minima, the harmonic frequency calculation is also performed at the same level of theory. The results are carried out without any symmetry constraints, using the software’s default convergence criteria. The Gaussian 03 routine is used to perform the molecular calculations in this paper. Coordination compounds and organic molecules have both derived from this computational approach. Chemical potential is defined by DFT as the first derivative

\[ \mu = \left( \frac{\partial E}{\partial N} \right) \vartheta(r) \]

a measure of energy in terms of the number of electrons where \( E \) is the maximum energy of the system, \( N \) is the number of electrons in the system at constant external strain, and Chemical hardness \( n \) is half of the second derivative of energy with respect to the number of electrons, so it is the first derivative of energy with respect to the number of electrons.

\[ n = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right) \vartheta(r) \]
respect to number of electrons[32].

However, in most cases, chemical potential($\mu$) and chemical hardness($n$) are measured in terms of ionization potential(IP) and electron affinity(EA), and thus [33].

$$\mu = -\left(\frac{IP+EA}{2}\right) \text{ and } n = \left(\frac{IP-EA}{2}\right)$$

According to Koopman's theorem, IP and EA are compared to the energies of the highest occupied molecular orbital (EHOMO) and the lowest occupied molecular orbital (ELUMO). $EA = -E_{LOMO}$, and $IP = -E_{HOMO}$

$$\mu = \left(\frac{ELUMO-EHOMO}{2}\right) \text{ and } n = \left(\frac{ELUMO-EHOMO}{2}\right)$$

Electrophilicity was proposed by Parr and coworkers as a measure of a compound's electrophilic ability. Electrophilicity can be described as

$$\omega = \frac{n^2}{2n}$$

Table-6 shows the chemical potential($\mu$), chemical hardness($n$), electrophilicity, and dipole moment of the ligand and complexes. The minimum electrophilicity theory can be used to estimate the ligand's and metal complexes' reactivity. According to the theory of minimal electrophilicity, compounds with the lowest electrophilicity have the highest stability. The HOMO and LUMO values of the ligand(Fig7-15) and its complexes (Fig8-16) are used to measure the chemical potential($\mu$), chemical hardness($n$), and electrophilicity($n$) (Table.6).

Fig.6.LOMO Ligand  Fig.7.HOMO Ligand

Fig.8.LOMO of Fe(II)-Complex  Fig.9.HOMO of Fe(II)-Complex
Fig. 10. LOMO of Co(II)-Complex

Fig. 11. HOMO of Co(II)-Complex

Fig. 12. LOMO of Hg(II)-Complex

Fig. 13. HOMO of Hg(II)-Complex

Fig. 14. LOMO of Zn(II)-Complex

Fig. 15. HOMO of Zn(II)-Complex

Table 6. The investigated compounds’ global reactive indices and dipole moment

| Compounds                  | HOMO  | LUMO  | n    | η    | μ (eV) | III   |
|----------------------------|-------|-------|------|------|--------|-------|
| Azo-pyr-m-Ap               | -1.977| -1.956| 1.966| 0.0105| -1.9665| 0.020302 |
| [Fe (L)](pheon)(H₂O)ClCl   | -12.305| -11.591| 11.774| 0.357| -11.948| 25.48171 |
| [Co (L) (pheon)]Cl₂       | -11.639| -10.915| 11.277| 0.362| -11.277| 23.0179 |
| [Ni(L) (pheon) Cl₂]       | -11.812| -10.8813| 11.366| 0.46535| -11.3467| 29.95608 |
4. Antibacterial study

The investigated compounds’ in-vitro biological screening effects were checked against bacteria using the disc diffusion method and nutrients agar as the medium. Table 6 summarizes the results, with DMSO serving as a negative control and Amoxicillin acting as a positive normal.

Table 7. The synthesized compounds’ minimum inhibitory concentrations against the growth of four bacteria (MIC in µg/mL)

| Compound                | Escherichia coli | Pseudomonas aeruginosa | Staphylococcus aureus | Klebsiella pneumonia |
|-------------------------|------------------|------------------------|-----------------------|----------------------|
| Azo-pyrm-Ap             | 20               | 14                     | 18                    | 16                   |
| [Fe (L)(pheon)(H$_2$O)Cl] | 34               | 26                     | 30                    | 32                   |
| [Co (L)(pheon)Cl$_2$]   | 26               | 22                     | 24                    | 26                   |
| [Ni(L)(pheon)Cl$_2$]    | 38               | 30                     | 32                    | 32                   |
| [Cu (L)(pheon)Cl$_2$]   | 22               | 24                     | 24                    | 26                   |
| [Zn (L)(pheon)Cl$_2$]   | 22               | 20                     | 26                    | 24                   |
| [Hg (L)(pheon)Cl$_2$]   | 38               | 32                     | 38                    | 32                   |
| Amoxicillin             | 8.8              | 6.8                    | 12                    | 10                   |

The zone of inhibition region for metal chelates is much greater than the ligand, as shown in Table 6. Chelation theory may describe the increased activity of metal chelates in this way. Due to the overlap of the ligand orbitals, the polarity of the metal ion would be decreased to a greater degree during chelation. It also promotes the delocalization of π-electrons over the entire chelate ring and increases the complexes’ lipophilicity [34,35]. This increased lipophilicity causes the cell’s permeability barrier to break down, slowing down normal cell processes.

![Fig. 16. Results of antibacterial screening.](image)

5. Conclusions

The authors of this paper describe the synthesis and spectral characterization of a new heteroarylazo dye derived from 2-aminopyrimidine with Antipyrine (Azo-pyrm-Ap) and its metal complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) ions. Analytical, physical, and spectral data from the chalet complexes, such as IR, 1H-NMR, UV-Vis., and Xrd,
revealed the ligand (azo-pyr-mp-Ap) mixed ligand with(N,N) from free ligand 1,10-phenanthroline, acts as Bidentate N, O coordination involving one of the azo nitrogen which is the farthest of Azo group between pyrazole ring and Pyrimidine ring, and the oxygen of Carbonyl group of pyrazole ring. Both complexes have been proposed to have an octahedral geometry. The Fe(II) complex is ionic, resulting in a [1:1] electrolyte, but the Co(II),Ni(II),Cu(II),Zn(II), and Hg(II) complexes are non-ionic. XRD and SEM studies revealed that the ligand and its complexes had different structures and morphologies. TGDSC diagrams were used to investigate the thermal stability of ligand and its complexes, and it was discovered that the Theoretical Calculation (HOMO and LOMO) Orbitals and thermal stability were both successful in the complexes. The prepared complexes have important applications in industrial fields like dyes, as well as medical fields like pharmacology, toxicology, and biochemistry.

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