Synthesis and characterization of some metals complexes with new heterocyclic azo dye ligand 2-[2\(-\)5-nitrothiazolyl(azo)]-4- methyl-5-nitro phenol and their biological activities

Ziyad T Al-Khateeb\(^1\), Faiq F. Karam \(^1\) and Khalid Al-Adilee\(^2\)

\(^1\)Department of Chemistry, College of Science, University of Al-Qadisiyah, Al-Diwaniya 58002, Iraq
\(^2\)Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya 1753, Iraq
Email: ziyad.ttt@gmail.com

Abstract. A series of Cu(II), Fe(III), Pb(II), Mn(II) metals complexes have been synthesized with the new thiazole azo dye containing tridentate [N.N.O] donor ligand 2-[2\(-\)5-nitro thiazolyl(azo)]-4-methyl-5-nitro phenol (5-NTAMNP) derived from 2-amino-5-nitrothiazole and 3-methyl-4-nitrophenol by the diazotization operation and the adizonium chloride salt solution of 2-amino-5-nitrothiazole reacting with 3-methyl-4-nitrophenol as a coupling compound in alkaline alcoholic solution. The structures of synthesized novel ligand was identified and confirmed via resorting to various spectroscopic techniques which included, \(^1\)H NMR, Mass spectrum, UV–visible, Fourier-transform infrared (FTIR), X-Rays diffraction (XRD), the surface nature and morphology and size average and elemental composition of individual ligand particles were examined using a field emission scanning electron microscope (FESEM) coupled with an energy dispersive X-ray system (EDX), in addition to above the physical properties of ligand have been studied via check its melting point and the purity of the ligand also was checked by TLC in presence of a certain solvent system. As for the consistency positions available in (5-NTAMNP) and the manner of its association with these metallic ions it's likely that the pattern of complexity as a tridentate chelating agent with the formation of a coordination number for all metallic ions found equal to six and have Octahedral shape for all metallic ion. The optimal condition for complexation have been studied, the prepared metallic complexes were identified via UV–visible & FT-IR spectra. All metallic complex and (5-NTAMNP) ligand were screened for their biological activities.

Keyword: Thiazole azo; NNO donor ligand; Biological activities; FESEM; TLC

1. Introduction

The heterocyclic coordinating compounds which are concerned with azo ligands especially thiazole azo ligands and with their metallic ions in their coordinated chelate pattern, these ligands have a pivotal and vital role in coordination chemistry. They are of great importance to their specific properties which make them very important in industrial technology, biological systems and routine, they are essential to life as they play a very important role in the metabolism of many living cells. The metal chelates of ligands with hetero-atom donor sets have physicochemical properties [1-5]. Thiazole azo ligands having a stable and intensely colored metal complexes.
owning to hard nitrogen, oxygen and soft sulfur donor atoms thereby have capability for coordinating with a wide range of metallic ions [6]. Metallic ions ligand complexes have uniqueness shapes compared with organic molecules thus, its forms are a span a range of coordination geometries [7]. The study of compounds containing S and N atoms is interesting due to their significant antifungal, antibacterial and anticancer activities [8]. Thiazolylazo complexing agents have been successfully employed in determinations of many metal ions and have attracted much attention as they are sensitive chromogenic reagents for spectrophotometric, liquid chromatography and extraction-photometric such as solid phase, liquid – liquid and cloud point extraction [9]. Thiazolyl azo compounds are important in intermediates for the preparation of some applications such as biological activity [10]. Thiazolylazo reagents as analytical reagents owing to the high sensitivity and selectivity therefore these azo reagents have attracted much attention in analytical field [11-13]. This category of azo dyes being a (π-acidic) azo imine (-N=N-C=N-) for this reason a number of these dyes were synthesized and their abilities as chelating reagents [14]. The objective of this work, synthesis of novel thiazolyl azo ligand with a series of Cu(II), Mn(II), Fe(III) and Pb(II) complexes of the azo dye ligand (5-NTAMNP) and characterized via various analytical and spectroscopic techniques further, the bioactive significance of the ligand and its metal complexes was investigated.

2. Experimental

2.1. Materials and instrumentation

All solvents, organic chemicals and inorganic salts those used in this work, were all highly purified and directly used without any further purification, chemicals supplied from Sigma-Aldrich, Merck, BDH, Fluka, Scharlau, Companies, The 1H NMR spectra were carried out on a Bruker model 500-UltraShield 300 MHZ spectrometer using DMSO-d$_6$ as solvent for measurement and using TMS as an internal standard reference. Mass spectra were collected on a Shimadzu Agilent Technologies model 5973C. Fourier Transform Infrared (FT-IR) spectra were recorded on a Shimadzu model 8400s FT-IR spectrometer scanning at range between (4000-400 cm$^{-1}$) via a KBr pellets. UV-Visible spectra were measured on a Shimadzu model UV-1650 UV-Visible spectrophotometer Double beam scanning at range of (200-1100 nm) using absolute ethanol as solvent for measurement. X-ray diffraction were performed on Shimadzu model XRD-6000 spectroscopy. And also used JENWAY, England model 3505 digital pH meter for the pH adjustment. The field emission scanning electron microscope and the energy dispersive X-ray were taken on a TESCAN model MIRA3 (FE-SEM). The Melting points were taken in open capillary tube by using OMEGA Digital Melting Point Apparatus model MPS10-120.

2.2. Synthesis of azo dye ligand

2-[2'-(5-nitro thiazolyl) azo]-4-methyl-5-nitro phenol (5-NTAMNP)

Synthesized of the novel azo ligand according to the method proposed by Al-Adilee et al. [15-16], with some modification via the diazotization coupling reaction (Scheme 1). This method of action included dissolving (1.45g, 0.01mol) from 2-amino-5-nitrothiazole in mixture contain (5ml of concentrated HCL) and (35ml of distilled water) then the all mixture was cooled to (0-2)°C, then to this solution was added drop wise a solution of sodium nitrite prepared by dissolving (0.9g, 0.013mol of NaNO$_2$) in 30ml of distilled water, and stirred for (30min) at (0-5)°C. The resulting diazonium chloride solution was added also drop wise while maintaining temperature at (0-5)°C , with stirring continuously into a 500 mL beaker containing (1.53g, 0.01mol of 3-methyl-4-nitrophenol in the mix contains on 50ml of absolute ethanol and 18ml of 10% NaOH) and coolant to (0-5)°C , after completion of the add-on process the final mixture was stirring at least for (2h) then complete the precipitate of the ligand by modifying the acidic function of the solution to pH=6.5. and allowed to stand overnight. The precipitate was filtered off, washed with distilled water and finally recrystallized. The ligand is spectrally studied and check of purity via TLC techniques. The melting point of azo ligand point found to be (129-131°C) and the yield was of about 82%. The ligand appearance was as a reddish brown rod crystals. The following chart illustrates the method of preparation azo dye (5-NTAMNP):
2.3. General method for the preparation of metallic ions complexes

The metallic ions complexes were prepared using corresponding metal chlorides for Mn(II), Fe(III), Cu(II), except Pb(II) was as acetate anhydrous and the azo ligand (5-NTAMNP). Amount of 0.6 g (0.002mol) from azo ligand, dissolved in 50 mL of absolute ethanol was gradually added in drops wise with stirring a stoichiometric to (0.001mol) amount of [1:2 M:L for Fe(II), Cu(II), pb(II) and Mn(II), chloride and acetate salt dissolved in 40 mL hot buffer solution (ammonium acetate) (of the required pH for each metallic ions), at optimum pH for each metal ions. The mixture was heated to (50-70)°C at 50 min until the precipitated product, then left over night. The separated solid complexes were filtered off, washed with distilled water and little warm ethanol to remove any traces of unreacted materials. The complexes obtained were finally dried under vacuum desiccators over combined CaCl₂ dehydrated. The analytical and physical data of ligand and its metal complexes are collected in Table-1.

3. Result and discussion

3.1. Physical and chemical properties of azo dye ligand (5-NTAMNP)

The azo dye ligand (5-NTAMNP) is characterized by the fact that his amorphous look is on the form of a fine brownish-red powder, while its crystalline appearance is show as like a micro needle/rod-shaped crystals, giving the color red-purple when dissolved with ethanol. This synthesis
thiazolylazo ligand is easily soluble in most solvents [Acetone, THF, DMSO, DMF, Methanol, Ethanol] but it is sparingly soluble in water. The obtained metallic ions complexes and azo (5-NTAMNP) ligand were stable in air. The purity of the ligand was confirmed by thin layer chromatography (TLC) technique via using certainly solvent system methanol: acetic acid (12:3:7 v/v) [17], this ligand conferred a single red purple color spot when its adsorbed onto silica chromatography plates.

| Compound                         | Colour             | M.P. (°C) | M.F. (M.W.)                          |
|----------------------------------|--------------------|-----------|--------------------------------------|
| Red Purple                       | 130                | C_{60}H_{67}N_{32}O_{32}S (309.26) | 5-NTAMNP(LD) [Fe(LD)_{2}]. H_{2}O |
| Red Orange                       | >290               | C_{50}H_{41}N_{10}O_{10}S_{2} Fe (674.37) | [Mn(LD)_{2}]. H_{2}O |
| Light Red                        | >290               | C_{40}H_{31}N_{10}O_{10}S_{2} Mn (673.46) | [Cu(LD)_{2}].H_{2}O |
| Yellowish Green                  | >290               | a C_{20}H_{14}N_{10}O_{5}S_{2} Cu (682.07) | [Pb(LD)_{2}].H_{2}O |
| Golden Yellow                    | >290               | a C_{20}H_{14}N_{10}O_{5}S_{2} Pb (825.73) | [Pb(LD)_{2}].H_{2}O |

3.2. Effect of pH

Values of pH for metallic ions complex's solutions was studied in order to detected the optimum pH medium to prepare the metallic complexes, wide range of pH scale were used from 5 to 10 and the required value of the pH was reached via adjusted the solution by using dilute solutions (0.1M) of ammonium acetate, acetic acid and ammonia solution, and the effect of pH on absorbance was carried out by measured the absorbance of these solutions at each λ-max for all metallic complexes with the change with solution pH. This study show the absorption of all chelate complexes solutions did not change over the whole range and very stable at pH= 6-7.5. As the results are illustrate in Figure.1,2.

3.3. Mole ratio [Metal: ligand] ratio

The mole ratio method were used in order to identify spectrophotometrically of the composition of metal chelate complexes and to finding possible structural formula of prepared metallic ions complexes, this method is based on the measurement of absorbance of each complexes solution at fixed optimum pH and concentration at the maximum absorbance wavelength. The intensity of the colors for the solution of prepared metallic ions complexes was increase as approach point of intersection [M:L] ratio, and the continued stability of color after the point of intersection indicating on formation of the metallic complexes [18-19]. The suggested molar ratio founded to be a [2:1] for all formation of metallic complexes, and maximum absorbance was obtained in pH range given in Table-2.
Effect of pH on absorbance values of chelate complexes.. Figure. 1, 2

3.4. Calculation of the metal complexes stability and dissociation constants:

According to this equation, $\beta = (1 - \frac{3}{4} C_i^2)$, $\text{Am-As/Am)$, the stability constants of complexes in their solutions was studied depending on spectroscopic methods for 1:2 (M:L) metal complexes, where As and Am are the absorbance of the partially and fully formed complexes respectively at optimum concentration, the stability constants are obtained by measuring the absorbance of solution mixture of ligand and metal ion at fixed wavelength ($\lambda\text{-max}$) and optimum pH values to each metallic ion [20]. The calculated $\beta$ values for the complexes are given in Table.3. The stability constants of metallic complexes follows the sequence $\text{Mn(II)} > \text{Cu(II)} > \text{Pb(II)} > \text{Fe(III)}$. The sequence of metal ions of the first row transition metal agree with Irving-Williams series of stability constant [21].

3.5. $^1H$ NMR spectra

The $^1H$ NMR spectra for novel ligand (5-NTAMNP) [22] was obtained in DMSO-d$_6$ as solvent with TMS as an internal reference (300MHZ). The spectrograph which is illustrated in Figure.3 and as the proton NMR interpreted listed in Table.4.

3.6. Mass spectra

The mass spectral of free novelty ligand (5-NTAMNP) are presented in Figure.4, the mass spectra show the base peak $M^+$ at $M/Z^+ = (309.26)$ correspond to the original molecular weight of ligand molecular ion, the molecular ion of the reagent with reactive abundance equal to (1.4%), where the mass spectrum was given to ligand a number of fragmentation and these fragmentation represented in the mass spectra in term of relative abundance compared to $M/Z^+$, and the main peak show via mass spectrum is relatively to molecular weight of ligand $[C_{10}H_{7}N_{5}O_{5}S]^+$, the schem.2, explains the proposed mass fragmentation products for ligand (5-NTAMNP) [23-24].
Table 2: Metal: ligand (M: L), Stability Constant Values (β), Optimum pH, Optimal Concentration & Wave Length with Absorption (λ<sub>max</sub>) of Complexes.

| Ligand                  | Metal ion | Optimal pH | λ<sub>max</sub> (nm) | Optimal Conc. × 10<sup>-4</sup> M | Molar absorptivity (ε) × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup> | Stability constant (β) L<sup>2</sup> mol<sup>-2</sup> | Log (β) |
|------------------------|-----------|------------|----------------------|-----------------------------------|-------------------------------------------------|-----------------------------------------------|--------|
| (5-NTAMNP)             | Mn(II)    | 7.5        | 534                  | 2                                 | 1.1                                             | 26×10<sup>12</sup>                           | 13.42  |
|                        | Fe(III)   | 6.5        | 612                  | 2                                 | 0.615                                           | 9×10<sup>7</sup>                              | 7.96   |
|                        | Cu(II)    | 6          | 601                  | 1.5                               | 0.0933                                          | 16×10<sup>10</sup>                            | 11.22  |
|                        | Pb(II)    | 7          | 618                  | 1.5                               | 0.1267                                          | 13×10<sup>10</sup>                            | 13.42  |

λ<sub>max</sub> = 518 nm
ε = 0.52×10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>
Conc. = 1.5×10<sup>-4</sup> M

Figure 3. 1H NMR spectrum of thiazolylazo dye ligand (5-NTAMNP).
Figure. 4. Mass spectrum of thiazolylazo dye ligand (5-NTAMNP).

Table 3: $^1$H NMR SPECTRA OF THIAZOLYLAZO DYE LIGAND (5-NTAMNP).

| Ligand (5-NTAMNP) δ, ppm | $J$-$J$ coupling | H atoms | peak |
|-------------------------|------------------|---------|------|
| 2.505-2.510             | –                | 3H      | d    |
| 6.788-6.772             | 2.053            | 2H      | t    |
| 8.006-7.966             | 1.000            | 1H      | m    |
| 10.789                  | 0.962            | 1H      | s    |
Scheme 2. Mass spectrum fragmentation of thiazolylazo dye ligand (5-NTAMNP).

3.7. Electronic spectra measurements

The electronic absorption spectra of thiazolylazo dye ligand (5-NTAMNP) and its' chelates complexes were measure at (10⁻³M) via used absolute ethanol as solvent to them, the ligand and its chelates appearing many of specific absorbance bands at differ wavelength due to the electronic transitions for them [25-27]. The all-electronic transition were explain for each spectrum and this data is summarized in Table.4. The U.V spectrum of (5-NTAMNP) and its’ chelates complexes were obtained in absolute ethanol solution are given in Figure (5, 6, 7, 8 and 9).
3.8. Infrared spectra measurements

The FT-IR spectra data for thiazolylazo dye ligand (5-NTAMNP) and its chelates complexes with Mn(II), Fe(III), Cu(II), and Pb(II) are given in Table 5. The FT-IR spectrum of the chelates complexes and free ligand shows a number of variable absorbance bands in them is due to this transitions responsible for FT-IR bands are due to molecular vibrations, these absorbance bands that appeared on FT-IR spectrum were due to active functional groups present [28-30]. Through this study shows that the shifts and change were occurred on absorbance bands at certainly wavenumber when these bands are compared with those that corresponding into free azo dye ligand and that it is pointing into formation a new shapes and coordination for metallic ions with of free azo ligand to created metallic chelates complexes and suggest the possible bonding modes in the complexes. Through the results of the spectral and analytical studies that have been reached that the ligand (5-NTAMNP) is likely to have a correlation pattern as a Tridentate chelating agent and be the coordination with metallic ions through by a phenolic oxygen, azo nitrogen which is the farthest of thiazole ring and nitrogen atom in thiazole ring to forming two five membered chelating ring [31]. The infrared spectra of azo dye ligand and some metal complexes are shown in Figures (10, 11, 12, 13 and 14). And the proposed stereotypical shapes and geometrical structures for the chelates complexes prepared in Figure 15.
Table 4: ELECTRONIC SPECTRA (nm, cm\(^{-1}\)) FOR THIAZOLYLazo DYE LIGAND (5-NTAMNP) & CHELATES COMPLEXES , PROPOSED GEOMETRY.

| Compounds       | \(\lambda_{\text{max}}\) (nm) | Absorption bands (cm\(^{-1}\)) | Transitions | Geometry       |
|-----------------|-------------------------------|-------------------------------|-------------|----------------|
| Ligand (5-NTAMNP) | 519                           | 19268                         | n-\(\pi^*\) | —              |
|                 | 408                           | 24510                         | \(\pi-\pi^*\) |                |
|                 | 236                           | 42373                         | n-\(\sigma^*\) |                |
| \([\text{Mn}(L)_2]\) | 972                           | 10288                         | \(2\text{A}_2g\rightarrow 4\text{T}_1g(\text{G})\) | Octahedral |
|                 | 528                           | 18939                         | \(2\text{A}_1g\rightarrow 2\text{T}_2g(\text{G})\) |          |
|                 | 415                           | 24096                         | \(2\text{A}_1g\rightarrow 2\text{T}_2g(\text{G})\) |          |
|                 | 258                           | 38760                         | Center Ligand |                |
| \([\text{Fe}(L)_2]\) | 960                           | 10417                         | \(2\text{A}_2g\rightarrow 4\text{T}_1g(\text{G})\) | Octahedral |
|                 | 612                           | 16340                         | \(2\text{A}_2g\rightarrow \text{E}_{\text{g}}, \text{A}_{1g(\text{G})}\) |          |
|                 | 377                           | 26525                         | \(2\text{A}_2g\rightarrow \text{T}_{2g(\text{P})}\) |          |
|                 | 253                           | 39526                         | Center Ligand |                |
| \([\text{Cu}(L)_2]\) | 601                           | 16639                         | \(3\text{B}_{1g}\rightarrow \text{E}_{\text{g}}\) | Octahedral |
| \([\text{Pb}(L)_2]\) | 618                           | 16181                         | M—L,CT       | Octahedral     |
Figures (10, 11, 12, 13 and 14) FTIR analysis of ligand and its chelates complexes.
M= Fe (III) ; n=1 M= Mn(II), Cu(II), Pb(II) ; n=0

Figure. 15. The suggest structural formula of

Table 5: Complexes

| Group | Ligand | Cu(II)          | Fe(III) | Pb(II)   | Mn(II)   |
|-------|--------|-----------------|---------|----------|----------|
| γ(O-H) | 3309.62 s.shr | 3448.49-        | –       | 3170.76 s.br | 3390.97 s.br |
| γ(C=N) | 1589.23 Vs. | 1566.09 m      | 1564.32 m | 1550.66 w | 1545.03 w |
| γ(N=N) | 1473.51 m.shr | 1411.80 m     | 1411.80 m | 1404.08 s.shr | 1450.52 m |
| γ(C=C) | 1419.51 w.shr | 1388.65 w    | 1391.04 w | 1326.93 w | 1157.33 m |
| γ(C-S) | 1257.50 m | 1265.22 w     | 1257.50 m | 1249.79 w | 1251.57 w |
| γ(M-N) | –     | 486.03 w    | 466.79 w | 424.31 w | 422.42 s |
| γ(M-O) | –   | 518.87 w   | 621.10 w | 609.46 s.br | 507.30 Vs. |

V - very , w - weak, s - strong, m - medium, br - broad , shr - sharp.

3.9. X-ray diffraction study (XRD)

The (XRD) of ligand (5-NTAMNP) were recorded in the range of 2θ = (10-80 deg) value in its solid state using the (Cu-κα) copper spectrum band as a generator of the X-ray with wavelength λ =1.54056Å. X-ray diffraction spectroscopy was used to identify the crystalline structure and to
determine the (grain size) crystal size, d-spacing between the atomic levels of the ligand. The Figure.16, of (XRD) spectra shows that the ligand appeared as a (Poly-crystalline) system and these systems are of different sizes and random distribution in nature [32], the XRD spectra of pure ligand display three main sharp peak at \[2\theta = 27.1249, 13.6297, 13.9383\] that corresponded to d-spacing of \[d= 3.28479, 6.49158, 6.34854 \text{Å}\], these major peaks represented the preferred orientation of crystal growth of the ligand molecule. The appearance of high intensity peak indicates a high crystalline nature. To calculate d-spacing reflections were obtained using Bragg’s equation \(n \lambda = 2dsin\Theta\), where d is the spacing between the crystalline levels, n is an integer (1,2,3 \ldots), \(\lambda\) is the wavelength of X-ray Cu-\(k\alpha = 1.54056 \text{Å}\), \(\Theta\) is the diffraction angle [33]. The grain size of the particles were evaluated by the Debye–Scherrer [34]. \(D = \frac{k \lambda}{\Theta \cos \Theta}\), where D is the average grain size, k is Blank’s constant (0.94), \(\lambda\) is the X-ray wavelength (0.154059 nm), and \(\Theta\) and \(\Theta\) are the diffraction angle and full width at half maximum of an observed peak, respectively. Table.6, shows the diffraction angles, d-spacing values, and the crystalline size of prepared ligand.

Table 6: \(2\Theta\) value of each peak, relative intensity, d-spacing FwHM, lattice strain & crystallite size.

| Compounds            | \(2\Theta\)  | FWHM | I/I₁ % | Lattice Strain | D(nm) | d-spacing |
|----------------------|--------------|------|--------|----------------|-------|-----------|
| Ligand(5-NTAMNP)     | 13.6297      | 0.23970 | 100    | 0.0088         | 34.88 | 6.49158   |
|                      | 27.1249      | 0.25970 | 84     | 0.0047         | 32.88 | 3.28479   |
|                      | 13.9383      | 0.19860 | 45     | 0.0071         | 42.11 | 6.34854   |

Figure. 16. XRD spectra of ligand(5-NTAMNP).
3.10. **EDX and FE-SEM analysis**

The morphology and the Topography for ligand (5-NTAMNP) is identified using FE-SEM, the Figure.17(a, b). Show FE-SEM and EDX spectra analysis of ligand. FE-SEM image shows the ligand (5-NTAMNP) where the nature of homogeneity of the surface and the distribution of particles and collected in a regular order, and illustrated the surface shape of the ligand on it as horizontal Micro-slices with granular appearance and has average size up to 96.91nm, these slices had different diameters and contain cavities containing pores and possess a high degree of ruggedness.

The EDX image shows that the prepared ligand includes only sulfur, carbon, nitrogen, and oxygen is similar to the chemical composition for azo ligand. This indicates a match in the atomic structure and to the purity of the synthesis azo ligand (5-NTAMNP). The EDX spectrum referred to weight percentage of each element within the composition of the ligand.

![Figure 17. (a) EDX spectra of ligand(5-NTAMNP).](image)
3.11. Antibacterial and antifungal activity

The antimicrobial activity of thiazolylazo dye ligand (5-NTAMNP) and its chelates complexes have been recorded in Tables.7. The biological activity (antibacterial and antifungal) have been carried out on selective two types of bacteria against Gram-positive bacteria: *Staphylococcus aureus*, *Streptococcus*. Antifungal studies were also carried out on selective four fungal like: *Alternaria alternata*, *Aspergillus niger*, *Mucor*, *Penicillium*. This biological activity completed via use Disc diffusion assay method [35], via using DMSO as a solvent, a certain range of optimal concentrations (1-2×10^{-4}M) of both ligand and its chelates complexes was prepared. The inhibitory zone diameter (IZD) was measured in centimeters (cm) and the assessment of activity was based on the measurement of the diameter of inhibition zone (IZD) around the wells and the results were tabulated. All of tested ligand and its chelates complexes show a remarkable antifungal activity against tested fungal. In detailed manner, the chelates complexes showed full inhibition of all growth fungi, while the ligand and its chelates complexes did not show any significant effectiveness against growth bacteria. The results of biological activity have been statistical presented in Figure.12.
Table 7: antimicrobial activity of the ligand and of its metal complexes.

| Compounds          | Staphylococcus S. aureus | Aspergillus-niger | Penicillium | Muor  | Alternaria |
|--------------------|--------------------------|------------------|-------------|-------|------------|
| Ligand (5-NTAMNP)  | +                        | +                | +           | +     | +++        |
| [Mn(L)₂]          | _                        | _                | +++         | ++    | +++        |
| [Fe(L)₂]          | _                        | _                | +++         | +++   | +++        |
| [Cu(L)₂]          | _                        | _                | +++         | +++   | +++        |
| [Pb(L)₂]          | _                        | _                | +++         | +++   | +++        |

_ = 00 mm, + = 25 mm, ++ = 45 mm and +++ = 85 mm.

4. Conclusions

Based on this experimental study, the following conclusions were reached: we have prepared and structurally characterized of new azo chelating ligand (5-NTAMNP) derived from thiazole. The structure of analytical reagent has been confirmed by the analytical data (EDX), mass spectrum, 1H NMR, FT-IR and electronic spectra. The azo ligand have different morphologies as appeared in XRD and SEM. The formation of the chelates metal complexes by the analytical data FT-IR and electronic spectra, the geometry proposed for all metallic complexes is octahedral structure (fig.15). The antimicrobial tests of the prepared ligand and its complexes has been studied and showed high activity and sensitivity against all fungal. The ligand and its metallic complexes are found to have higher biological activities toward antifungal and with full inhibition zone for metal complexes compared with free ligand (5-NTAMNP) toward the fungi used. but, the prepared ligand and its metallic complexes did not show any activity against the typed selective of bacteria tested against Gram-positive bacteria. We can conclude that all the metallic ion compounds synthesized were more active than the free ligand (5-NTAMNP).

References

[1] Peters, A. T., & Freeman, H. S. (1991). Colour chemistry: the design and synthesis of organic dyes and pigments. Elsevier Applied Science. Sole distributor in the USA and Canada, Elsevier Science Pub. Co.
[2] Roblin Jr, R. O., Williams, J. H., Winnek, P. S., & English, J. P. (1940). Chemotherapy. II. Some Sulfanilamido Heterocycles1. Journal of the American Chemical Society, 62(8), 2002-2005.
[3] J.D. Edward, M.N. Hughes and K.J. Rutt, J. Chem. Soc. (A), 2101-2105 (1969).
[4] Sharma, S. (2017). 2-(5-Chlorobenzo [d] thiazol-2-ylimino) thiazolidin-4-one derivatives as an antimicrobial agent. Arabian Journal of Chemistry, 10, S531-S538
[5] Ali, M. A., Mirza, A. H., Ting, W. Y., Hamid, M. H. S., Bernhardt, P. V., & Butcher, R. J. (2012). Mixed-ligand nickel (II) and copper (II) complexes of tridentate ONS and NNS ligands derived from S-alkylthiocarbazates with the saccharinate ion as a co-ligand. Polyhedron, 48(1), 167-173.
[6] Biswas, S., Pramanik, A. K., & Mondal, T. K. (2015). Palladium (II) complex with thiazole containing tridentate ONN donor ligand: Synthesis, X-ray structure and DFT computation. Journal of Molecular Structure, 1088, 28-33.

[7] Haas, K. L., & Franz, K. J. (2009). Application of metal coordination chemistry to explore and manipulate cell biology. Chemical reviews, 109(10), 4921-4960.

[8] Jana, S., Jana, M. S., Sarkar, D., Paiya, M. K., & Mondal, T. K. (2013). Ruthenium carbonyl complexes of 3-(2-(methylthio) phenylazo)-4-hydroxy-3-penten-2-one: Synthesis, spectral characterization, electronic structure and catalytic activity. Journal of Molecular Structure, 1054, 83-88.

[9] Bazel, Y., Tupys, A., Ostapiuk, Y., Tymoshuk, O., Imrich, J., & Šandrejová, J. (2018). A simple non-extractive green method for the spectrophotometric sequential injection determination of copper (ii) with novel thiazolylazo dyes. RSC Advances, 8(29), 15940-15950.

[10] Yadav, P. S., & Senthilkumar, G. P. (2011). Benzothiazole: different methods of synthesis and diverse biological activities. International journal of pharmaceutical sciences and drug research, 01-07.

[11] Fan, X., Zhu, C., & Zhang, G. (1998). Synthesis of 2-[2-(5-methylbenzothiazolyl) azol]-5-dimethylaminobenzoic acid and its application to the spectrophotometric determination of nickel. Analyst, 123(1), 109-112.

[12] Karipcin, F., Dede, B., Percin-Ozkorucuklu, S., & Kabalcilar, E. (2010). Mn (II),Co (II) and Ni (II) complexes of 4-(2-thiazolylazo) resorcinol: Syntheses, characterization, catalase-like activity, thermal and electrochemical behaviour. Dyes and Pigments, 84(1), 14-18.

[13] Wang, M., Lin, J. M., Qu, F., Shan, X., & Chen, Z. (2004). On-capillary complexation of metal ions with 4-(2-thiazolylazo) resorcinol in capillary electrophoresis. Journal of Chromatography A, 1029(1-2), 249-254.

[14] Al-Adilee, K. J., Abedalrazaq, K. A., & Al-Handiny, Z. M. (2013). Synthesis and Spectroscopic Properties of Some Transition Metal Complexes with New Azo-Dyes Derived From Thiazole and Imidazole. Asian Journal of Chemistry, 25(18).

[15] Al-Adilee, K., & Kyhoiesh, H. A. (2017). Preparation and identification of some metal complexes with new heterocyclic azo dye ligand 2-[2-(1- Hydroxy-4-Chloro phenyl) azol]-imidazole and their spectral and thermal studies. Journal of Molecular Structure, 1137, 160-178.

[16] J. Al-Adilee, Khalid & A. Jaber, Sudad. (2018). Synthesis, Characterization and Biological Activities of Some Metal Complexes Derived from Azo Dye Ligand 2-[2-(5-Methyl thiazoil)azol]-5-dimethylamino Benzoic Acid. Asian Journal of Chemistry. 30. 1537-1545. 10.14233/ajchem.2018.21222.

[17] Maradiya, H. R., & Patel, V. S. (2001). Synthesis and dyeing performance of some novel heterocyclic azo disperse dyes. Journal of the Brazilian Chemical Society, 12(6), 710-714

[18] Al-Adilee, K. J., & Fanfon, D. Y. (2012). Preparation, Spectral Identification and Analytical Studies of Some Transition Metal Complexes with New Thiazolylazo Ligand and Their Biological Activity Study. Journal of Chemistry and Chemical Engineering, 6(11), 1016.

[19] K.J. Al-Adilee, Res. J. Pharm. Chem. Sci. 6 (5) (2015) 1297e1308. 19.

[20] A. Skooge, D.M. West and F.J. Holler, Fundamentals of Analytical Chemistry, Saunders College Publishing, New York, edn. 5 (1988).

[21] Irving, H., & Williams, R. J. P. (1953). The stability series for complexes of divalent ions. J Chem Soc, 1953, 3192-3205.
[22] Mubarak, A. T. (2013). Novel complexes of zirconium and uranium derived from bifunctional azodyes donor ligands containing hydrogen bonds. *Journal of Saudi Chemical Society*, 17(4), 409-418.

[23] Al-Adilee, K. J. (2015). Preparation and Characterization of Some Transition Metal Complexes with Novel Azo-Schiff base Ligand Derived from 2(E)-1H-benzo[d] imidazole-2-yl diazenyl)-5-(E)-benzylideneimino) phenol (BIADPI). *RESEARCH JOURNAL OF PHARMACEUTICAL BIOLOGICAL AND CHEMICAL SCIENCES*, 6(5), 1297-1308.

[24] J. Al-Adilee, Khalid & A. Atyha, Saad. (2018). Synthesis, Spectral, Thermal and Biological Studies of Some Metal Complexes Derived from Heterocyclic Mono Azo Dye Ligand 2'(2'-Hydroxy-4-methyl phenylazo)imidazole. *Asian Journal of Chemistry*. 30. 280-292. 10.14233/ajchem.2018.20889.

[25] Al-Adilee, K. J., Abass, A. K., & Taher, A. M. (2016). Synthesis of some transition metal complexes with new heterocyclic thiazolyl azo dye and their uses as sensitizers in photoreactions. *Journal of Molecular Structure*, 1108, 378-397.

[26] Al-Adilee, K. J., & Shaimaa, A. (2017). Synthesis and spectral Properties studies of novel Hetro Cyclic Mono Azo dye Derived from Thiazole and Pyridine with Some Transition Complexes. *Oriental journal of chemistry*, 33(4), 1-14.

[27] Hankare, P. P., & Chavan, S. S. (2003). Studies on Some Binuclear Metal Complexes with Tetradentate Ligand Derived from 5-(2'-Thiazolylazo) salicylaldehyde and 2-Aminophenol. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 33(3), 423-434.

[28] Pavia, D. L., & Gary, M. (2001). Lampman George, S. Kriz, *Introduction to Spectroscopy third edition*, Brookscole.

[29] Stafford, U., Gray, K. A., & Kamat, P. V. (1996). Heterogeneous Chem. *Rev*, 3, 77.

[30] Karipcin, F., Kabalcilar, E., Ilican, S., Caglar, Y., & Caglar, M. (2009). Synthesized some 4-(2-thiazolylazo) resorcinol complexes: Characterization, thermal and optical properties. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 73(1), 174-180.

[31] Abazari, R., Mahjoub, A. R., & Sanati, S. (2014). A facile and efficient preparation of anatase titania nanoparticles in micelle nanoreactors: morphology, structure, and their high photocatalytic activity under UV light illumination. *RSC Advances*, 4(99), 56406-56414.

[32] Al-Adilee, K. J. (2018). Synthesis, Spectral and Biological Studies of Metal Complexes with Heterocyclic Ligand Derived from Thiaziolylazo Dye. *Journal of Global Pharma Technology*.

[33] Bai, S., Hu, J., Li, D., Luo, R., Chen, A., & Liu, C. C. (2011). Quantum-sized ZnO nanoparticles: synthesis, characterization and sensing properties for NO2. *Journal of Materials Chemistry*, 21(33), 12288-12294.

[34] Cruickshank R (1986) Medical microbiology: a guide to diagnosis and control of infection. E&S. Livingston Ltd, Edinburgh and London, p 888