Mn(II), Fe(III), Co(II) and Rh(III) complexes with azo ligand: Synthesis, characterization, thermal analysis and bioactivity

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Received 4/4/2022, Revised 20/5/2022, Accepted 22/5/2022, Published Online First 20/11/2022
Published 1/6/2023

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Abstract

New series of metal ion complexes have been prepared from the new ligand [4-Amino-N-(5-methyl-isoxazol-3-yl)benzenesulfonamide] derived from Sulfamethoxazole and 3-aminophenol. Accordingly, mono-nuclear Mn(II), Fe(III), Co (II), and Rh(III) complexes were prepared by the reaction of previous ligand with MnCl₂, 4H₂O, CoCl₂, 6H₂O, FeCl₃, 6H₂O and RhCl₃ H₂O, respectively. The compounds have been characterized by Fourier-transform infrared (FTIR), ultraviolet–visible (UV–vis), mass, ¹H–, and ¹³C–nuclear magnetic resonance (NMR) spectra and thermo gravimetric analysis (TGA&DSC) curve, Bohr magnetic (B.M.), elemental microanalyses, metal ions, chloride containing, and molar conductance. These reviews uncovered octahedral geometries for complexes. The investigation of complexes development by means at molar proportion and occupation strategy in DMF solution has been researched, and results were reliable to those found in the solid complexes with a proportion of (M:L) as (1:2).

Keywords: Azo complexes, Bioactivity, Mass spectroscopy, Spectroscopic studies, Thermal analysis.

Introduction:

The coordination compounds resulting from azo compounds are of increasing importance in the various fields of industry, agriculture, medicine, and medicine, and as auxiliary factors, and what helped them in this is the effective groups present in the compound originally, which gave them additional stability and effectiveness at the same time. Antibiotics are substances which, even at low concentrations, inhibit the growth and reproduction of bacteria. Infectious disease treatment would have been inconceivable today without antibiotics. In this work, we have tried in using diazotization coupling reaction between sulfamethaxazole (sulfur-containing organic compound) and 3-aminophenol(m-aminophenol)forming (E)-3-((4-amino-2-hydroxyphenyl)diazenyl)-N-(4-methylisoxazol-3-yl)benzenesulfonamide can be classified as azo compound that in turn coordinate with each of Mn(II), Fe(III), Co(II) and Rh(III) metal ions in 2:1 ratio. In such reactions, the use of acidic media to prepare the intermediate compound is the basis for the preparation of important azo compounds with widespread uses in various fields. The aim of this work is to synthesize a novel azo ligand from an aromatic amine with spectroscopic analysis of (NMR, Mass, IR, UV-Vis) and studying of thermal decomposition and thermal stability by using TGA and DSC, its composition as well as to synthesize Mn(II), Fe(III), Co(II) and Rh(III) complexes with spectroscopic analysis and studying of thermal decomposition and thermal stability by using TGA and DSC.

Material and methods:

Materials and instrumentation

The Sulfamethoxazole, Hydrochloric acid, Sodium Nitrite NaNO₂, 3-aminophenol, Sodium Hydroxide NaOH, ethanol, methanol, DMSO, DMF, MnCl₂.4H₂O, CoCl₂.6H₂O, FeCl₃, 6H₂O and RhCl₃ H₂O Equipped with (Sigma-Aldrich, Merck, and others). The complexes' molar conductances were measured by using a Conductometer WTW at 25°C at a concentration of 1×10⁻³M. DMSO was used to dissolve all of the complexes (DMSO). On a mass spectrometry (MS) QP50A: DI Analysis

642
ShimadzuQP-2010-Plus (E170Ev) spectrometer, the UV–Vis spectrophotometer UV-1800 Shimadzu was used to analyze the spectra in the ultraviolet–visible (UV–Vis) range, and the IR Prestige-21 was used to investigate the (FTIR) spectra, and the PerkinElmer Pyris Diamond TGA&DSC was used to conduct thermogravimetric studies. A Brucker500 MHz was used to record the proton nuclear magnetic resonance (1H&13C-NMR) spectra for ligand in DMSO-d6. The Euro vector model EA/3000, single-V.3.O-single, was used to conduct elemental analyses (C, H, N, S and O). Metal ions were estimated as metal oxides using a gravimetric method, mass spectra for substances were recorded.

**Synthesis of azo dye ligand**

The ligand in Scheme 1, was synthesized according to the suggested method10. Dissolving (1g, 3.948 mol) of Sulfamethoxazole in a mixture composed of 37% (2ml) concentrated Hydrochloric acid HCl, (15ml) distilled water and 15 ml of ethanol. The solution is cooled from 0°C up to 5°C then a gradual addition of (10%, 1g, 14.49mmol) hydrated Sodium Nitrite NaNO2 to the solution occurs with continuous stirring and avoid any increasing in temperature up to 5°C. Then leaving the solution for about 45 min. to perform the diazotezation process resulting in diazonium salt, salt solution is adding gradually with continuous stirring onto (0.43g, 3.948mmol) of 3-aminophenol dissolved in 20ml of ethanol. Change in solution's color into dark color is observed keeping on stirring about 30 min. to perform the reaction. The solution isolates until being stable then adding few drops of Sodium Hydroxide NaOH solution in order to equivalence the middle of reaction till reaching to 6.8pH at which the perfect precipitating of ligand occurs. Finally, the former is filtered and making recrystallization by methanol and dried resulting in 1.34g, 90.70%, 192-194°C m. p and orange precipitate., The yield is (1.34g), 90.97%, mp.192-194°C.1H-NMR (DMSO-d6, ppm) Ar-OH (11.14, 1H, singlet) , N-H (9.51,1H , singlet)Ar-H(7.78-7.80, 4H, multiplet) C-H(aromatic) besides OHC-H(aromatic) besides NH2(6.87, 2H, douplet) Ar-NH2 (5.94, 2H, singlet) C-H (aromatic) besides CH3 (5.49, 1H, singlet) CH3 (2.51, 3H, singlet) DMSO (solvent) (2.55 – 2.64) : 13C-NMR (DMSO , ppm, ): 15.16(C-1), 174.60(C-2), 107.50(C-3), 167.70(C-4), 162.15(C-5), 131.97(C-6 C-7), 132.02(C-8), 146.94(C-9), 148.76(C-10), 157.27(C-11), 134.31(C-12), 115.39(C-13), 121.95(C-14), 151.10(C-15), 153.24(C-16)11-13. Fig.1, show the 13C-NMR spectrum of ligand.

**General method for the preparation of metallic ions complexes**

The metallic ions complexes were made with metal chlorides for Mn(II), Fe(III), Co(II) and Rh(III). An amount of (0.373g, 1m.mol) from azo ligand, dissolved in 10 mL absolute ethanol, was gradually added in drops wise with stirring to a (0.5m.mol) amount of [1:2] M:L for Mn(II), Fe(III), Co(II) and Rh(III), MnCl2.4H2O, CoCl2.6H2O, FeCl3.6H2O and RhCl3.H2O. The mixture was heated for 2 hours at (50-70)°C, then chilled in an ice bath until precipitated, then left overnight. To remove any unreacted components, the solid complexes were separated and washed with distilled water and a little amount of hot ethanol. Finally, vacuum desiccators were used to dry the complexes. The analytical and physical properties of the ligand and its metal complexes are summarized in Table 1.
Scheme 1. Synthesis of ligand and its complexes

Figure 1. $^{13}$C-NMR spectrum of ligand
Result and Discussion:
Physical and chemical properties of azo dye ligand

Microscopic analysis of the elements, the infrared spectrum, the proton NMR spectrum, carbon NMR spectrum, the malar conductivity, TGA & DSC and Mass, and the azo complexes was used to identify the prepared ligands and their complexes. Table 1 shows this with some physical properties.

| Comp. | Chemical Formula | Color | m.p. | Elemental microanalysis % |
|-------|-----------------|-------|------|---------------------------|
|       | M.Wt |                 |      | C     | H     | N      | O      | S      | M      | Cl    |       |
|       |       |                 |      | Foun. | Foun. | Foun.  | Foun.  | Foun.  | Foun.  | Foun. |
| LH    | C₁₆H₁₅N₆S₂O₅S | Orange | 192  | 52.44 | 4.99  | 20.01  | 16.1   | -      | -      | -     |
|       | 373.39 |       |      | 194   | 51.47 | 4.05   | 18.76  | 17.1   | 8.59   | -     |
| [Mn(L)₂(H₂O)]₂ | C₉₂H₃₂N₁₀CoO₁₀ | Dark brown | 266 | 44.89 | 4.60  | 17.09  | 20.2   | 7.12   | 5.96   | -     |
|     | 835.73 |       |      | 45.99 | 3.86  | 16.76  | 19.1   | 7.39   | 6.57   | -     |
| [Fe(L)₂(H₂O)₂Cl] | C₉₂H₃₀N₁₀CoO₁₀ | Brown | 256 | 45.04 | 4.23  | 17.21  | 16.3   | 7.79   | 6.33   | 4.88  |
|     | 854.07 |       |      | 257   | 45.00 | 3.54   | 16.40  | 16.8   | 7.51   | 6.54   | 4.15  |
| [Co(L)₂(H₂O)₂] | C₉₂H₃₂N₁₀CoO₁₀ | Brown | 213 | 46.24 | 4.15  | 17.07  | 18.8   | 7.89   | 6.75   | -     |
|     | 839.72 |       |      | 215   | 45.77 | 3.84   | 16.68  | 19.0   | 7.64   | 7.02   | -     |
| [Rh(L)₂(H₂O)₂Cl] | C₉₂H₃₀N₁₀RhO₁₂ | Red brown | 301 | 43.05 | 2.98  | 14.89  | 14.9   | 8.08   | 8.08   |       |
|     | 901.13 |       |      | 42.65 | 3.36  | 15.54  | 15.9   | 7.12   | 7.12   |       |

D = decompose

Electronic spectra measurements

The UV–Vis spectra of the ligand LH and its complexes. With absorption maxima at (253 nm, 38759.6 cm⁻¹) ascribed to the π→π* transition and two peaks at (435 nm, 22988.5 cm⁻¹) attributed to the n→π* transition a peak with a high intensity band formed with absorption maxima. There were six absorption peaks in the electronic spectra of the [Mn(L)₂(H₂O)₂] complex. The peaks at 275nm and 360nm is ascribed to the ligand, while the (π→π*) complex, the peak at 402 nm is ascribed to the ligand, while the n→π* complex and three peaks in the (602nm) (713nm) and (809nm) while the one peak at are attributed to the (d-d) electronic transitions types ⁶A₁₇→⁴A₁₇, ⁴E₉(G), ⁶A₉→²T₂₃(G) and ⁶A₉→²T₁₅(G) respectively. Furthermore, the magnetic moment of the Mn(II) (d⁵) complexes is found to be (3.71 B.M)⁹⁻¹⁰. All the above mentioned data correspond to an octahedral geometry. The electronic spectrum of the paramagnetic (3.66B.M)Fe(III) complex was ascribed to the peak at 280nm and 360nm is ascribed to the ligand, while the(π→π*) and (n→π*), and the three peaks at 684nm, 850nm and 996nm was assigned to the ⁶A₁₇→²A₁₇, ⁶E₉(G), ⁶A₉→²T₂₃(G) and ⁶A₉→²T₁₅(G)transitions, respectively, indicating an Octahedral geometry Fig.2. While the electronic spectra of the Co(II) complex revealed to the peak at 267nm and 451nm is ascribed to the ligand, while the (π→π*) and [n→π* & C.TML] and three peaks at 730nm, 922nm and 1027nm corresponding to²T₁₅→²T₁₅, ²T₁₅→²A₂₅ and ²T₁₅→²T₂₅, respectively indicating an octahedral geometry and the Co(II) complex was paramagnetic (3.88 B.M.)¹⁷⁻¹⁹. The electronic spectrum of the diamagnetic Rh(III) complex was ascribed to the peak at 268nm and 446nm is ascribed to the ligand, while the (π→π*) and [n→π* & C.TML], and the three peaks at 752nm 900nm and 998nm was assigned to the ¹A₁₇→¹T₁₇, ¹A₁₇→¹T₂₃ and ¹A₁₇→¹T₂₅ transitions, respectively Fig.3, indicating an Octahedral geometry diamagnetic²⁰. Table 2 show the data of complexes electronic spectra and molar conductivity.

645
Figure 2. Electronic spectra of Fe-complex

Figure 3. Electronic spectra of Rh(III)complex
Liquid chromatography–mass spectrometry (LC–Mass) measurements

The electron impact of fragmentation was used to acquire mass spectra of the ligand and metal complexes. High-resolution MS of the free azo ligand and its complexes, as well as large fragments linked to breakdown products, was obtained in general. The electron impact mass spectrum of ligand LH. This ligand molecular weight is calculated to be 373.39g/mol. The spectra showed a peak at 373 m/z, which was attributed to [M]+ and corresponded to a novel azo moiety C₁₈H₁₃N₅O₅S. Their brightness indicates the pieces’ stability Fig.4 depicts the mass spectrum of the Mn(II) complex. The complex moiety C₃₂H₃₂S₂N₁₀MnO₁₀ had a peak at 836 m/z, which corresponded to the complex moiety C₃₂H₃₂S₂N₁₀MnO₁₀ in the spectrum. Fig.5 depicts the mass spectrum of the Fe(III) complex. The compound moiety C₃₂H₃₀N₁₀O₆FeClS₂ was identified by a peak at 854 m/z in the spectra. The electron impact mass spectrum of the Co(II) complex. The complex moiety C₃₂H₃₂N₁₀O₆CoCl₂ was identified by a peak at 839 m/z in the spectra. The electron impact mass spectrum of Rh(III). This complex molecular weight is calculated to be 901.13/mol. The spectra showed a peak at 901 m/z, which was attributed to [M]+ and corresponded to a novel azo moiety C₃₂H₃₀N₁₀O₆S₂RhCl₂. In Schemes 2–6, suggested fragmentation routes and structural assignments of pieces are given.

Table 2. Electronic spectral data of the metal complexes with LH ligand and molar conductivity in DMSO (1 × 10⁻³ M)

| Complexes Geometry | λmax (nm) | vcm⁻¹ | ABS | εmax L mol⁻¹ cm⁻¹ | Assignment | v cm⁻¹ | Ω mol⁻¹ |
|-------------------|-----------|--------|-----|------------------|------------|--------|--------|
| LH                | 258       | 38759.6| 1.182| 1182             | π* → π     | 1.182  |        |
| [Mn(L)₂(H₂O)₂]   | 275       | 36363.6| 2.061| 2061             | π* → π     | 2.061  |        |
| Octahedral        | 360       | 27777.7| 3.200| 3200             | π* → π     | 3.200  |        |
|                   | 402       | 24875.6| 3.298| 3298             | π* → π     | 3.298  |        |
|                   | 602       | 16611.2| 0.197| 197              | π* → π     | 0.197  |        |
|                   | 713       | 14025.2| 0.225| 225              | π* → π     | 0.225  |        |
|                   | 809       | 12360.9| 0.180| 180              | π* → π     | 0.180  |        |
| [Fe(L)₂(H₂O)Cl]  | 280       | 35714.2| 2.661| 2661             | π* → π     | 2.661  |        |
| Octahedral        | 360       | 27777.7| 1.500| 1500             | π* → π     | 1.500  |        |
|                   | 684       | 14619.8| 0.350| 350              | π* → π     | 0.350  |        |
|                   | 850       | 11764.7| 0.180| 180              | π* → π     | 0.180  |        |
|                   | 996       | 10040.0| 0.151| 151              | π* → π     | 0.151  |        |
| [Co(L)₂(H₂O)₂]   | 267       | 37453.1| 0.480| 480              | π* → π     | 0.480  |        |
| Octahedral        | 451       | 22172.9| 0.998| 998              | π* + C.TML → n | 0.998  |        |
|                   | 730       | 13698.6| 0.110| 110              | π* → π     | 0.110  |        |
|                   | 922       | 10845.9| 0.108| 108              | π* → π     | 0.108  |        |
|                   | 1027      | 9737   | 0.130| 130              | π* → π     | 0.130  |        |
| [Rh(L)₂(H₂O)Cl]  | 268       | 37313.4| 1.753| 1753             | π* → π     | 1.753  |        |
| Octahedral        | 446       | 22421.5| 2.100| 2100             | π* + C.TML → n | 2.100  |        |
|                   | 752       | 13297.8| 0.098| 98               | 1T₁g → 1A₁g | 0.098  |        |
|                   | 900       | 11111.1| 0.113| 113              | 1T₂g → 1A₁g | 0.113  |        |
|                   | 998       | 10020  | 0.196| 196              | 3T₂g → 1A₁g | 0.196  |        |
Figure 4. (LC–Mass) spectrum of Mn-complex

Figure 5. (LC–Mass) spectrum of Fe complex
Scheme 2. Fragmentation pattern of ligand

Scheme 3. Fragmentation pattern of Mn complex
Scheme 4. Fragmentation pattern of Fe complex Scheme

Scheme 5. Fragmentation pattern of Co complex
Infrared spectra measurements

The azo ligand spectra and their metal chelates complexes with Mn(II), Fe(III), Co(II) and Rh(III) have been compiled, and the data has been organized in Table 3. The ligand displayed bands at 3377, 3318 and 1618 cm\(^{-1}\) that were ascribed to the stretching vibration \(\nu(NH_2)\), \(\nu(NH_2)\), and out of plane of \(\delta(NH_2)\), but these bands were reduced to a non lower frequency in the spectra of all generated compounds, indicating not coordination with a metal ion\[24\]. The \((N=N)\) stretching vibration was attributed to the band seen at 1467, 1406 cm\(^{-1}\) in the unbound azo ligand (LH). This band was discovered in the compounds' spectra around (1464-1442),(1444-1411) cm\(^{-1}\). The engagement of the azo group in chelation was verified by a change in the azo group of the azo ligand\[25\]. In addition, prior study has shown that in the presence of transition metals, the azo-dye nitrogen is always more likely to favor complication\[26\]. Because of the presence of coordinated water molecules in the complexes, it was difficult to confirm that this group was involved in chelate formation. The existence of coordinated water molecules in the coordination sphere was ascribed to the appearance of OH bands in the IR spectra of the Ni(II) complex in the (3733-3655)cm\(^{-1}\). In addition, stretching vibrations in the range of (1544-1579) and (737-768) cm\(^{-1}\) were shown to correlate to \(\nu(M-OH_2)\) in (500-569) cm\(^{-1}\).

This is a strong evidence that water molecules are involved in the coordination process\[27\]. For the unbound ligand, the IR spectra revealed a wide stretching vibration band at 3492 cm\(^{-1}\), which might correlate to \(\nu(OH)\) of the phenolic group\[28\]. The band at 1284 cm\(^{-1}\) was assigned to the \(\nu(C-O)\) stretching vibration of the phenolic group of the free azo-dye ligand. After this, the IR spectra of all produced compounds revealed that the azo-dye ligand connected to metal ions through two sites: the azo group's nitrogen site, and oxygen site via deprotonation of the phenolic group\[29\]. As a result, in the all complexes, the ligand behaved as an N, O bidentate ligand.
Table 3. The IR spectra bands (cm\(^{-1}\)) of the ligand azo and its complexes

| Compounds                  | (H\(_2\)O) aquav | (NH\(_2\))v | (NH)v | (N=H)v | (SO\(_2\))v | (M-O)v | (M-N)v |
|---------------------------|------------------|-------------|--------|---------|-------------|--------|--------|
| LH                        | -                | 3377        | 3142   | 3042    | 1467        | 1035   | -      |
|                           |                  | 3318        |        | 2927    | 1406        |        |        |
|                           |                  | 1618        |        |         | 1091        |        |        |
| [Mn(L)\(_2\)(H\(_2\)O)]\(_2\)] | 3733            | 3443        | 3285   | 3079    | 1457        | 1041   | 508    |
|                           | 1579             | 3332        |        | 2929    | 1411        |        | 1096   | 569    |
|                           | 762              | 1625        |        |         |             |        |        |
| [Fe(L)\(_2\)(H\(_2\)O)]Cl | 3742             | 3311        | 3191   | 3053    | 1464        | 1021   | 500    |
|                           | 1566             | 3287        |        | 2917    | 1444        |        | 1119   | 686    |
|                           | 768              | 1642        |        |         |             |        |        |
| [Co(L)\(_2\)(H\(_2\)O)]\(_2\)] | 3655            | 3330        | 3174   | 3098    | 1442        | 1078   | 569    |
|                           | 1565             | 3267        |        | 2922    | 1159        |        | 639    |
|                           | 737              | 1615        |        |         |             |        |        |
| [Rh(L)\(_2\)(H\(_2\)O)Cl] | 3739             | 3322        | 3122   | 3055    | 1464        | 1014   | 514    |
|                           | 1544             | 3287        |        | 2917    | 1123        |        | 669    |
|                           | 768              | 1644        |        |         |             |        |        |

Study of Thermo Gravimetric Analysis for compounds by TGA & DSC Curve

The results of DSC and TGA of ligand and Fe and Co complexes are given in Table 4 and Fig.6-8. The thermograms have been carried out in the range of 25–700°C at a heating rate of 10°C/min in nitrogen atmosphere, the ligand showed little thermal stability at 41°C, similar to the little stability complexes in the range of 48.623°C for Fe and 74.433°C for Co complexes, indicating the presence of water molecules in the Co and Fe complexes, whether water hydrate or aqua and as well as DCS the determination of the exothermic and endothermic given in table. 4. They show an agreement in weight loss between their results obtained from the thermal decomposition and the calculated values, which supports the results of elemental analysis and confirms the suggested formulae

![Graph showing DSC and TGA results](image-url)
Figure 6. DSC & TGA curve of Ligand
Figure 7. DSC & TGA curve of Co-complex
Figure 8. DSC & TGA curve of Fe-complex

Scheme 7. Tentative decomposition reaction of complexes
Table 4. DSC data TGA records for the ligand and its complexes

| Compound     | T$_1$ / °C | T$_d$ / °C | T$_{DTG}$ Max | % (calculated) Mass loss | Estimated Total mass loss | Assignm ent | $\Delta$H J/g | Maximum temperature point C and Type |
|--------------|------------|------------|---------------|--------------------------|--------------------------|-------------|----------------|-------------------------------------|
| (HL)         | 119.634    | 597.547    | 306.76        | 97.976                   | 97.976                   | C$_{15}$H$_{12}$N$_3$O$_4$S, C | -37.45     | -17.08, C | 66.8-endothermic, 150.79-endothermic |
|              | 2.024      | (3.214)    |               |                          |                          | C           | 238.78        | 189.75-endothermic, 254.77-endothermic |
| [Fe(L)$_2$(H$_2$O)Cl] | 48.623     | 166.89     | 106.11        | 5.987(5.386)             | 92.245                   | -H$_2$O      | -115.03      | 99.62-endothermic                  |
|              | 7          | 3          |                |                          | (91.501)                 | -CO          | -222.66      |                                     |
|              | 166.89     | 246.4      | 202.20        | 10.451(10.7)            | 61.574                   | -SO$_2$       | -125.67      |                                     |
|              | 7          | 6          | 71            |                          |                          | SO           | 50.47        |                                     |
|              | 246.4      | 392.13     | 298.66        | 49.897(48.1)            | 39.37                   | -SO$_2$, NO, Cl | -9.22       |                                     |
|              | 2          | 3          | 81            |                          |                          | CI           | 157.80-endothermic |                                     |
|              | 392.13     | 596.75     | 483.62        | 26.000(27.1)            |                         | C$_{14}$H$_{10}$N$_8$ | 215.11-endothermic |                                     |
|              | 2          | 5          | 64            |                          |                         | C$_{16}$H$_{10}$N$_3$ | 251.01-endothermic |                                     |
| [Co(L)$_2$(H$_2$O)$_2$] | 74.433     | 118.70     | 93.642        | 4.745(4.287)            | 91.568                   | FeO          | -2.09        | 75.44-endothermic                  |
|              | 0          | 118.70     |                |                          | (90.981)                 | -H$_2$O      | -3.03        | 267.34-endothermic                  |
|              | 0          | 311.70     | 256.66        | 17.983(17.3)            | 15.70                   | -CO$_2$, C$_{14}$H$_{10}$N | -9.22       | 392.40-endothermic                  |
|              | 331.10     | 596.70     | 392.29        | 68.840(69.3)            |                         | C$_{20}$H$_{22}$N$_9$O$_4$S | 15.70       |                                     |
|              | 5          | 4          | 80            |                          |                         | CoO          | 16           |                                     |

Vital diagnosis

The findings showed that the produced ligand and its constituents were biologically efficient, since the experiment was carried out in aerobic circumstances at a temperature of 37°C. Drilling was used to exposing every pathogenic active compound pathogenic bacteria to two different types of pathogenic bacteria S aureus, P aeruginosa and Fungi P. expansum, F. graminearum, M. phasealina, and C albicans which were used the DMF solvent with 1×10$^{-3}$M concentrations and showed different efficacy to the negative and positive stain-bacteria of the compounds. The data are shown in the table 5 below in (mm)$^{35-38}$.

Table 5. vital returns

| Compounds         | Positive and negative bacteria | Fungi |
|-------------------|--------------------------------|-------|
|                   | S.T                           | P.A   | Pe.  | F.M  | M.P | Ca.a |
| Conc.             |                                |       |      |      |     |      |
| MnCl$_2$.4H$_2$O  | 15 A                          | 12 B  | 16 A | 15 B | 38  | 28   |
|                  | 16 B                          | 16 B  | 15 B | 15 B | 38  | 33   | A    |
| MnL$_2$(H$_2$O)$_2$ | 12                             | 12    | 12    | 12  | 12  |      | A    |
|                  |                                |       |      |      |     |      | B    |
| CoCl$_2$.6H$_2$O  | 40                             | 25    | 23    | 18  | 30  | 18   | 26   |
|                  | 15                             | 0     | 15    | 0   | 13  | 0    | 0    | 0    |
| CoL$_2$(H$_2$O)$_2$ | 20                             | 0     | 15    | 0   | 13  | 0    | 0    | 0    | 0    |
| Control           | 0                              | 0     | 0     | 0   | 0   | 0    | 0    |

S.T = Staphylococcus aureus, P.A = Pseudomonas aeruginosa, Pe. = Penicillium expansum, M.P = Macrophomina phaseolina and Candida albicans = Ca.a, A= conc $1*10^{-3}$, B= dilute $1*10^{-4}$.

Study complexes in gas stat (theoretical studies)

The Theoretical study for the formed entity (LH) was accomplished at its gaseous state in order to detect the stretching vibrations and Fourier transform spectra and make a competition for them with the practical returns and detect the mistake percentage, and so forth for the complexes, show as electrostatic potential (HOMO and LUMO) as 2D& 3D Fig. 9.
Optimized geometries of LH and their complexes
The expected geometric shapes of the prepared compounds were also drawn according to the results of the analyzes Fig.10.

HOMO = -8.64499 Ev
LUMO = -2.079227 eV

Figure 9. Electrostatic potential (HOMO and LUMO) as 2D & 3D contours for (LH)
Conclusion
The ligand chemical is a brand-new azo dye that has never been made before. $^1$H & $^{13}$C-NMR, IR, UV-Vis, TGA, DSC and Mass spectrum techniques were used to identify the ligand and its complexes. The estimated values and the results of the elemental micro analysis were found to be in good agreement. The ligand bidentate character was suggested by IR measurements. Complexation happens through –NO moiety, according to multinuclear NMR data. Complex molecules are more stable, therefore the process requires less equipment to advance. The biological activity of some prepared compounds against two types of bacteria and four type's fungi was also studied, and it gave varying inhibition values.

Author's declaration:
- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors Contribution:
Al-Hamdani AAS presented the idea, analysis, discussion of the results and writing of the manuscript. Shaimaa Mohammed Reda contributed to the design and implementation of the esearch, laboratory work, verified the analytical methods and discussed the results and contributed to the final manuscript

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معقدات المنغنيز الحديد الكوبلت الروديوم مع ليكاندازو : تحضير، تشخيص، تحليل حراري وفعالية حيوية

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الخلاصة:
حضرت سلسلة من معقدات من ايونات المعادن من الليكاند الجديد 4-امينو-5-(إثنامينوفرمازول-3-يل) بنزينيل 4-امينوفنيل و 6-امينوفينول، المعقدات احادية النوى لكل من المنغنيز الثنائي وال الحديد الثلاثي والكوبلت الثنائي والروديوم الثلاثي كمكملات مع تفاعلك تفاعلا مع أملاح ايونات المعادن. المركبات فحصت بأطوار تحت الحمراء وفوق البنفسجية، وكميات الكتلة ورنين نووي المغناطيسي للمريخ والكربون وكميات الكتلة والتخليل الحراري الوزني والمسح الحراري التفاضلي وحساسية المغناطيسية وتحليل دقيق للعناصر، ونسبة الهيدروكسيد النيكل والكروم والنيكل والكربون، وفقاً للدراسات التحليلية أعطت المعقدات شكل ثماني السطح (6:6:6) (ليكاند مختلي). وبناء على الدراسات الحرارية فإن المعقدات تحوي جزيئات متصلبة.

الكلمات المفتاحية: معقدات الازو، فعالية حيوية، مطيافية الكتلة، دراسات طيفية، التحليل الوزني الحراري.