Journal of Advances and Scholarly Researches in Allied Education
Vol. 19, Issue No. 1, January-2022, ISSN 2230-7540

Synthesis of Novel Complexes with Interaction of Ligand and Metal Ions Such as Mn (II), Fe (III), Co (II), Ni (II) and Cu (II)

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Abstract - Sulfuric acid and a Compounds of cobalt, nickel, copper, cadmium, and iron have been created by combining a Schiff base obtained from 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (1). The ligand and its complexes have been analyzed using techniques such as infrared and 1H nuclear magnetic resonance spectra, elemental investigations, The techniques used include ultraviolet-visible spectroscopy and discrepancy current investigation using thermogravimetry (TGA-DTA). Analytical data shows that the metal-to-ligand proportion in Cu (II) complexes is 2:2, but in Co (II), Ni(II), Cd(II), and Fe(II) complexes, it is 1:2. N- [5' -Amino-2,2' -bis(1,3,4-thiadiazole)-5-yl] is the chemical name of the substance. With the exception of Ni (II) and Cu (II), the predicted structures for the formation of Fe (II), Co (II), and Cd (II) are octahedral, tetrahedral, and square-planar features, respectively. The synthesis of novel Two distinct ligands, Benzaldehyde with two carbon and hydrogen bonds Cobalt (II), nickel (II), copper (II), and zinc (II) were among the metallic compounds reacted with Benzaldehyde picolinoyl hydrazine (CBPH) and 4-methylbenzoylhydrazone (CBMH) are two examples. This reaction led to the formation of metal complexes. Condensation reactions using Hydrazide, 2-carboxy benzaldehyde, 4-methylbenzoyl, and picolinoyl estersindividually, were used to produce CBMH and CBPH. [M(L-H)2] complexes are genuine. The characterization of xH2O was performed using spectral measurements, including UV-Vis, IR, molar conductance, and chemical analysis. All the complexes involving the hydrazones CBMH and CBPH have the ligand function, exhibiting monobasic tridentate characteristics.

Keywords - Transition Metal Complex, 1,3,4-Thiadiazole, Salicylaldehyde, Schiff Base and Complexes.

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INTRODUCTION

Schiff bases and complexes display a great deal of diversity in inorganic chemistry. Therefore, it is crucial for the progress of biochemistry, pharmacy, and medicine to find novel organic and inorganic chemicals that exhibit outstanding anti-fungal, anti-bacterial, and anticancer properties. While Schiff bases and their derivatives have been studied extensively across many scientific domains, amino acid imines have been given much less attention because of their difficulty in column purification. The conformational flexibility of their backbones facilitates the generation of new compounds in simpler coordination forms, and they outperform conventional Schiff bases in terms of stability and solubility in organic solvents. Several published research have examined the biological consequences of d-group metal complexes containing nitrogen and oxygen donor atoms.

Infectious diseases caused by microbes have seen a dramatic increase in frequency. Despite several significant advances in antimicrobial therapy, the evolution of bacteria resistant to antibiotics has resulted from their misuse and abuse, posing a serious threat to public health. Staph infections that are resistant to methicillin, streptococcus aureus that are resistant to vancomycin, and enterococci that are resistant to vancomycin are example of the multidrug-resistant gram-positive bacteria that have recently emerged as a big problem in the field of bacterial illness treatment. Therefore, finding new compounds that can fight bacteria that have evolved resistance is one of the main objectives of contemporary antibacterial research.

The function of a thiazole ring is essential in the natural environment. Thiamine is one example of a coenzyme that is necessary for the process of oxidatively removing a carboxyl group from α-keto acids. One of the earliest and crucial broad-spectrum antibiotics, penicillin, is structurally related to a tetrahydrothiazole. Some of the most helpful drugs include thiazoles and thiazolamines. A molecule's potential biological function is immediately obvious when it has a thiazole ring. In a similar vein, 2-aminothiazoles are acknowledged as physiologically active compounds with a broad range of activity; they are used as intermediate products in the production of antibiotics and dyes. 2-Aminothiazole derivatives have widespread use in the pharmaceutical industry. Antibacterial and antioxidant capabilities are shown by aminothiazole. A number of substituted aminothiazole derivatives have antioxidant properties that might be useful in a variety of applications, including mineral processing, hydrocarbon fuels, solid paraffin, polyolefins, and vegetable fats. The addition of 2-aminothiazole fragment substituents to sym triazine derivatives improves lubricating lubricants by making them more resistant to corrosion, wear, and scuffing.

LITERATURE REVIEW

Soleimani, Esmaiel. (2010) This is the description of the process for making The compound The evolution of 1,2-dibromobenzilmonoxime (BBOH) Sodium bibromide trihydrate. According to the results obtained from the infrared, hydrogen, and carbon nuclear magnetic resonance (IR) spectroscopy of Mn (II), Co (II), and Cu (II) seem to be compounds with oxygen atoms from carbonyl and nitrogen atoms from oxime groups establish a connection between 4,4′-dibromobenzilmonoximate and metal (II) ions. Electronic spectra collected from M(II) complexes in DMSO provide significant evidence for octahedral coordination.

Tas, E & Kilic (2010) Various complexes including steric hindered Schiff-base ligands and their mononuclear Cu (II), Co (II), Ni (II), Mn (II), and Fe (II) ions are detailed in this paper, including their chemical make-up, physical composition, and electro-spectrochemical properties (LH (2)). By reacting 3,5-Bu(t)(2)-salicylaldehyde with 3,4-diaminobenzophenon, a new asymmetrical Schiff-base ligand with bulky steric hindrance and a donor set including nitrogen and oxygen atoms was synthesized. A variety of A stoichiometric ratio of metal salts to an ethanolic ligand solution was used to produce metal complexes. Magnetic susceptibility, electrochemistry, spectro-electrochemistry, molar conductivity, Thermal analysis, ultraviolet-visible spectroscopy, nuclear magnetic resonance, elemental analysis, and (1)H spectroscopy utilizing Fourier transform infrared were among the methods used to describe the ligand and its complexes.The tetradentate and mononuclear metal complexes were generated by combining a little amount of metal acetate with an N,N'-(3,4-benzophenon)-3,5-Bu(t)(2)-salicylaldimine (LH(2)) in a mole ratio of one to one. Metal complexes are likely not electrolytes, according to the molar conductance measurements.

Lidia Zapała (2021) The minimum formula for the compounds was determined to be $M(nif)_2 \cdot nH_2O$ using the findings The techniques used include quantitative analysis using elemental analysis (EA), TG/DTG-DSC, and complexometric titration with EDTA. In this context, M represents the metal ion, nif represents the niflumate ion, and n ranges from 1 to 2.25. There is one particular example that is very notable: the compound including Fe(III) ions, denoted as $Fe(nif)_3 \cdot H_2O$. The results showed that there are two distinct binding modes for niflumate ligands to metal ions. Based on the results of the TG/DTG-DSC research, the thermal breakdown of the compounds was shown to be a multi-stage process that is atmosphere and metal ion dependent. A two-step process is required for the dehydration of these compounds, according to the comprehensive DSC study. Using combined TG-FTIR-MS methods, we were able to determine the aim is to analyze the gaseous byproducts produced during the pyrolysis and thermal oxidation of the compounds, and to study the mechanisms by which the synthetic compounds break down. Several of the synthesized complexes exhibited more activity than the ligand in the antibacterial analysis. The effectiveness against the microorganisms Pseudomonas aeruginosa and Escherichia coli is more pronounced in the combination containing Zn(II) ions. This chemical has 31-fold lower MIC values against E. coli compared to niflumic acid. Moreover, when compared to the reference medications against P. aeruginosa, kanamycin and chloramphenicol, this molecule was five and 1.25 times more effective, respectively.

RESEARCH METHODOLOGY

The following substances were acquired from Merck: thiosemicarbazide, the substances used, salicylaldehyde, oxalic acid, phosphorous oxychloride, sodium hydroxide, and glacial acetic acid, were not subjected to any further purification prior to their usage. All our solvents were procured exclusively from either Merck or Aldrich. The salts of metals CuCl2 2H2O, NiCl2 6H2O, CdCl2 H2O, and FeCl2. 6H2O utilized after being bought from Merck precisely according to their provided descriptions. In a 100 mL round-bottom flask, 0.61 g of the ligand HL (equivalent to 2 millimoles, or mmol) was combined with 20 mL of N,N-dimethylformamide (DMF). The following metal salt solutions were added drop by drop while stirring continuously during a 15-minute period at room temperature: In 10 milliliters of pure ethanol, dissolve 0.6 grams of cobalt chloride, 0.2 grams of nickel chloride, 0.1 grams of copper chloride, 0.20 grams of cadmium chloride, and 0.41 grams of iron chloride. Subsequently, the reaction mixture underwent reflux for a further 6 hours at a temperature range of 100-120°C.

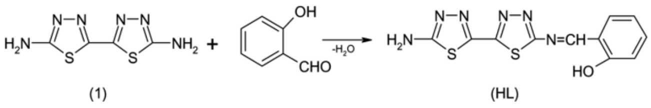


Figure 1: The ligand synthesis involves the formation of N-[5'-amino-2,2'-bis(1,3,4-thiadiazole)-5-y1].The compound is called -2-hydroxybenzaldehyde imine (HL1).

After filtering out the precipitates, they were cleaned using DMF and 100% ethanol, respectively, before being allowed to air dry.

Chemicals used in this project were sourced exclusively from B.D.H. and Fluka. We used an Electrothermal 9300 melting point equipment to find the melting points. The I.R. A KBr disc was used to record ranges within the 4000-400 cm-1 range using a Tensor 27 Bruker FT-IR spectrophotometer. The 1 cm quartz cruets were used to analyze room temperature The Labo Med, Inc. 1650Pc spectrophotometer was used to get UV-Vis spectra ranging from 1100 to 200 nm dissolved in dimethylformamide (DMF).At room temperature, the molar conductance was measured using a PMC3 Jeneway conductivity meter. With the use of a Cambridge balance made by Sherwood Scientific, the magnetic susceptibility was measured at room infection. The Euoro EA 3000 Instrument was used to conduct the C.H.N. fundamental analysis. The complexes were identified by atomic absorption spectroscopy using a Shimadzu AA670 instrument or by volumetric analysis with a standard EDTA solution and an appropriate indicator in the case of nickel and zinc.

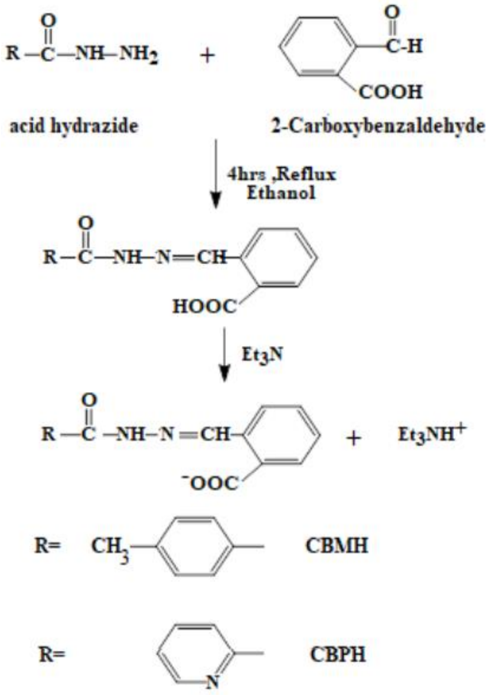
MIXTURE OF THE LIGANDS

Research of hydrazides:

Hydazine hydrate was used to create MBH and PH, or 4-methylbenzoyl hydrazine, are by reacting it with the appropriate ethyl ester in ethanol, as described in previous research. The following concentrations of ethylpicolinate or ethyl 4-methylbenzoate were added to 30 mL of ethanol: 0.05mol, 7.5g, or 8.2g, followed by 5g of excess hydrazine hydrate (80%), or 0.08mol, mixed continuously. The mixture was then cooked for seven hours under reflux. After the white crystalline precipitate cooled, it was filtered, followed by a 5-milliliter wash with cold ethanol and 5-milliliter diethyl ether, and finally dried at a temperature of 144–145ºC with a pH of 115–117ºC (MBH).

Synthesis of hydrazones:

The synthesis of 2-carboxy benzaldehyde picolinoylhydrazone and 4-methylbenzoyl hydrazine was carried out by following the directions provided in the literature. (Scheme 1) The reflux reaction was performed by continuously stirring a combination mixed with 4.5 grams of 2-carboxybenzaldehyde and 0.03 mole of acid hydrazide in 20 milliliters of pure ethanol were combined in 20 mL. After 4 hours, a white solid precipitated out. A 5-milliliter wash with 100% ethanol and subsequent drying in an oven set to 80 to 90 degrees celsius removed the solid.



Scheme 1 Research of hydrazones

Metal complex synthesis:

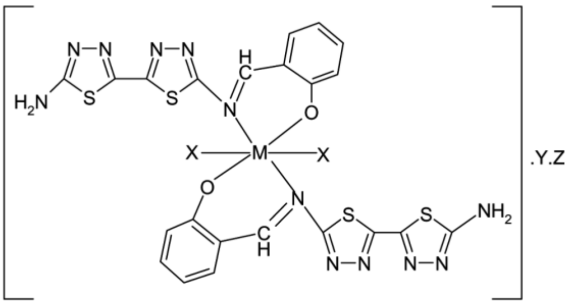
Add the correct metal salt (0.001mole) to a stirred, heated ethanolic solution (10 mL) of [0.20g $MnCl_2.4H_2O$, 0.25g $Co(CH_3COO)_2.4H_2O$, 0.25g $Ni(CH_3COO)$]Copper(II) hydroxide, 0.2 gram. The ligand, either 0.564g of CBMH or 0.538g of CBPH, was introduced into a solution containing 10 mL of pure ethanol and 0.202g (equivalent to 0.02mol) of triethylamine in addition to $2.H_2O$, or 0.22g $Zn(CH_3COO)_2.2H_2O$. After three hours of refluxing, the solid complexes were extracted by filtering out the mixture and washing it with five milliliters of ethanol. The mixture was then dried in an oven set at 80 to 90^oC.

DATA ANALYSIS

There were three phases to this research. The 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)- 1,3,4-thiadiazole (1) was initially produced according to the literature-described procedure. Step two involves the addition of the N-[5' -amino-2,2' -bis(1,3,4-thiadiazole)-5-yl]. The reaction between salicylaldehyde and 2-amino-5-(2-amino-1,3,4-thiadiazole-2-yl)-1-,3,4-thiadiazole (1) yielded -2-hydroxybenzaldehyde imine (HL). Finally, the complex compounds were made by reacting the ligand (HL^1) with the metal salts $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $CdCl_2.H_2O$, and $FeCl_2.6H_2O$.

The metal complexes and Schiff base exhibit color and air and moisture stable. A little amount of the Schiff base may be dissolved in heated acetone, chloroform, methanol, or ethanol. In most cases, however, DMF and DMSO will dissolve its metal complexes too.

We were able to determine theorganization mechanism of ligand HL in these complexes was determined by studying its essential composition and phantom data. The elemental studies of the novel complexes showed a deviation of just 0.4% from the theoretical data derived for the recommended formulae. The developments investigated included cobalt, nickel, cadmium, and iron, when faced with a The metal to ligand ratio is 1:2. A combination of ethanol and water was detected. It is composed of two chloride ions, two water ions, and two dimethylformamide molecules that constitute the Cu(II) complex. The ideal ratio of metal to ligand in the composite was 2:2. The complexes' likely architecture is shown in Figure 2.



M =	Co(II)	Ni(II)	Cd(II)	Fe(II)
X	$2C_2H_5OH$	_	$2C_2H_5OH$	$2H_2O$
Y	$4C_2H_5OH$	$3C_2H_5OH$	C_2H_5OH	$2H_2O$
Z	_	$2H_2O$	$4H_2O$	$3C_2H_5OH$

Figure 2:Proposed arrangement is generated by the ligand (HL) in complexes with octahedral Co (II), Co (II), Fe (II), and tetrahedral Ni (II).

Synthesis and characterization of ligands

As shown in Scheme 1, the ligands were successfully and accurately produced by condensing equimolar amounts.2-Carboxy benzaldehyde and 4-methylbenzoyl hydrazide or picolinoyl hydrazide are combined in the synthesis. The ligands' molecular structures were established using elemental and infrared investigations. The unbound ligands showed functional group characteristic features in their infrared spectra. The unconstrained elongation of the hydrogen-bonded υ(NH) in the carboxylic group is responsible for the faint wide bands seen in the ligand spectra within the region of 2400-3113 cm^{-1}. The carboxylic cluster carbonyl occurrence$υ_{(C=O)car}$ is responsible for the strong absorption bands seen between 1689 and 1688 cm $^{-1}$. For CBMH, the amide-I carbonyl $υ_{(C=O)\ (hydraz)}$ frequencies were measured at 1637-1622 cm^{-1}, whereas for CBPH, they were 1610-1599 cm^{-1}. The regions between 3209 and 3165 cm^{-1} and 1012 and 947 cm^{-1}, which show medium to weak intensity bands, are caused by the stretching vibrations of $υ_{(NH)}$ and $υ_{(N-N)}$, respectively.

Production and Analysis of Compounds

The hydrazones and their complexes that were synthesized are along with certain physical attributes and analytical data. The elemental analysis findings show that there is a 1:2 stoichiometry (metal: ligand) for all complexes. Analyses provide findings that are consistent with what is needed by the suggested formulae. All the produced compounds were discovered to have a non-electrolytic character, with a molar conductivity ($Λ_m$) ranging from 5.6-21.3 ohm^{-1} cm^2 mol^{-1}, as measured at ambient temperature in 10^{-3}M solutions in DMF. We have successfully obtained all the complexes in solid form. While they dissolve somewhat in ethanol, they are insoluble in chloroform, benzene, and diethyl ether among other organic diluters. However, they are more soluble in dimethyl sulfoxide and dimethyl sulfoxide. Complexes 6 and 8–10, when broken down, may be non-polymeric since they all melt within the temperature range of 162–275°C. Using a 1:2:2 molar proportion of metallic, ligand, and triethyl amine in absolute ethanol, the complexes described here were produced by reacting hydrous M(II) salts with appropriate ligands in the basic intermediate. Neutral compounds of the generic formulae $[M(L-H)_2]. xH_2O$ involving deprotonated ligands were used.x-hydrogen was extracted. One way to express the responses is as:

$$M(CH_3COO)_2.nH_2O + 2L + 2Et_3N \rightarrow [M(L\text{-}H)_2].xH_2O + 2Et_3NH^+CH_3COO^-$$

$$MnCl_2.4H_2O + 2L + 2Et_3N \rightarrow [Mn(L\text{-}H)_2].xH_2O + 2Et_3NH^+Cl^-$$

L=CBMH or CBPH x = 0,1,2 or 3

Electronic spectra

We may infer from the electronic spectra what the ligand field surrounding the metal ion is like.The electronic spectra provide trustworthy details on the compounds' electronic structures. Strong bands may be seen in the ligand spectra of DMF at 34246-33898 cm^{-1} and 31948-30674 cm^{-1}, respectively, because of the intraligand transitions involving the aromatic moiety's π→π* and the chromophore's (-C=N-NH-CO) n→π*. The groups at 33557-29498 cm-1 and 28901-26809 cm-1, individually, shifted to lower-frequency regions of the compounds' electronic spectrum, showing that the metal atoms had complexed with the hydrazone ligands. All complexes (1–10) have a new strong spectral band in the 26455-23474 cm^{-1} range. This band is perhaps associated with the change in charge transmission. The complexes (1,6) of Mn(II) show magnetic moments ranging from 5.90 to 5.60 B.M. The system exhibits a high spin state with five unmatched electrons, which are closely aligned with the estimated spin-only worth. Zinc (II) ions with a d10 electronic configuration and manganese (II) ions with a high-spin d5 electronic configuration do not exhibit d-d transitions., there is no significant absorption in the visible range for either compound. The Co(II) complexes (2,7) exhibit electronic spectra with three bands at ranges of 20703-18867, 15337-14388, and 10183-10141 cm^{-1}.These bands correspond to the changeovers of $^4T_1g(F)\rightarrow{}^4T_1g(P)$, $^4T_1g(F)\rightarrow{}^4A_2g(F)$, and $^4T_1(F)\rightarrow{}^4T_2g(F)$, one by one, and prefer octahedral shape centered around the ion. Cobalt (II) Complex magnetic moment values between 4.90 and 4.50 B.M. provide credence to the idea that the space around the Co(II) particles is octahedral. Due to a significant orbital contribution, the higher values for the high spin d7 system (3.87 B.M.) than for spin alone.

Three bands may be seen in the Ni(II) complexes (3,8) electronic spectra in the following regions: 23752-21739, 13192-12468, and 10121-9633 cm^{-1}. These correspond to transitions of $^3A_2g(F)\rightarrow{}^3T_1g(P)$, $^3A_2g(F)\rightarrow{}^3T_1g(F)$, and $^3A_2g(F)\rightarrow{}^3T_2g(F)$, in that orderThe changeovers reveal the octahedral geometry around the Ni(II) particles. The computed compellingminute of complexes with Ni(II), ranging from 3.08 to 2.92 B.M., aligns with the magnetic moment assortment of Ni(II) octahedral multiplexes (2.9–3.3 B.M.), providing more evidence to support this conclusion. Typical Cu(II) complex electronic spectra show a wide band within the county of 14471–14025 cm-1. This band may be ascribed to two or three transitions and is characteristic to the deformed octahedral stereochemistry of Cu(II) developments. The values of ^2B_1g are $-{}^2Eg$, $\rightarrow{}^2B_2g$, and $\rightarrow{}^2A_2g$. The complexes (4,9) have compellingminutes between 2.20 and 2.02 B.M., which is dependable with a monomeric octahedral geometry.

CONCLUSION

A unique tridentate hydrazone metal complexes with the ligand and covalent elements such as nickel, zinc, copper, and iron were created and studied using a range of spectroscopic methods. Two distinct coordination mechanisms exist for the hydrazones that are produced the monobasic tridentate ligands used are produced from Two-carboxy benzaldehyde with either CBMH or CBPH, which stands for 4-methyl benzoyl hydrazine.

REFERENCE

1. Jevtovic V, Alshamari Ak, Milenković D, Dimitrić Marković J, Marković Z, Dimić D. The effect of metal ions (Fe, Co, Ni, And Cu) on the Molecular-Structural, Protein Binding, And Cytotoxic Properties of Metal Pyridoxal-Thiosemicarbazone Complexes. Int j mol sci. July 25;24(15):11910. Doi: 10.3390/ijms241511910. Pmid: 37569285; pmcid: pmc10419307.

2. Ma. El-ghamry (2016).Synthesis of Co(II), Ni(II), Cu(II), Fe(III), vo^{2+} and uo^{2+}Complexes Derived From A New Bis(Pyridylurea) Ligand. Spectroscopic characterization, thermal, magnetic and 3d molecular modeling studies," ijpcbs 2016, 6(1), 76-96 ma el-ghamry et al. Issn: 2249-9504

3. Lidia zapała (2021).Green Synthesis Of Niflumic Acid Complexes with Some Transition Metal Ions (Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)). Spectroscopic, thermoanalytical and antibacterial studies," thermochimica actavolume 696, February 2021, 178814

4. Tas, E.&Kilic, Ahmet & Durgun, Mustafa & Küpecik, L.& Yilmaz, I.& Arslan, Sonmez. (2010). Cu(II), Co(II), Ni(II), Mn(II), and Fe(II) metal complexes containing N,N'-(3,4-diaminobenzophenon)-3,5-Bu-2(t)-salicylaldimine ligand: synthesis, structural characterization, thermal properties, electrochemistry, and Spectro electrochemistry. Spectrochimica acta. Part a, molecular and biomolecular spectroscopy. 75. 811-8. 10.1016/j.saa.2009.12.002.

5. Soleimani, Esmaiel. (2010). Novel complexes of Mn(II), Co(II), and Cu(II) with ligand derived from dibromobenziloxime. Journal of the Chinese chemical society. 57. 10.1002/jccs.201000091.

6. Suvarapu, L. N., Seo, Y. K., Baek, S. O., & Ammireddy, V. R. (2012). Review on analytical and biological applications of hydrazones and their metal complexes. E-Journal of Chemistry, 9(3), 1288-1304.

7. Rollas, Sevim, and S Güniz Küçükgüzel. "Biological activities of hydrazone derivatives." Molecules (Basel, Switzerland) vol. 12,8 1910-39. 17 Aug. 2007, doi:10.3390/12081910.

8. Verma, G., Marella, A., Shaquiquzzaman, M., Akhtar, M., Ali, M. R., & Alam, M. M. (2014). A review exploring biological activities of hydrazones. Journal of pharmacy & bioallied sciences, 6(2), 69-80. doi:10.4103/0975-7406.129170.

9. Jing-lin, W., Ya-qin, Z., & Bin-sheng, Y. (2014). Transition metal complexes of asymmetrical aroylhydrazone ligand: Syntheses, structures, DNA binding and cleavage studies. Inorganica Chimica Acta, 409, 484-496.

10. Aly, S. A., & Fathalla, S. K. (2020). Preparation, characterization of some transition metal complexes of hydrazone derivatives and their antibacterial and antioxidant activities. Arabian Journal of Chemistry, 13(2), 3735-3750.

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