

Synthesis of New Mono and Binuclear Transition Metal Complexes

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Abstract

Important pharmacological uses may be found for metal complexes made from amino acids and their derivatives. Using metalated phosphorus ylides has been shown to be useful in synthetic chemistry. This is reflected in increased morbidity and mortality, which allows them to endure the effects of the majority of antibiotics in use today. According to the elemental analysis, the ratio of metal to ligand is 2. Binuclear metal complexes were tested for antibacterial activity against *Escherichia coli*, *Klebsiella pneumonia*, and *Staphylococcus aureus*.

Keywords Binuclear, 3, 3'-Dihydroxy benzidine, 2-Amino thiophenol, Infrared, Electronic Spectra, DNA Cleavage Study, Antimicrobial Study

1. INTRODUCTION

Important pharmacological uses may be found for metal complexes made from amino acids and their derivatives. They have antimalarial action and have been explored for use in cancer treatment (Wang et al., 2005). However, little contemporary research has been conducted on the thiourea derivatives containing glycine, despite their potential medical use as powerful anti-cancer and anti-influenza medicines. This research investigates the spectroscopic properties and coordination chemistry of thiourea and its metal complexes, produced by reacting N-benzoyl-N-allylthiourea (BGH) with Cu (II), Co (II), Ni (II), Zn (II), and Fe (III) chlorides and/or Cu(II), Co(II), Ni(II), and Zn(II) acetates. This research is also conducted to better understand the ligand's dynamics during complex formation at various pH values.

In organic chemistry, phosphorus ylides have a significant role as reagents, particularly in the production of natural compounds having biological and pharmacological properties. The incoordination chemistry of these compounds has been used as reducing agents. Using metalated phosphorus ylides has been shown to be useful in synthetic chemistry. In 1965, a symmetric halide-bridged dimeric structure was proposed for hg halide complexes, while in 1995, kalyanasundari et al reported an asymmetric halide-bridged dimeric structure. Without providing any structural characterisation, sanehi et al. (1985) described a mononuclear hg complex of phosphorus ylides. As of late, our lab has been working on synthesizing complexes involving mercury salts and phosphorus ylides, including mononuclear, binuclear, and polynuclear species. r 3 p@ c(0)cor 00, a -keto-stabilized phosphorus ylide, with intriguing features including excellent stability and ambidentate character as a ligand (c- vs. O-coordination) A significant public health issue has emerged as a result of the overuse and abuse of antibiotics: microorganisms have become resistant to these drugs. Methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant enterococci (VRE) are only two examples of the superbugs responsible for a disproportionate share of hospital-acquired infections. This is reflected in increased morbidity and mortality, which allows them to endure the effects of the majority of antibiotics in use today. New and old antibiotic resistance have both emerged in the previous several decades, highlighting the urgent need for new classes of antimicrobial medicines despite the abundance of existing treatments (WHO, 2012a). Emerging infectious illnesses and an increasing number of multidrug-resistant microbiological pathogens are only two of the many reasons why treating infectious diseases remains difficult.

2. LITRATURE OF REVIEW

Voguri Haranath babu et.al (2017) The binding mode of the ligand to the metal, as well as the composition and geometry of the metal complexes, were investigated using elemental analysis, conductivity measurements, magnetic moments, IR, ¹H, ¹³C NMR, Mass and electronic spectroscopies, and TGA, DTA. The ligand used was

a binucleating new amino schiff base ligand with a phenylene spacer afforded by the condensation of amino acids witho-pthalaldehyd It was discovered that the complexes in the coordination sphere consist of $[M_2(L)(H_2O)_4]xH_2O$ (where $M=Mn$) (II). All of the aforementioned metal complexes exhibit some degree of antibacterial activity against both Gram-positive and Gram-negative bacteria.

Atakilt Abebe et.al (2020) Many researchers have focused on 1,10-phenantroline-containing cobalt (II) mixed ligand complexes because of the complexes' antibacterial properties. Here, we present three new mixed ligand cobalt (II) complexes with the following formulae: $[Co(L1)_2(H_2O)_2] Cl_2$, $[Co(L1)_2(L_2) (H_2O)]$. The combination of Cl_2 and $[Co_2(L1)_4(L_2)_2(L_3)]$ Elements such as conductivity measurement, infrared spectroscopy, and UV-Vis spectroscopy were used to manufacture and analyses Cl_4 ($L_1 = 1,10$ -phenanthroline, $L_2 =$ adenine, $L_3 = 1,3$ -diaminepropane). All the suggested complexes have octahedral geometry. Four harmful bacteria (*Staphylococcus aureus*, *Salmonella typhus*, *Escherichia coli*, and *Staphylococcus epidermis*) were used to investigate the in vitro antibacterial activity of the ligands, salts, and metal complexes using the disc diffusion technique. Cobalt (II) complexes are often used to combat gram-positive bacteria; however, it is noteworthy to note that the newly produced complexes are effective against gram-negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*).

Dr. Santosh Kumar Singh (2019) Chemical Elements and Compounds That Cannot Be Regenerated Many recently developed metal-based pharmaceuticals and cosmetics ingredients make use of binuclear metal (II) complexes. To better understand the role of inorganic chemistry in the delivery of drugs and cosmetics, this review provides a brief overview of the use of these metal complexes in the fields of pharmacy, microbiology, and cosmetics. This metal activity has kicked off the creation of metal-based medications that show great pharmacological promise and may provide novel therapeutic avenues. Improvements in inorganic chemistry have opened up new possibilities for using metal complexes in the beauty industry. Binuclear complexes affecting living things behave differently than those affecting inanimate objects.

Aziza Sarwa et.al (2018) Due to their possible use as luminous materials in today's technology displays, metal complexes have garnered a lot of attention. The structure-property connections of the various types of luminous transition metal complexes may be determined via careful analysis of the variety of ligands, structural, and bonding mechanisms of distinct metal centers. Herein, we describe the synthesis and luminescence investigations of several metal-diamine complexes. Examination reaction between diaminodiphenylether and salicylaldehyde in a 1:2 molar ratio yielded N, N'-bis-(salicylidene)-4,4'-diaminodiphenylether (3a), a diimine ligand. In the presence of base, the corresponding Zn (II) (4a) and Cd (II) (4b) complexes were produced with the metal:ligand:NaOH=1:1:2 stoichiometry. CHN elemental analysis, 1H and ^{13}C NMR, UV-Vis and FTIR spectroscopy data, and molar conductivity measurements were used to characterize the synthesized ligand and all the complexes. Spectroscopic evidence indicated that the ligands coordinated to the metal atom through both the azomethine N atoms and the hydroxyl O atoms, making them N_2O_2 -tetradentates. There was an examination of the metal complexes' fluorescence characteristics once they were produced. Intensified luminescence was seen in the 465–490 nm wavelength range for metal–diimine complexes, with the bands concentrated on these wavelengths because of charge transfer transitions between the ligand metal and metal (LMCT). The significant proportion the observed Stoke's shift suggests that the organic ligands effectively transmitted the energy they absorbed to the metal ions, which supports their potential application as emitters in organic light-emitting diodes.

3. METHODOLOGY

We bought 2-amino thiophenol and 3,3'-dihydroxy benzidene from Loba Chemicals. DMSO, DMF, and ethanol were used as solvents. To conclude our elemental study, we turned to the Carlo-Eraba 1106. The ELICO CM 185 conductivity Bridge was used to study the molar conductances of the metal complexes. The spectra in the Infrared range were obtained using a spectrometer of the Perkin Elmer FT-IR-8300 series. A Perkin Elmer Lambda-25 was used to capture UV-Visible spectra from 200 to 700 nm. Disc diffusion was utilized for antimicrobial testing.

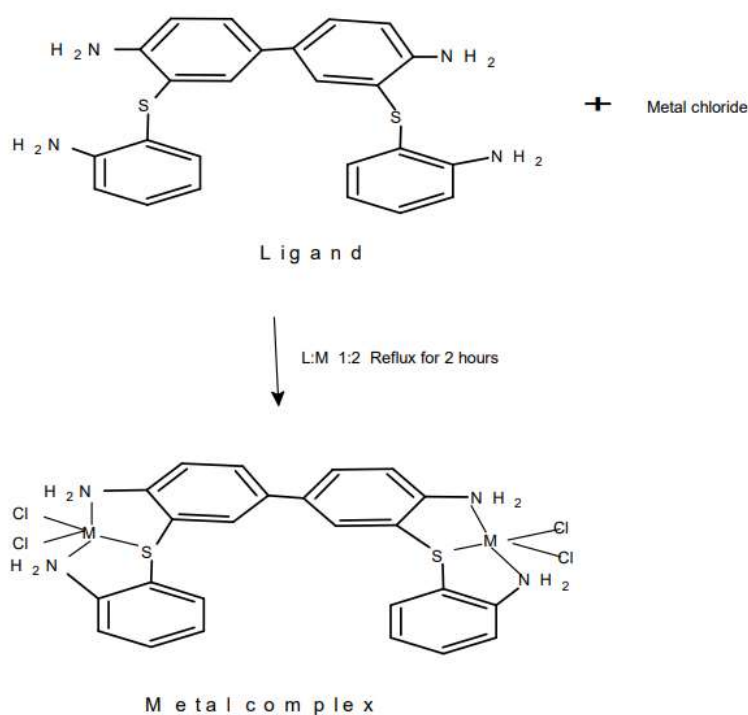
SYNTHESIS OF LIGAND



Gradually, while stirring constantly, the 3, 3'-dihydroxy benzidine solution was combined with the 2-amino thiophenol solution in alcohol. After mixing, this solution was heated for two hours in a condenser-equipped Rb flask. After the precipitate cooled, it was collected. It was desiccated after going through many ethanol purifications processes.

Synthesis of Metal Complexes

The ligand and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were blended together and allowed to reflux for 2 hours. It was cold outside. Metal complexes were gathered. After cooling, fused CaCl_2 was used to filter and dehydrate the mixture. Similar refluxing action was used with ligand and yet another metal salt (NiCl_2).



Scheme-2: Synthesis of Binuclear Metal Complex

4. DATA ANALYSIS

Elemental analysis

Table-1 displays the elemental analysis data. The data supports a 2:1 [M: L] ratio between metal and ligand. When writing out the formula, keep in mind that the "M" stands for the copper and nickel ions and the "L" stands for the ligand. For some time now, we have been aware of the close correspondence between theoretical and experimental values.

Table-1: Elemental Analysis of the Metal Complexes

Ligand/ Complexes	Molecular Weight	% C		% H		% N		μ_{eff} (B.M)	Λ_M^{-1} (Ohm^{-1} $\text{cm}^2\text{mol}^{-1}$)
		Cal.	Exp.	Cal.	Exp.	Cal.	Exp.		
($\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4$)	430.588	66.95	66.85	5.15	5.08	13.01	12.95		
$[\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	699.492	41.21	41.12	3.17	3.11	8.01	8.10	1.61	12.41
$[\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	689.780	41.79	41.70	3.21	3.18	8.12	8.19	2.72	13.74

Conductivity Studies

In the first step, DMF is used to dissolve the metal complexes. The conductivity of molecules is quantified. Table 1 lists the complicated values that were found. The conductivity of copper and nickel complexes is shown to be in the range of 12.41 to 13.74 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ (Table-1). Metal complexes are of a non-ionic, non-electrolyte nature, as shown here. Chloride ions are indeed located inside the inner sphere, as previously proven.

Infrared Spectroscopy

Carbon-carbon double bond (C=C) bands may be seen between 1510 and 1550 cm^{-1} . The bands seen between 452 and 455 cm^{-1} are indicative of a metal-nitrogen connection (M-N). In the frequency range 340–347 cm^{-1} , which was detected, the Sulphur bond of the metal was emitted (M-S). Within 350-355 cm^{-1} , 14-17, the bands that represent the metal-chloride bond (M-Cl) are most prominent. Below is Table-2, which details the various areas.

Table-2: Infrared Spectra of Ligand and Metal Complexes

Ligand/ Complexes	(C-C) (cm^{-1})	(M-N) (cm^{-1})	(M-S) (cm^{-1})	(M-Cl) (cm^{-1})
($\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4$)	1540	452	340	350
$[\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	1510	453	343	355
$[\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	1550	455	347	353

Ultraviolet Spectroscopy

UV spectra, which are shown in Figs. 1–3, validated the structural elucidation. It was determined that one or two peaks were produced between 290 and 320 nm, indicating the presence of an intra ligand charge transfer transition (*). It was determined that the 380-390 nm range was indicative of the charge transfer transition between the ligand and metal. The mononuclear nickel (II) complex exhibited d-d transitions in its ultraviolet spectrum that were consistent with the Ni (II)-d8 system in an octahedral environment. Due to its low absorption peak at 535 nm and d-d transition, the mononuclear copper (II) complex displayed a distorted octahedral geometry. As expected, the presence of a second metal ion in the complex results in a single broad absorption peak between 515 and 655 nm for the binuclear copper (II) and nickel (II) complex. 18-20 You can find the UV spectral data in Table-3 below.

Cyclic Voltammetry

Understanding how metal complexes interact with DNA was investigated using the cyclic voltametric method. Fig. 4 displays cyclic voltammograms (CV) obtained in DMF solution at a scan rate of 0.1 Vs1 for the complexes $[\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$ and $[\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$. From 1.2 V to -2.0 V was the potential. In a binuclear copper complex, the cathodic wave determines the redox characteristics of the individual nuclei. Thus, Cu (II) was reduced to Cu(I) in the center at -0.80 V, and copper was irreversibly reduced at -1.50 V. Support for two one-electron reductions in the binuclear copper complex is evidence of interaction between the two copper ions. In addition to $[\text{Mn}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$, $[\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$ yields same results.

Table-3: UV-Vis Spectra of the Ligand and Complexes

Ligand/ Complexes	$\pi-\pi^*$ [nm]	$n-\pi^*$ [nm]	L-M CT [nm]	d-d [nm]
($\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4$)	290	348	380	--
$[\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	300	357	385	610
$[\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_4)]$	320	365	390	620

Thermal analysis-TGA

The binuclear complexes have undergone TG and DTG analysis. The temperature may have been anything between 900 degrees and room temperature. We compared the weight losses that occurred throughout the various stages of breakdown of the synthetic substances. Table 4 lists the temperatures experienced by various objects. When compared with analytical data, the outcomes were quite similar. There was a single phase of breakdown for the binuclear Copper complex with the formula [Cu₂ (C₂₄H₂₂S₂N₄Cl₄)]. The predicted mass loss was 68.12% (the calculated mass loss was 69.24%). It was between 150 and 660 degrees Celsius. The elimination of four Cl atoms together with aniline and aromatic ligands was blamed. 23 The nickel binuclear complex (molecular formula: [Ni₂ (C₂₄H₂₂S₂N₄ Cl₄)) decomposed into its constituent atoms in three distinct stages during heat breakdown. The first phase took place between 170 and 330 degrees Celsius. A mass loss of 20.56 percent was determined (mass loss= 19.82). A loss of four Cl groups was to blame for this. The second phase took place between 330 and 420 degrees Celsius. There was a loss of 21.79 percent of mass (the calculated loss of mass was 22.56). As a result of the absence of aromatic ligands. Third, we find a mass loss of 26.73 percent (calculated mass loss = 25.88 percent). It was between 420 and 630 degrees Celsius. Aniline group release was proposed as a possible explanation. The final process was interrupted before it could end. For that reason, we skipped figuring out the residual after final breakdown.

Magnetic Measurements

The magnetic moment readings supported the structural analysis. Measurements were taken at ambient temperature. For copper (II) complexes with one nucleon, the value was 1.68 B.M. Accordingly, the +2-oxidation state of copper (II) complexes is due to the paramagnetic nature of these compounds. The binuclear combination [Cu₂ (C₂₄H₂₂S₂N₄Cl₄)] has a magnetic moment of 1.57 BM for Cu (II) complexes. The value of binuclear copper (II) complexes was less than that of mononuclear complexes. Good super exchange characteristics were characterized as the strong antiferromagnetic coupling seen for binuclear copper (II) complexes. Values of the binuclear complexes' magnetic moments may be attributed mostly to the antiferromagnetic intramolecular interaction brought about by the interaction of two copper metals.

DNA Cleavage Study

The results of the DNA cleavage experiment were analyzed using electrophoresis. Figure 5 provides a schematic representation of a gel electrophoresis experiment. By "super coiled form," I meant the form with the fastest migration. If one strand was cleaved, the super coils would transform into a slower moving open circular form, or Form II. If both strands were cleaved, then the Form III resulted in the generation and migration of a linear nicked form. DNA cleavage efficiency was mostly due to the compound's weak binding affinity to DNA. An effective cleavage activity was observed in the presence of a copper compound that completely destroyed DNA. Nickel compound demonstrated similar effective cleavage action to copper compound. An effective cleaving activity was confirmed for both the copper compound and the nickel compound.

Table-4: TG/ DTA Data for Binuclear Complexes

Complexes	TG Range (°C)	Estimated (Calculated) (%)		Assignment	Metallic Residue
		Loss of Mass	Total Loss of Mass		
Cu	150-660	68.12 (69.24)	68.12 (69.24)	Loss of four Cl groups and Loss of aromatic group and Loss of aniline groups	Decomposition is in progress
	170-330	20.56 (19.82)	69.08 (68.26)	Loss of four Cl groups and	
Ni	330-420	21.79 (22.56)		Loss of aromatic group and	Decomposition is in progress
	420-630	26.73 (25.88)		Loss of aniline groups	

Antimicrobial Activity

The metal complexes' antibacterial efficacy is determined using the disc diffusion method. Tests for antimicrobial efficacy were conducted using *Escherichia coli*, *Klebsiella pneumonia*, and *Staphylococcus aureus*. Table 5 provides the values for the minimal inhibitory concentration (MIC). Increased antibacterial activity of the complexes was validated by their MIC values.

Table-5: Antibacterial Activity of the ligand and metal Complexes

Compounds	Klebsiella pneumoniae(mm)				Escherichia coli(mm)				Staphylococcus aureus(mm)			
	Concentrations ($\mu\text{g/ml}$)											
	25	50	75	100	25	50	75	100	25	50	75	100
(C ₂₄ H ₂₂ S ₂ N ₄)	13	14	19	20	13	15	17	19	13	16	18	19
[Cu ₂ (C ₂₄ H ₂₂ S ₂ N ₄ Cl ₄)]	12	15	18	19	12	14	17	19	12	15	17	18
[Ni ₂ (C ₂₄ H ₂₂ S ₂ N ₄ Cl ₄)]	12	13	17	18	11	13	16	18	11	13	16	17

Binuclear complexes suppress bacterial growth in the following order: Cu(II)>Ni (II). To a greater extent than with regular Streptomycin, binuclear complexes are inhibiting microbial development. The action of the copper complex may be explained by chelation theory. Metal complexes completely shut down cellular respiration, prevented protein synthesis, and stunted the growth of the organisms.

Biological studies

Antimicrobial activity against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Pseudomonas fluorescens*) bacteria and one pathogenic fungus was investigated for the Schiff base ligand H₄L and its metal complexes. Table 6 displays the findings from the ligand and complex-related biological research. Antibiotics like chloramphenicol and cephalothin serve as benchmarks against which the results may be evaluated. The fungicidal standard of cycloheximide was utilized. The complexes exhibit greater antimicrobial activity than the ligand did in in vitro tests of bacteria and fungi.

Table 6 Antimicrobial activity of the Schiff base ligand H₄L and its metal complexes

Compound	Mean of zone diameter/mm mg cm ⁻³		
	Gram—positive bacteria <i>Staphylococcus aureus</i>	Gram—negative bacteria <i>Pseudomonas phaseolicol</i>	Fungi <i>Fusarium oxysporium</i>
H ₄ L	22 ± 0.2	13 ± 0.1	17 ± 0.2
1 [Co(H ₃ L)(NO ₃)]·2H ₂ O	24 ± 0.6	23 ± 0.1	26 ± 0.2
2 [Ni(H ₃ L)(H ₂ O)]NO ₃	28 ± 0.2	28 ± 0.3	25 ± 0.2
3 [Cu(H ₂ L)]·2H ₂ O	36 ± 0.3	30 ± 0.2	31 ± 0.3
4 [(VO) ₂ (H ₂ L) ₂]·2H ₂ O	33 ± 0.1	24 ± 0.3	25 ± 0.3
5 Fe ₂ (H ₂ L) ₂ (NO ₃) ₂ (H ₂ O) ₂	37 ± 0.4	26 ± 0.1	31 ± 0.2
6 Co ₂ (H ₂ L)(NO ₃) ₂ (H ₂ O) ₂	27 ± 0.4	22 ± 0.1	23 ± 0.2
7 Ni ₂ (H ₂ L)(NO ₃) ₂ (H ₂ O) ₄	20 ± 0.6	20 ± 0.1	29 ± 0.3
8 [Cu ₂ (H ₂ L)(H ₂ O) ₄](NO ₃) ₂	31 ± 0.1	29 ± 0.2	24 ± 0.3
9 [(VO) ₂ (H ₂ L)(SO ₄)]·3H ₂ O	30 ± 0.1	22 ± 0.2	34 ± 0.3
10 Fe ₂ (L)(H ₂ O) ₄ (NO ₃) ₂	32 ± 0.2	23 ± 0.1	30 ± 0.2
Antibiotic	42	36	40

This allows for the potential delocalization of p-electron throughout the whole chelate ring. The core metal atom may become more lipophilic after chelation. As a result, it is more likely to pass through the lipid bilayers of the cell membrane, where it could potentially obstruct a microbe's enzyme's metal binding site.

5. CONCLUSION

Herein, we investigate the spectroscopic properties and coordination chemistry of thiourea and its metal complexes, which are produced by reacting N-benzoyl-N-allylthiourea (BGH) with Cu (II), Co (II), Ni (II), Zn (II), and Fe (III) chlorides and/or Cu (II), Co (II), Ni (II), and Zn (II) acetate. Emerging infectious illnesses and an increasing number of multidrug-resistant microbiological pathogens are only two of the many reasons why treating infectious diseases remains difficult. N₂S-donor containing 3,3'-dihydroxy benzidine and 2-amino thiophenol were used to synthesize the binuclear copper and nickel complexes. Researchers looked into whether or not the metal complexes might kill germs. Binuclear metal complexes were tested for antibacterial activity against *Escherichia coli*, *Klebsiella pneumoniae*, and *Staphylococcus aureus*.

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