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BINUCLEAR TRANSITION METAL COMPLEXES DERIVED FROM 3, 3'-DIHYDROXY BENZIDIENE AND 2-AMINO THIO PHENOL: SPECTROSCOPIC, THERMOGRAVIMETRIC, DNA CLEAVAGE, AND ANTIMICROBIAL STUDIES

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ABSTRACT

In this novel paper, we synthesized binuclear complexes of metal chloride of Cu(II), Ni(II) with organic compounds 3,3'-dihydroxy benzidiene and 2-amino thiophenol. The type of complex is $[LM_2Cl_4]$. The characterization had been found from elemental analysis, molar conductivity, Infrared, Ultraviolet-visible, cyclic voltammetry, TG-DTA, magnetic measurements, DNA cleavage study and antimicrobial study. The elemental analysis suggested that the metal-ligand ratio is 2:1. The microbes *Escherichia coli, Klebsiella pneumonia and Staphylococcus aureus* were used to find out antimicrobial activity of binuclear metal complexes.

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

INTRODUCTION

In general, transition metals exercise many interesting properties and play a vital role in our life. Among transition metals, Copper and nickel are used in many fields. Copper has biostatic property. There is no chance for bacteria and many other forms of life in it. Copper alloys play a vital role as netting materials in the aquaculture industry due to their antimicrobial and bio fouling properties. It has strong structural and corrosion-resistant properties in Ocean environments. Copper protein has important roles in biological electron transport and oxygen transportation because of the interconversion of Cu(I) and Cu(II). The first pure metal carbonyl produced is Nickel tetracarbonyl. Nickel forms simple binary compounds with non metals including halogens. Many double salts containing nickel with another cation are acknowledged. Nickel can be part of a negatively charged ion called nickelate. Since nickel is present nearer to Copper and Ferrum, compounds with the same structure as the high-temperature superconductors that are known.

Transition metal complexes are not only important as potential drugs like treatment of cancer, but also used for analytical and diagnostic purposes in biological systems, in construction materials, tools, vehicles and as a catalyst. They are used as antimicrobial[1-2], antioxidant[3-4], antifungal[5], antitumour[6], anti-inflammatory[7], anticancer[8-9] and antibiotic[10] applications. The ligands containing Nitrogen and sulphur can act as effective chelating agents for transition metal ions.[11] Antibacterial activity against microbes such as *Escherichia coli, Klebsiella pneumonia, and Staphylococcus aureus* by metal complexes are calculated.[12] We synthesized and characterized the novel binuclear complexes by means of 3,3'-dihydroxy benzidiene and 2-amino thiophenol and Cu(II), Ni(II) salts.

EXPERIMENTAL

We purchased chemicals 3, 3'-dihydroxy benzidiene and 2-amino thiophenol from Loba chemicals. The solvents used were ethanol, DMSO and DMF. We completed the elemental analysis by using Carlo-Eraba

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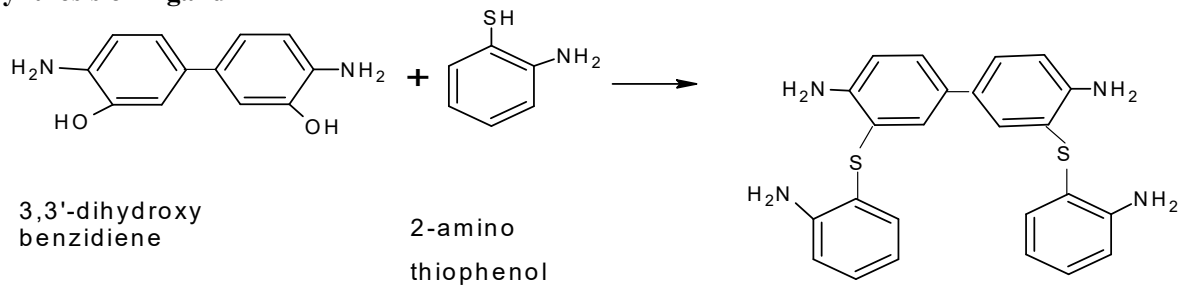
1106 instrument. Molar conductances of the metal complexes were analyzed with ELICO CM 185 conductivity Bridge. The Infrared spectra were collected by using the Perkin Elmer FT-IR-8300 model spectrometer. The UV-Visible spectra were recorded by means of Perkin Elmer Lambda-25 between 200-700 nm. The disc diffusion technique was used for antibacterial activities.

Synthesis of Ligand

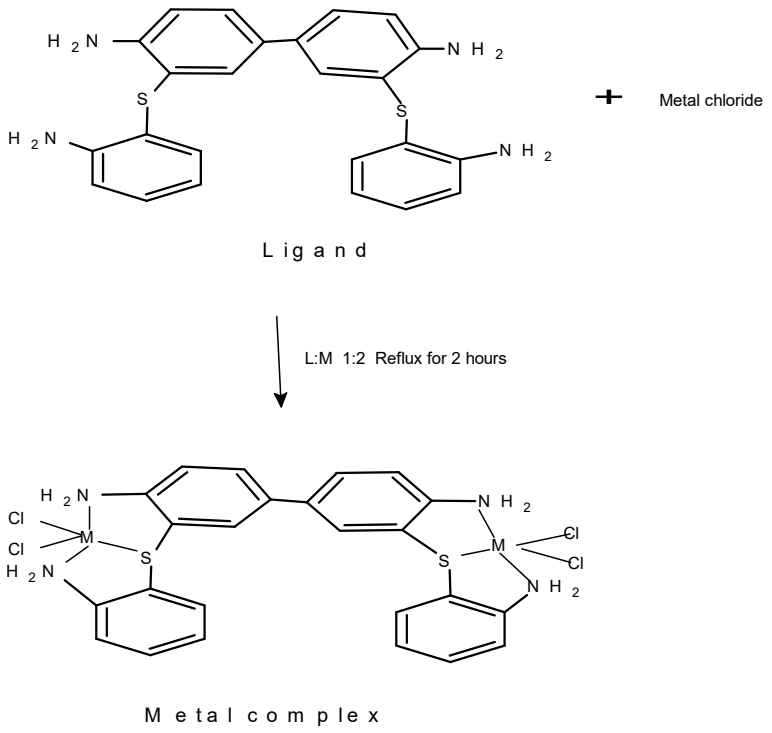


Scheme-1: Synthesis of Ligand

The solution of 3, 3'-dihydroxy benzidiene and solution of 2-amino thiophenol with alcohol were assorted slowly with constant stirring. This mixture was heated in Rb flask fitted with condenser for two hours. The precipitate was collected after cooling. It was purified many times with ethanol and further, it was desiccated.

Synthesis of Metal Complexes

Ligand and $CuCl_2$ $2H_2O$ were mixed and refluxed for 2 hours. It was chilled. The metal complexes were collected. After cooling, it was filtered and desiccated by using fused $CaCl_2$. Similarly, ligand and another metal salt (i.e. $NiCl_2$) were refluxed.



Scheme-2: Synthesis of Binuclear Metal Complex

RESULTS AND DISCUSSION

Elemental analysis

The data of elemental analysis are mentioned in Table-1. The metal and ligand ratio 2:1 [M: L] is confirmed from the data. The formula is ML, where M means copper and nickel ions, while L means ligand. We have known that the theoretical values and experimental values are more or less the same.

Table-1: Elemental Analysis of the Metal Complexes

Ligand/ Complexes	Molecular Weight	% C		% H		% N		μeff (B.M)	Λ_M (Ohm^{-1} cm^2mol^{-1})
		Cal.	Exp.	Cal.	Exp.	Cal.	Exp.		
$(C_{24}H_{22}S_2N_4)$	430.588	66.95	66.85	5.15	5.08	13.01	12.95		
$[Cu_2(C_{24}H_{22}S_2N_4Cl_4)]$	699.492	41.21	41.12	3.17	3.11	8.01	8.10	1.61	12.41
$[Ni_2(C_{24}H_{22}S_2N_4\ Cl_4)]$	689.780	41.79	41.70	3.21	3.18	8.12	8.19	2.72	13.74

Conductivity Studies

The metal complexes are dissolved in DMF initially. Molar conductivities are measured. The values of the complexes are mentioned in Table 1. It is proved that the copper and nickel complexes have a conductivity range of 12.41 – 13.74 Ohm^{-1} cm^2 mol^{-1}(Table-1). It shows the metal complexes are non-ionic nature and non-electrolytes. It is confirmed that the chloride ions are in inside sphere.[13]

Infrared Spectroscopy

.The bands corresponding to carbon-carbon double bond υ (C=C) appear within 1510–1550 cm^{-1}. The bands obtained in the range 452-455 cm^{-1}corresponds to metal nitrogen bond υ (M-N). The bands received in the range 340-347 cm^{-1} corresponds to metal sulphur bond υ (M-S). The bands corresponding to metal Chloride bond υ (M-Cl) appear within 350-355 cm^{-1} [14-17]. The regions are given in the following Table-2.

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})
$(C_{24}H_{22}S_2N_4)$	1540	452	340	350
$[Cu_2(C_{24}H_{22}S_2N_4Cl_4)]$	1510	453	343	355
$[Ni_2(C_{24}H_{22}S_2N_4\ Cl_4)]$	1550	455	347	353

Ultraviolet Spectroscopy

Structural elucidation was confirmed by UV spectra and they are shown in Figs.-1 to 3. Intra ligand charge transfer transition ($\pi \rightarrow \pi^*$) was confirmed by one or two peaks obtained in the range of 290-320 nm. The ligand to metal charge transfer transition was confirmed by the range of 380-390 nm. UV spectra of the mononuclear nickel (II) complex showed d-d transitions corresponding to Ni (II)-d^8 system in an octahedral field. The mononuclear copper (II) complex exhibited a distorted octahedral geometry due to low absorption peak at 535 nm and d-d transition. Only one broad absorption peak obtained in the binuclear copper (II) and nickel (II) complex in the region 515–655 nm, because of one more metal ion present in complexes.[18-20] The UV spectral data was given in the following Table-3.

Cyclic Voltammetry

The cyclic voltammetric technique was applied to know the reaction between metal complexes with DNA. The cyclic voltammograms (CV) of complexes $[Cu_2\ (C_{24}H_{22}S_2N_4Cl_4)]$ and $[Ni_2\ (C_{24}H_{22}S_2N_4Cl_4)]$ were got in DMF solution at a scan rate of 0.1 Vs^{-1} and are shown in fig 4. The potential range was from 1.2 to –2.0 V. The cathodic wave of the binuclear copper complex gives redox properties of the own units by them. Thus, there was a reduction of central Cu (II) to Cu(I) at –0.80 V and irreversible copper reductions at–1.50 V. The support of two one-electron reductions is observed for the binuclear copper complex, suggesting that the two copper ions have some sort of interaction with each other. Same reports are obtained in the following complexes also $[Ni_2\ (C_{24}H_{22}S_2N_4Cl_4)]$ and $[Mn_2\ (C_{24}H_{22}S_2N_4Cl_4)]$.[21-22]

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

Ligand/ Complexes	π-π* [nm]	n-π* [nm]	L-M CT [nm]	d-d [nm]
($C_{24}H_{22}S_2N_4$)	290	348	380	--
[Cu_2($C_{24}H_{22}S_2N_4Cl_4$)]	300	357	385	610
[Ni_2($C_{24}H_{22}S_2N_4$ Cl_4)]	320	365	390	620

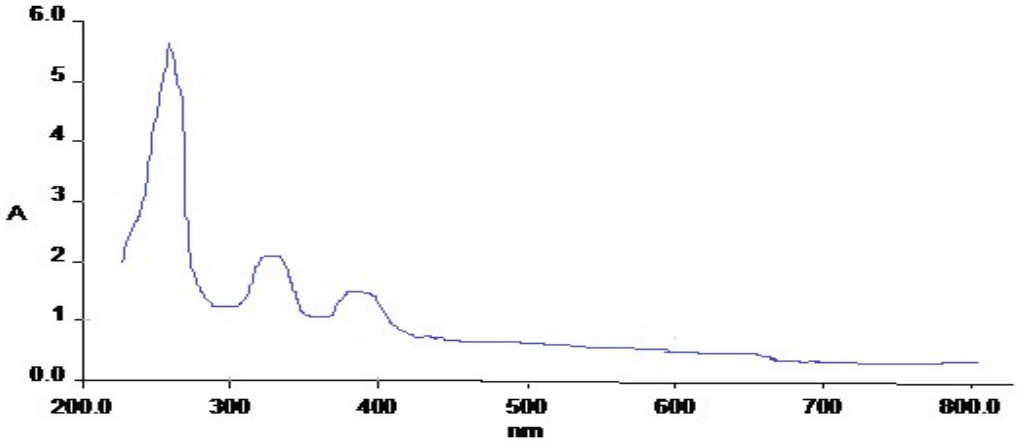


Fig.-1: UV Spectrum for Ligand ($C_{24}H_{22}S_2N_4$)

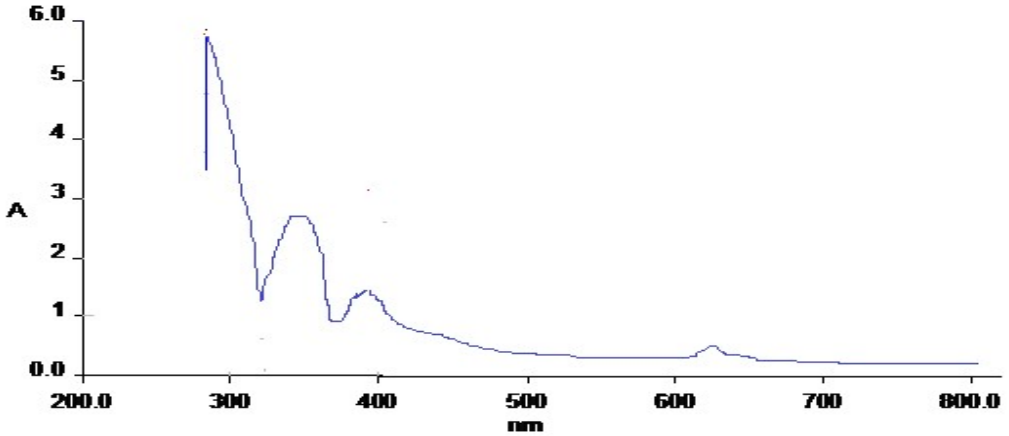


Fig.-2: UV Spectrum for [Cu_2 ($C_{24}H_{22}S_2N_4Cl_4$)]

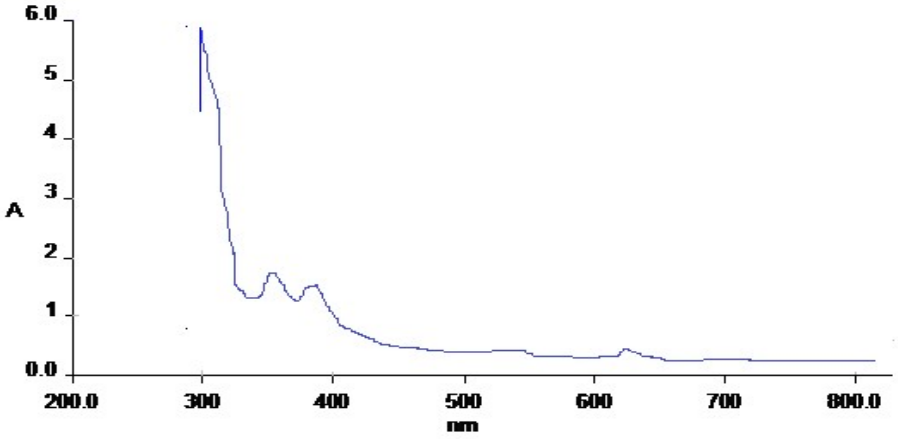


Fig.-3: UV Spectrum for [Ni_2 ($C_{24}H_{22}S_2N_4$ Cl_4)]

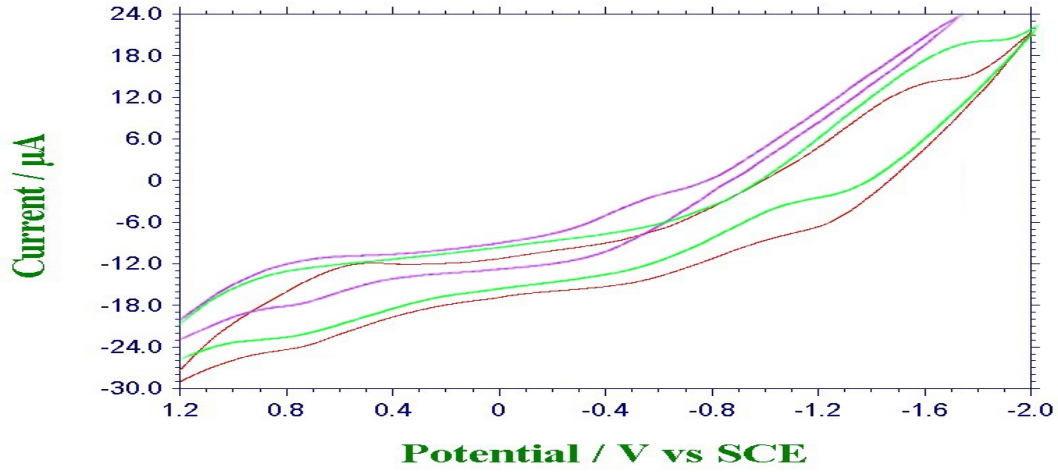


Fig.-4: Cyclic Voltagram of Ligand and complexes
Where, Violet- ($C_{24}H_{22}S_2N_4$), Red- [Cu_2 ($C_{24}H_{22}S_2N_4Cl_4$)] and Green- [Ni_2 ($C_{24}H_{22}S_2N_4$ Cl_4)]

Thermal analysis-TGA

TG and DTG analyses were completed for the binuclear complexes. The temperature range was from ambient temperature to 900°C. The decomposition steps of the synthesized compounds with the corresponding weight losses were compared. The thermal behaviour was mentioned in Table 4. The results were more or less the same when compared with analytical data.

The binuclear Copper complex having the formula [Cu_2 ($C_{24}H_{22}S_2N_4Cl_4$)] was decomposed only one decomposition step. The loss of mass estimated was 68.12% (calculated loss of mass = 69.24%). The temperature range was 150–660°C. It was attributed to the loss of four Cl, aniline and aromatic ligand groups.[23]

The thermal decomposition of the binuclear Nickel complex with the molecular formula [Ni_2 ($C_{24}H_{22}S_2N_4$ Cl_4)] proceeded with three steps. The first step occurred within the temperature range of 170–330°C. The estimated loss of mass was 20.56% (calculated loss of mass= 19.82). This was because of the loss of four Cl groups. The second step occurred within the temperature range of 330–420°C. The loss of mass was 21.79% (calculated loss of mass = 22.56%). It was due to the loss of aromatic ligand groups. The third estimated loss of mass was 26.73% (calculated loss of mass = 25.88%). The temperature range was 420–630°C. It was attributed to the liberation of aniline groups. The last step did not finish completely. Therefore, the last decomposition residue was not calculated.[24]

Magnetic Measurements

The structural investigation was confirmed by the magnetic moment values. It was measured at room temperature. The value for mononuclear copper (II) complexes was 1.68 B.M. Hence complexes were paramagnetic, which is responsible for the +2 oxidation state of copper (II) complexes. The magnetic moment of binuclear Cu (II) complexes are 1.57 BM for the binuclear complex [Cu_2 ($C_{24}H_{22}S_2N_4Cl_4$)]. The Binuclear copper (II) complexes had lower value compared to the mononuclear copper (II) complexes. The strong antiferromagnetic coupling that was established for binuclear copper (II) complexes were described as the good super exchange properties. Antiferromagnetic intramolecular interaction because of copper metal-copper metal interaction was the main reason for magnetic moment values of the binuclear complexes.[25-26]

DNA Cleavage Study

Electrophoresis method was used to analyse DNA cleavage study. Gel electrophoretic model is given in figure-5.Form I meant fastest migration for super coiled form. Form II meant super coils turned into slower moving open circular form if one strand was cleaved. Form III meant a linear nicked form was

generated and migrated if both strand were cleaved. The dissimilar binding attraction of the compound to DNA was main reason for DNA cleavage efficiency. Copper compound degraded DNA wholly and showed efficient cleavage activity. Next to copper compound, efficient cleavage activity was shown by nickel compound. Both copper compound and nickel compound confirmed efficient cleavage activity [27-28].

Table-4: TG/ DTA Data for Binuclear Complexes

Complexes	TG Range (^oC)	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
Ni	170-330 330-420 420-630	20.56 (19.82) 21.79 (22.56) 26.73 (25.88)	69.08 (68.26)	Loss of four Cl groups and Loss of aromatic group and Loss of aniline groups	Decomposition is in progress

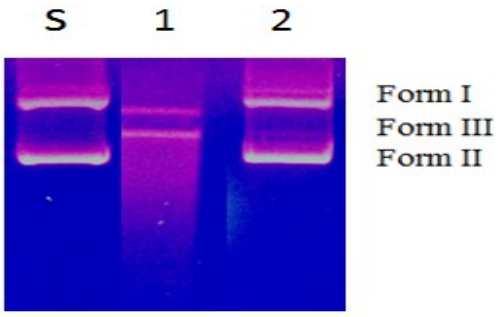


Fig.-5: Gel Electrophoretic Model of pUC18 DNA induced by H_2O_2 and Metal Compounds
Lane s: Standard-pUC18DNA + H_2O_2; Lane 1: pUC18DNA +Cu compound + H_2O_2 ; Lane 2: pUC18DNA +Ni compound + H_2O_2

Antimicrobial Activity

Disc diffusion technique is used to calculate the antibacterial activity of the metal complexes. The microbes *Escherichia coli, Klebsiella pneumonia and Staphylococcus aureus* were used for antimicrobial activity. The minimum inhibitory concentration (MIC) values are given in Table 5. MIC values confirmed that the complexes have higher antimicrobial activity.[29-30]

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

Compounds	Klebsiella pneumoniae(mm)				Escherichia coli(mm)				Staphylococcus aureus(mm)			
	Concentrations (µg/ml)											
	25	50	75	100	25	50	75	100	25	50	75	100
$(C_{24}H_{22}S_2N_4)$	13	14	19	20	13	15	17	19	13	16	18	19
$[Cu_2(C_{24}H_{22}S_2N_4Cl_4)]$	12	15	18	19	12	14	17	19	12	15	17	18
$[Ni_2(C_{24}H_{22}S_2N_4\ Cl_4)]$	12	13	17	18	11	13	16	18	11	13	16	17

The order of bacterial growth inhibition capacity of the binuclear complexes is Cu(II)>Ni(II). Binuclear complexes are having larger MIC values against the growth of microorganisms when compared to

standard Streptomycin. Chelation theory is used to explain the activity of the copper complex. The respiration process of the cell is collapsed by metal complexes and the synthesis of proteins is fully avoided and growth of the organisms was restricted.[31-32]

CONCLUSION

From the elemental analysis, molar conductance measurements, infrared and ultraviolet-visible spectra, cyclic voltammetry, TG-DTA, magnetic measurements of the complexes, the above-mentioned diagram is fixed and complexes are distorted octahedral. The molar conductance measurements confirm that the synthesised complex is non electrolytic in nature. The binuclear copper and nickel complexes were prepared from 3,3'-dihydroxy benzidiene and 2-amino thiophenol having N_2S donors. The antibacterial activity of the metal complexes was examined. The microbes *Escherichia coli, Klebsiella pneumonia and Staphylococcus aureus* were used to find out antimicrobial activity of binuclear metal complexes. Copper and nickel complexes have got more DNA cleavage activity and antimicrobial action.

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