BINUCLEAR TRANSITION METAL COMPLEXES DERIVED FROM 3, 3'-DIHYDROXY BENZIDIENE AND 2-AMINO THIOPHENOL: 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 [LM₂Cl₄]. 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 antimicrobial¹⁻², antioxidant³⁻⁴, antifungal⁵, antitumour⁶, anti-inflammatory⁷, anticancer⁸⁻⁹ and antibiotic¹⁰ 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
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**

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\(_2\)O 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.
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) | ΛM (Ohm⁻¹ cm² mol⁻¹) |
|------------------|------------------|-----|-----|-----|------------|-----------------------|
| (C₂₄H₂₂S₂N₄)    | 430.588          | 66.95 | 66.85 | 5.15 | 13.01      | 12.95                 |
| [Cu₂(C₂₄H₂₂S₂N₄Cl₄)] | 699.492        | 41.21 | 41.12 | 3.17 | 3.11       | 12.41                 |
| [Ni₂(C₂₄H₂₂S₂N₄Cl₄)] | 689.780        | 41.79 | 41.70 | 3.21 | 3.18       | 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 cm² 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) |
|------------------|--------------|--------------|--------------|-------------|
| (C₂₄H₂₂S₂N₄)    | 1540         | 452          | 340          | 350         |
| [Cu₂(C₂₄H₂₂S₂N₄Cl₄)] | 1510        | 453          | 343          | 355         |
| [Ni₂(C₂₄H₂₂S₂N₄Cl₄)] | 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 (π→π*) 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)-d⁸ 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.¹⁶⁻²⁰ 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 [Cu₂(C₂₄H₂₂S₂N₄Cl₄)] and [Ni₂(C₂₄H₂₂S₂N₄Cl₄)] 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 [Ni₂(C₂₄H₂₂S₂N₄Cl₄)] and [Mn₂(C₂₄H₂₂S₂N₄Cl₄)].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] |
|------------------------|-----------|-----------|-------------|---------|
| (C₂₄H₂₂S₂N₄)          | 290       | 348       | 380         | --      |
| [Cu₂(C₂₄H₂₂S₂N₄Cl₄)]  | 300       | 357       | 385         | 610     |
| [Ni₂(C₂₄H₂₂S₂N₄Cl₄)]  | 320       | 365       | 390         | 620     |

Fig.-1: UV Spectrum for Ligand (C₂₄H₂₂S₂N₄)

Fig.-2: UV Spectrum for [Cu₂(C₂₄H₂₂S₂N₄Cl₄)]

Fig.-3: UV Spectrum for [Ni₂(C₂₄H₂₂S₂N₄Cl₄)]
The binuclear Copper complex having the formula \([\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_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.

The thermal decomposition of the binuclear Nickel complex with the molecular formula \([\text{Ni}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{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.

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 \([\text{Cu}_2(\text{C}_{24}\text{H}_{22}\text{S}_2\text{N}_4\text{Cl}_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.

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.

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 |
| Ni        | 170-330       | 20.56 (19.82) | 21.79 (22.56) | Loss of four Cl groups and Loss of aromatic group and Loss of aniline groups | Decomposition is in progress |
|           | 330-420       | 21.79 (22.56) | 26.73 (25.88) | Loss of aromatic group and Loss of aniline groups |                  |
|           | 420-630       | 21.79 (22.56) | 26.73 (25.88) | Loss of aromatic group and Loss of aniline groups |                  |

Fig.-5: Gel Electrophoretic Model of pUC18 DNA induced by H₂O₂ and Metal Compounds
Lane s: Standard-pUC18DNA + H₂O₂; Lane 1: pUC18DNA + Cu compound + H₂O₂; Lane 2: pUC18DNA + Ni compound + H₂O₂

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.

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

| Compounds | Klebsiella pneumoniae(mm) | Escherichia coli(mm) | Staphylococcus aureus(mm) |
|-----------|---------------------------|----------------------|---------------------------|
|           | Concentrations (μg/ml)    |                      |                           |
| (C₂₄H₂₂S₂N₄) | 25  50  75  100           | 25  50  75  100      | 25  50  75  100           |
|           | 13  14  19  20            | 13  15  17  19       | 13  16  18  19            |
| [Cu₂(C₂₄H₂₂S₂N₄Cl₄)] | 12  15  18  19       | 12  14  17  19       | 12  15  17  18            |
| [Ni₂(C₂₄H₂₂S₂N₄Cl₄)] | 12  13  17  18       | 13  14  16  18       | 13  16  17  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 N₂S 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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