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Synthesis, characterization and antimicrobial analyses of nickel (II) complexes of 2,3-(Diimino-4-antipyrynyl) butane

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Abstract

Nickel (II) complexes of the Schiff base ligand 2,3-(diimino-4'-antipyrynyl)butane (BDAP) have been synthesized and the characterization were done by elemental analysis, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as thermogravimetry. An octahedral geometry around the Nickel (II) ion in all the complexes have been suggested by electronic spectra and magnetic moment data. The above observations were confirmed by thermogravimetric analysis. Biological screening analyses of the ligand and the complexes reveal that the metal complexes show significantly higher activity than the ligand against microorganisms. The structure activity analysis of the complexes shows that, nitrate complexes have highest activity against tested bacteria and perchlorate complexes have highest activity against fungus.

Keywords: 2,3-(diimino-4' antipyrynyl)butane, antipyryne, Ni(II) metal complexes, antimicrobial studies, octahedral, bacteria, fungus

1. Introduction

Antipyryne and its significant Schiff base derivatives were investigated and effectively applied in analytical, clinical, biological, and pharmaceutical areas [1-4]. 4-aminontipyryne derivatives were reported to exhibit analgesic and anti-inflammatory effects [5, 6], antiviral [7] and antibacterial [8] activities. These compounds have been used in the determination of metal ions spectrophotometrically. Most of these reagents give intense colours with transition metal ions, acts as sensitive probes [9] and some of them can coordinate to rare earth metal ions to form metal complexes with fascinating structures [10]. Many complexes derived from such ligands possess physiological properties with varying intensity. Also most of the metal complexes were showing antitumor activities [11]. In the present investigation we have synthesized complexes of nickel (II) with varying counter ions with the Schiff base ligand 2,3-(diimino-4' antipyrynyl) butane (BDAP). All the complexes were characterized using different analytical and spectral techniques. The biological studies of these compounds such as the antimicrobial studies were also done.

2. Experimental

2.1 Materials

Five metal salts of nickel were used for the synthesis of complexes. The 4-aminoantipyryne and 2, 3-butanedione were supplied by Sigma Aldrich Chemical Co. USA. These chemicals were used without further purification. The solvents were further purified by distillation.

2.2 Complex Analysis

Nickel present in the complexes was estimated by EDTA titration [12]. Chloride content was estimated by Volhard's method is used for the estimation of chloride content [12] and perchlorate content by Kurz's method [13]. The CHN analyses of the complexes were done using a Heraeus-CHN-Rapid Analyzer. Molar conductance of 10⁻³M solutions of the complexes was measured using a Systronics conductivity bridge with a dip conductance cell having two platinum electrodes. The infrared spectra were recorded in a Shimadzu FTIR 8400 S spectrophotometer in the range 4000-400 cm⁻¹ using KBr pellet technique and in a Bruker IFS 66v FTIR spectrometer in the range 500-100 cm⁻¹ using polyethylene powder.

Electronic spectral studies of the Schiff base and the complexes in solid state were carried out on a Shimadzu UV-visible spectrometer UV-2450. Magnetic susceptibility measurements were done at room temperature.

2.3 Synthesis of ligand

The Schiff base ligand, 2, 3-(diimino-4' antipyrinyl) butane (BDAP) was prepared by the condensation between 2,3-

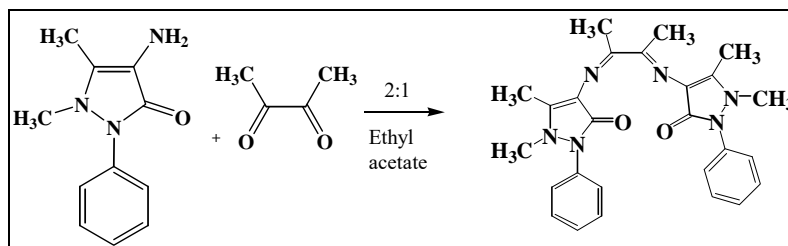


Fig 1: synthesis of 2, 3-(diimino-4' antipyrinyl) butane (BDAP).

The purity of the ligand was checked by TLC, Infrared, mass and NMR spectra and by elemental analysis. The melting point of the compound was found to be 245 °C. The molecular formula and molecular weight of the ligand were $C_{26}H_{28}N_6O_2$ and 456.44 respectively. The elemental analysis data is as shown below

$$C = 68.38 (68.41), H = 5.34 (6.18) N = 18.11 (18.40)$$

2.4 Preparation of Cobalt (II) complexes

To a boiling suspension of 1.2mmol of ligand in ethyl acetate(100mL) add a quantity of one mmol of $Ni(ClO_4)_2 \cdot 6H_2O$ in ethyl acetate (10mL) or $Ni(NO_3)_2 \cdot 6H_2O$ or $NiBr_2 \cdot 6H_2O$ in acetone (10mL) or $NiCl_2 \cdot 6H_2O$ in methanol (10mL) or $NiI_2 \cdot 6H_2O$ in isopropyl alcohol (10mL) was added to a boiling suspension of. The mixture obtained was refluxed for 5 hours. The precipitated complexes formed were filtered and washed repeatedly with hot ethyl acetate to remove the excess ligand and recrystallized from ethanol. It was then dried over phosphorous (V) oxide under vacuum.

2.5 Antimicrobial studies

The in vitro antimicrobial screening of the nickel (II) complexes were tested for their effect on certain human pathogenic bacteria and fungus by well diffusion method [14, 15]. $10^{-3}M$ solutions of all the complexes were prepared in DMSO. Nutrient agar medium was used for growing both the

butanedione and 4-aminoantipyrine in ethyl acetate medium for about 5 hours in 1:2 molar ratio. The yellow precipitated ligand thus obtained was filtered and washed with hot ethyl acetate to remove the excess reactants. The ligand was then recrystallized from ethanol. The yield was about 65%. The scheme of synthesis is represented in figure 1.

Gram negative (*Vibrio parahaemolyticus*, *Salmonella typhi*, *Salmonella weltevreden*, *Aeromonas hydrophila*) and Gram positive (*Escherichia coli* and *Bacillus subtilis*) bacteria, and was incubated at 37 °C for 48h followed by frequent subculture to Muller Hinton agar medium and were used as test bacteria. The fungi, *Trichophyton tonsurans* grown into the Sabouraud dextrose agar medium, incubated at 27 °C for 72h were used to test fungus. Then the petridishes were inoculated with a loop of bacterial or fungal culture and spread throughout uniformly with a sterile spreader. The test samples (10 mg/mL) and reference streptomycin (1 mg/mL for bacteria) or chlorothalonil (10 mg/mL for fungus) were added in the wells of each plate with a sterile micropipette. For bacteria and fungus the petridishes were incubated at 35 ± 2 °C and 27 ± 1 °C for 24–48h respectively. By measuring the diameter of the inhibitory zone after the period of incubation and the average values were noted after repeated twice.

3. Results and Discussion

3.1 Elemental Analyses

The metal, bromide, chloride, perchlorate, carbon, nitrogen and hydrogen content in the nickel (II) complexes were determined and presented in table 3.1. The data suggests that the complexes may be formulated as $Ni(BDAP)X_2$ where $X = ClO_4, NO_3, Cl, Br$ or I

Table 1: Analytical data^a of the Nickel (II) complexes of BDAP

| Complex/ Molecular formula/ Formula weight | Metal (%) | Anion (%) | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Melting point °C |
|---|------------------|------------------|------------------|----------------|------------------|------------------|
| $[Ni(BDAP)(ClO_4)](ClO_4)$ $C_{26}Cl_2H_{28}N_6NiO_8$ (714.03) | 9.42 (9.5) | 32.32 (32.49) | 43.77 (43.73) | 4.02 (3.92) | 11.79 (11.76) | 168 |
| $[Ni(BDAP)(NO_3)](NO_3)$ $C_{26}H_{28}N_8NiO_6$ (639.1) | 9.18 (9.22) | - | 48.67 (48.86) | 4.09 (4.3) | 17.42 (17.52) | 166 |
| $[Ni(BDAP)Cl_2]$ $C_{26}Cl_2H_{28}N_6Ni$ (586.03) | 10.14 (10.01) | 12.13 (12.09) | 53.12 (53.23) | 4.96 (4.75) | 14.42 (14.33) | 170 |
| $[Ni(BDAP)Br_2]$ $Br_2C_{26}H_{28}N_6Ni$ (674.74) | 8.79 (8.69) | 23.64 (23.67) | 46.28 (46.22) | 4.24 (4.14) | 12.52 (12.45) | 165 |
| $[Ni(BDAP)I_2]$ $C_{26}H_{28}I_2N_6Ni$ (768.93) | 7.67 (7.63) | 33.12 (33.0) | 40.37 (40.57) | 3.84 (3.64) | 10.89 (10.92) | 167 |

a: calculated values in parentheses

3.2 Electrical conductance

The molar conductance values of Nickel (II) complexes ($10^{-3}M$ solution) of BDAP were measured in acetonitrile, DMF, ethanol and methanol and the values are given in table 3.2. The molar conductance values fall in the range suggests 1:1

electrolytes for perchlorate and nitrate complexes and non-electrolyte for chloride bromide and iodide complexes¹⁶. Thus the complexes may be formulated as $[Ni(BDAP)X]X$ ($X = ClO_4$ or NO_3) and $Ni(BDAP)X_2$ ($X = Cl, Br$ or I)

Table 2: Molar Conductance^a data of the Nickel (II) Complexes^b of BDAP

| Complex | Molar conductance | | | | |
|--|-------------------|-------|----------|---------|---------------------|
| | Acetonitrile | DMF | Methanol | Ethanol | Type of electrolyte |
| [Ni(BDAP)(ClO ₄)](ClO ₄) | 156.2 | 76.24 | 114.9 | 61.95 | 1:1 |
| [Ni(BDAP)(NO ₃)](NO ₃) | 129.5 | 88.46 | 114.1 | 50.65 | 1:1 |
| [Ni(BDAP)Cl ₂] | 64.8 | 30.28 | 60.34 | 24.24 | non-electrolyte |
| [Ni(BDAP)Br ₂] | 100.34 | 24.26 | 58.16 | - | non-electrolyte |
| [Ni(BDAP)I ₂] | 29.5 | 45.28 | 75.28 | - | non-electrolyte |

^a ohm⁻¹cm²mol⁻¹ ^b 10⁻³ M solution

3.3 Infrared Spectra

The important infrared spectral bands of BDAP and its nickel(II) complexes together with the tentative assignments are given in Tables 3.3. The infrared spectrum of the ligand BDAP shows strong bands at 1649 and 1593cm⁻¹, characteristic of both carbonyl [17] and azomethine [18, 19] groups respectively. The infrared band observed at 1649 cm⁻¹, characteristic of carbonyl groups in BDAP is found to be shifted to the region 1622-1610 cm⁻¹ in all the complexes showing that both the carbonyl oxygens are coordinated in these complexes [20]. Also the intense band due to azomethine nitrogen is shifted to the region 1583-1571 cm⁻¹ in all the complexes indicating the coordination of both the azomethine nitrogens [21].

From the infrared spectral data it is concluded that the Schiff base BDAP acts as a neutral tetradentate ligand, coordinating through both the azomethine nitrogens and both the carbonyl oxygens and resulting in the formation of three five membered rings, there by imparting considerable stability to the complexes.

In the perchlorate complex, the triply split band maxima observed at 1135, 1112 and 1020 cm⁻¹ are due to ν_8 , ν_6 and ν_1 vibrations respectively of the perchlorate ion of C_{2v} symmetry indicating the coordination of perchlorate ion in a bidentate fashion [22]. But the band observed at 1091 cm⁻¹ is assigned to the ν_3 vibration of uncoordinated perchlorate ion of T_d symmetry [23]. Thus indicate the presence of both the bidentately coordinated and uncoordinated perchlorate ion.

The vibrational frequencies corresponding to ν_2 and ν_3 vibrations of the perchlorate (C_{2v}) ion is observed at 930 and 640 cm⁻¹ respectively and ν_4 vibration of the perchlorate (T_d) ion is observed at 624 cm⁻¹, also support the coexistence of both uncoordinated and bidentately coordinated perchlorate ion in the complex [24].

In the nitrate complex, two medium bands at 1492 and 1309 cm⁻¹ are observed which are attributable to the ν_4 and ν_1 stretching vibrations respectively of the nitrate ion of C_{2v} symmetry. Since the difference between ν_4 and ν_1 is 183 cm⁻¹, the nitrate ion is bidentately coordinated [23]. A very strong band observed at 1384 cm⁻¹ indicates the presence of uncoordinated nitrate ion in this complex which is due to ν_3 vibration of the nitrate ion of D_{3h} symmetry [25]. This is supported by another medium intensity band observed at 833 cm⁻¹ which is attributed to the ν_2 vibration of the uncoordinated nitrate ion of D_{3h} symmetry.

In the far IR spectrum of the chloro and bromo and iodo complexes the Ni-Cl, Ni-Br and Ni-I bands are observed at 314,312 and 311 cm⁻¹ respectively which are not present in the spectrum of the ligand.

The above IR spectral results are in conformity with the conductance data that one of the perchlorates and nitrates as well as both the chlorides, bromides and iodides are coordinated to the metal ion in these complexes. Further the ν_{Ni-O} and ν_{Ni-N} stretching vibrations are observed at about 554 and 454 cm⁻¹ respectively in all the complexes [23].

Table 3: Important infrared spectral bands (cm⁻¹) of BDAP and its Nickel (II) complexes

| BDAP | [Ni(BDAP)(ClO ₄)](ClO ₄) | [Ni(BDAP)(NO ₃)](NO ₃) | [Ni(BDAP)Cl ₂] | [Ni(BDAP)Br ₂] | [Ni(BDAP)I ₂] | Assignments |
|------|--|--|----------------------------|----------------------------|---------------------------|--|
| 1649 | 1610 | 1616 | 1622 | 1622 | 1618 | $\nu_{C=O}$ |
| 1593 | 1583 | 1583 | 1583 | 1583 | 1571 | $\nu_{C=N}$ |
| | 1145 | | | | | ν 8 coordinated ClO ₄ |
| | 1115 | | | | | ν 6 coordinated ClO ₄ |
| | 1020 | | | | | ν 1 coordinated ClO ₄ |
| | 932 | | | | | ν 2 coordinated ClO ₄ |
| | 636 | | | | | ν 3 coordinated ClO ₄ |
| | 1091 | | | | | ν 3 uncoordinated ClO ₄ |
| | 624 | | | | | ν 4 uncoordinated ClO ₄ |
| | | 1492 | | | | ν 4 coordinated NO ₃ |
| | | 1309 | | | | ν 1 coordinated NO ₃ |
| | | | | | | ν 2 coordinated NO ₃ |
| | | 1384 | | | | ν 3 uncoordinated NO ₃ |
| | | 833 | | | | ν 2 uncoordinated NO ₃ |
| | 314 | | 314 | | | ν_{Ni-Cl} |
| | | | | 312 | | ν_{Ni-Br} |
| | | | | | 311 | ν_{Ni-I} |
| | 554 | 552 | 554 | 554 | 553 | ν_{Ni-O} |
| | 454 | 453 | 454 | 450 | 454 | ν_{Ni-N} |

3.4 Electronic spectral studies

The electronic spectra of the ligand BDAP shows two absorption maxima at 26810 and 42735 cm⁻¹ corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively [26]. The electronic spectral bands of the complexes with tentative assignments

are listed in table 3.4. In all the nickel(II) complexes the $n \rightarrow \pi^*$ transitions are found to be blue shifted to the regions 27624-28248 cm⁻¹ and the $\pi \rightarrow \pi^*$ transitions are red shifted to the region 37453-38314 cm⁻¹ [27]. The absorption bands observed in the region 21413-23866 cm⁻¹ and 14367-15822

cm^{-1} are attributed to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ transitions respectively consistent with octahedral geometry around Ni(II) ion in all the complexes [28].

Furthermore a low energy band observed in the region 9149-10964 cm^{-1} may be attributed to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transition further supported octahedral geometry around Nickel (II) ion in all the complexes. Also an intense band observed in the region 34013-35211 cm^{-1} may be due to charge transfer transitions.

Table 4: Electronic Spectral data and magnetic moment values of Nickel (II) complexes of BDAP

| Complex | Abs.Max. (cm^{-1}) | Tentative Assignments | μ_{eff} (BM) |
|--|--|--|-------------------------|
| [Ni(BDAP)(ClO ₄)](ClO ₄) | 27,933 38314 35211 23,866 14992 9,250 | n → π* π → π* Charge Transfer ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ | 2.57 |
| [Ni (BDAP)(NO ₃)](NO ₃) | 27,624 37735 35087 23,041 15822 9,149 | n → π* π → π* Charge Transfer ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ | 3.1 |
| [Ni (BDAP)Cl ₂] | 27,933 37594 34013 22026 14367 9398 | n → π* π → π* Charge Transfer ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ | 2.81 |
| [Ni (BDAP)Br ₂] | 28011 38759 34482 21,645 15243 10,649 | n → π* π → π* Charge Transfer ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ | 2.91 |
| [Ni (BDAP)I ₂] | 28,248 37453 34843 21413 15503 10,964 | n → π* π → π* Charge Transfer ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ | 2.97 |

3.5 Magnetic Behaviour

The magnetic susceptibility measurement values of all the complexes are presented in Table 3.4 along with electronic spectral data. The magnetic moment values of the nickel (II) complexes are in agreement with an octahedral geometry around the Ni(II) ion. The values of μ_{eff} are observed in the range 2.57-3.1 BM [29]. These values are in agreement with the expected magnetic moment value, except the perchlorate complex, which is due to metal-metal interaction [30].

3.6 Thermogravimetric Analyses

The TG analysis of nickel (II) complexes of BDAP were done and the phenomenological data of all the complexes are presented in tables 3.5.

The Nickel (II) complexes of BDAP are formulated as [Ni(BDAP)X]X where X= ClO₄⁻ or NO₃⁻ and [Ni(BDAP)X₂] where X= Cl⁻, Br⁻ or I⁻. All the complexes undergo a two stage decomposition pattern.

In perchlorate complex there is no mass loss up to 210 °C indicating the absence of water or any solvent molecules. The

first stage starts at 210 °C and ends at 425 °C. The corresponding mass loss (27.97%) is due to the decomposition of two perchlorate ions. The maximum rate of mass loss occurs at 314 °C as indicated by DTG peak. The second stage starts at 425 °C and ends at 585 °C with a DTG peak at 496 °C. The corresponding mass loss (63.93%) is due to the decomposition of the BDAP molecule. The decomposition gets completed at 590 °C and the final residue is qualitatively proved to be anhydrous NiO.

In Nitrate complex there is no mass loss up to 196 °C indicating the absence of water or any solvent molecules. The first stage starts at 196 °C and ends at 458 °C. The corresponding mass loss (55.16%) is due to the decomposition of two nitrate ions and half molecule of BDAP. The maximum rate of mass loss occurs at 386 °C as indicated by DTG peak. The second stage starts at 458 °C and ends at 552 °C with a DTG peak at 468 °C. The corresponding mass loss (34.84%) is due to the decomposition of half molecule BDAP molecule. The decomposition gets completed at 555 °C and the final residue is qualitatively proved to be anhydrous NiO.

In chloro complex there is no mass loss up to 195 °C indicating the absence of water or any solvent molecules. The first stage starts at 195 °C and ends at 254 °C. The corresponding mass loss (11.99%) is due to the decomposition of two chloride ions. The maximum rate of mass loss occurs at 214 °C as indicated by DTG peak. The second stage starts at 254 °C and ends at 533 °C with a DTG peak at 496 °C. The corresponding mass loss (77.41%) is due to the decomposition of the BDAP molecule. The decomposition gets completed at 620 °C and the final residue is qualitatively proved to be anhydrous NiO.

In bromo complex there is no mass loss up to 186 °C indicating the absence of water or any solvent molecules. The first stage starts at 186 °C and ends at 312 °C. The corresponding mass loss (23.16%) is due to the decomposition of two bromide ions. The maximum rate of mass loss occurs at 256 °C as indicated by DTG peak. The second stage starts at 312 °C and ends at 599 °C with a DTG peak at 521 °C. The corresponding mass loss (67.58%) is due to the decomposition of the BDAP molecule. The decomposition gets completed at 600 °C and the final residue is qualitatively proved to be anhydrous NiO.

In iodide complex there is no mass loss up to 180 °C indicating the absence of water or any solvent molecules. The first stage starts at 180 °C and ends at 406 °C. The corresponding mass loss (32.99%) is due to the decomposition of two iodide ions. The maximum rate of mass loss occurs at 258 °C as indicated by DTG peak. The second stage starts at 406 °C and ends at 572 °C with a DTG peak at 446 °C. The corresponding mass loss (59.44%) is due to the decomposition of the BDAP molecule. The decomposition gets completed at 572 °C and the final residue is qualitatively proved to be anhydrous NiO.

From the above results we can conclude that all the complexes undergo two stage decomposition and the mass loss found is in good agreement with the calculated values with a final residue NiO. The bromide complex is the most stable and the chloride complex is the least stable. The thermal stability of the complexes is in the order bromide > perchlorate > iodide > nitrate > chloride.

Table 5: Phenomenological data for the thermal decomposition of the Nickel (II) complexes of BDAP

| Complexes | Stages of Decomposition | Temp. (K) | DTA peak (°C) | Residual species | Decomposition species | Total Mass Loss (%) | |
|--|-------------------------|-----------|---------------|------------------|--|---------------------|------------|
| | | | | | | Found | Calculated |
| [Ni(BDAP)(ClO ₄)](ClO ₄) | I | 210-425 | 314 | NiO | Two perchlorate ions | 27.97 | 27.85 |
| | II | 425-585 | 496 | | One molecule BDAP | 63.93 | 63.92 |
| [Ni (BDAP)(NO ₃)](NO ₃) | I | 196-458 | 386 | NiO | Two nitrate ions + half molecule of BDAP | 55.16 | 55.11 |
| | II | 458-552 | 468 | | half molecule BDAP | 34.84 | 35.70 |
| [Ni (BDAP)Cl ₂] | I | 195-254 | 214 | NiO | Two chloride ions | 11.99 | 12.09 |
| | II | 254-533 | 496 | | One molecule BDAP | 77.41 | 77.88 |
| [Ni (BDAP)Br ₂] | I | 186-312 | 256 | NiO | Two bromide ions | 23.16 | 23.68 |
| | II | 312-599 | 521 | | One molecule BDAP | 67.58 | 67.64 |
| [Ni (BDAP)I ₂] | I | 180-406 | 258 | NiO | Two iodide ions | 32.99 | 33.00 |
| | II | 406-572 | 446 | | One molecule BDAP | 59.44 | 59.36 |

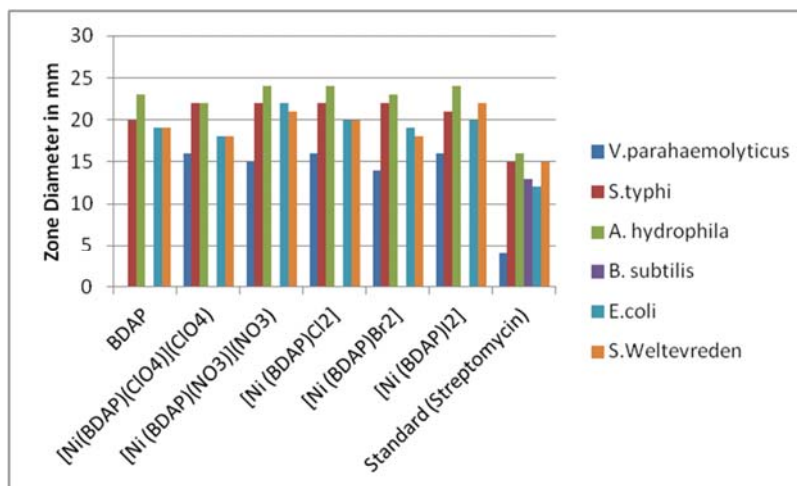
4. Biological study of Nickel (II) complexes

4.1 Antibacterial Study: The antibacterial analyses results of Ni(II) complexes are presented in Table 3.6. The Schiff base ligand BDAP and All the complexes were showing a very good antibacterial activity against all the six gram positive and gram negative bacteria compared to the standard. Generally, the complexes have higher activity than the Schiff base ligand. The positive charge of the metal in chelated complex is partially shared with the ligand's donor atoms so that there is an electron delocalization over the whole chelate

ring. This is the possible explanation for the observed increased activity upon chelation. So the lipophilic character of the metal ^[31] will increase. The graphical representation of their activity against bacteria is shown in fig 2. From the figure we can see that the antibacterial activity of BDAP and its Ni(II) complexes are [Ni(BDAP) ClO₄]ClO₄ > [Ni (BDAP) NO₃](NO₃) > [Ni (BDAP)Cl₂] > [Ni (BDAP)Br₂] > [Ni (BDAP) I₂] > BDAP. All the complexes seem to be promising as they showed antibacterial activity higher than standard streptomycin.

Table 6: Antibacterial activity of BDAP and its Nickel (II) Complexes (Zone diameter in mm)

| Compound | <i>V. parahaemolyticus</i> | <i>S. typhi</i> | <i>A. hydrophila</i> | <i>B. subtilis</i> | <i>E. coli</i> | <i>S. weltevreden</i> |
|--|----------------------------|-----------------|----------------------|--------------------|----------------|-----------------------|
| BDAP | 0 | 20 | 23 | 0 | 19 | 19 |
| [Ni(BDAP)(ClO ₄)](ClO ₄) | 16 | 22 | 22 | 0 | 18 | 18 |
| [Ni (BDAP)(NO ₃)](NO ₃) | 15 | 22 | 24 | 0 | 22 | 21 |
| [Ni (BDAP)Cl ₂] | 16 | 22 | 24 | 0 | 20 | 20 |
| [Ni (BDAP)Br ₂] | 14 | 22 | 23 | 0 | 19 | 18 |
| [Ni (BDAP)I ₂] | 16 | 21 | 24 | 0 | 20 | 22 |
| Standard (Streptomycin) | 4 | 15 | 16 | 13 | 12 | 15 |

**Fig 2:** Graphical representation of Antibacterial Analyses of BDAP and its Ni(II) complexes

4.2 Antifungal study: The antifungal analysis results of Ni(II) complexes are summarized in Table 3.28. All the complexes were showing a very good antifungal activity against *Trichophyton Tonsurans* compared to the standard. Generally, the complexes have higher activity than the Schiff base ligand. The graphical representation of their activity against fungus is shown in fig 3.31. From the fig we can see that the antifungal activity of the bromo and iodide complexes of Ni(II) complexes is higher than other complexes.

Table 6: Antifungal activity of BDAP and its Nickel (II) Complexes (Zone diameter in mm)

| Compound | <i>Trichophyton tonsurans</i> |
|--|-------------------------------|
| BDAP | 14 |
| [Ni(BDAP)(ClO ₄)](ClO ₄) | 23 |
| [Ni (BDAP)(NO ₃)](NO ₃) | 18 |
| [Ni (BDAP)Cl ₂] | 19 |
| [Ni (BDAP)Br ₂] | 20 |
| [Ni (BDAP)I ₂] | 21 |
| Chlorothalonil | 34 |
| DMSO | 0 |

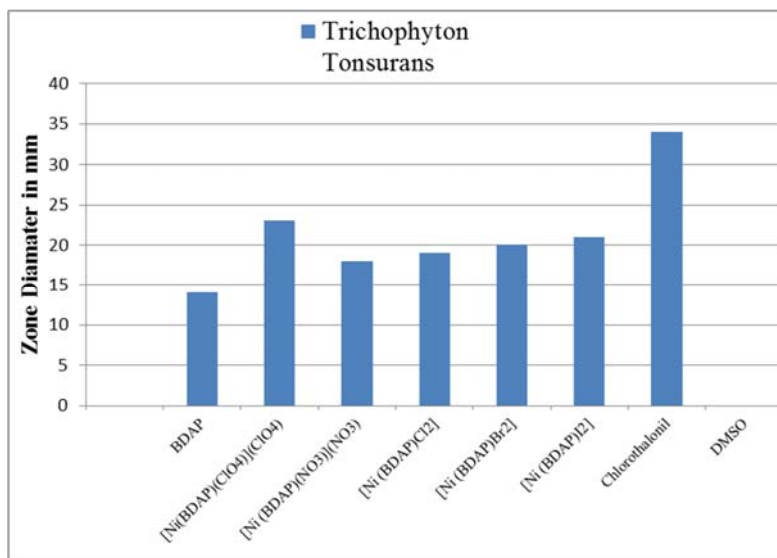
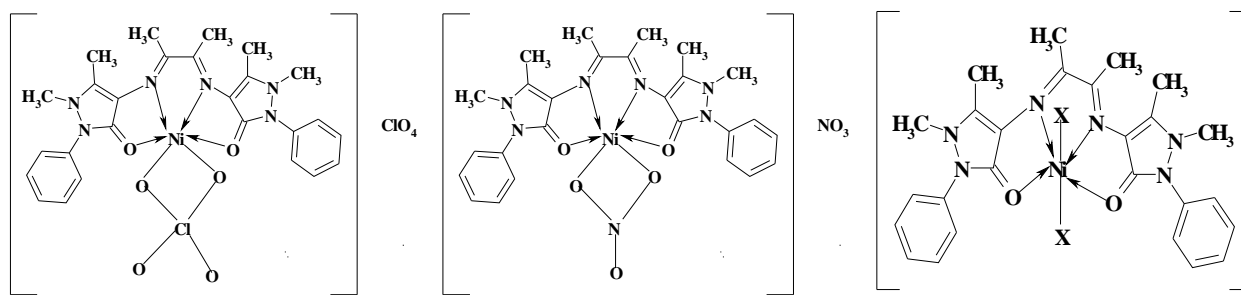


Fig 3: Graphical representation of Antifungal Analyses of BDAP and its Ni (II) complexes

5. Conclusion

The elemental analyses and molar conductance data suggests that the nickel (II) complexes of BDAP may be formulated as $[\text{Ni}(\text{BDAP})\text{X}]$ (where $\text{X} = \text{ClO}_4^-$ or NO_3^-) and $[\text{Ni}(\text{BDAP})\text{X}_2]$ (where $\text{X} = \text{Cl}^-$, Br^- or I^-). The infrared spectral data suggest that BDAP acts as a neutral tetradentate ligand coordinating through both the azomethine nitrogens and both the carbonyl oxygens. The molar conductance and the infrared spectral studies reveal that one of the perchlorate and one of the nitrate

ions are coordinated bidentately. In the case of halide complexes, both the chloride, both the bromide and both the iodide ions are coordinated. The electronic spectra and magnetic moment suggest a octahedral geometry around the Nickel (II) ion in all the complexes. The thermogravimetric analyses data also confirmed the above observations. Based on the results of the present study, the tentative structures of the complexes are shown in fig. 4.



(Where X = Cl⁻, Br⁻ or I⁻)

Fig 4 Tentative structures of Nickel(II) complexes of BDAP

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7. References

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