A New Mannich base, Ni (MOTTP) (H₂O)₄ NO₃] NO₃.H₂O and Ni (MDTTP)(H₂O)₄NO₃]NO₃.H₂O: Crystal structure, Thermal behavior, Solid state, FTIR, NMR Spectral analysis and Antimicrobial activity

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Abstract : Singal crystal of Ni complex, an organic material, were grown by slow solvent evaporation technique at room temperature. DMSO was used as solvent. The nickel crystal obtained by the above technique were subjected to different characterization analyses. The functional groups and optical behavior of the crystal was identified from FTIR and UV analysis. The correlation between crystal structure and thermal stability of nickel complex is observed. In all compounds the fragments of ligands donor atoms go in the last steps. Additionally, antimicrobial activities of compounds were carried out against certain gram positive and gram negative bacteria were also determined.
Keywords : nickel complex, FTIR, Antimicrobial studies.

Highlights

Single step synthesis of a new mannich base
Physicochemical characterization from UV, FTIR and NMR
Thermalanalysis were performed using TG-DTA
Antimicrobial and thermal properties of the compounds were completely investigated

Introduction

The design and synthesis or organic compounds with delocalized electronic clouds have got much attention in the recent past, due to their potential application in nonlinear optics like opto-eletronics, optical communication, dynamics image processing, optical computing, optical switching and light emitting diodes[1]. Organic crystals are mainly employed for optical applications owing to their high conversion efficiency,   transparency

in the UV- region, large optical susceptibilities and inherent ultrafast response time. An organic molecules with significant fluorescence and nonlinear optical activity generally consists of a delocalized pi electronic cloud with an electro donor on one end and an electron acceptor an the other end, forming a 'push-pull' nature in the molecular structure. Careful selection donor-acceptor groups in the conjugated system ultimately leads to increased molecular hyperpolarizability. Mannich bases are group of compounds derived by the condensation of aromatic aldehydes or ketones with animes. The crystal engineering of mannich bases for optical application is feasible by incorporating suitable donor-acceptor moieties. Groups attached to both ends of mannich bases facilities asymmetric electron distribution in either the ground or the excited state, leading to an increased optical nonlinearity. The presence of (anil-linkage) -HC=N- in the mannich base acts as a precursor for the synthesis of antibiotics, antitumor and antiphlogistic drugs. A large of mannich base crystals eith high seconds and thirds orders nonlinear optical properties (both macroscopic and microscopic) have been studied recently. In the presents investigation, we reports the synthesis, grouth and characterization of a new mannich base singalcrystal() carring electron pushing and electron pulling groups on either sides of the pi conjugation. The structure-property relations for our studies suggest that nickel compounds may be used as an inhibitor of some antimicrobial growth and probably in development of new preparation that may suppress the growth of microoraganism caused by bacterial infectiom.

Physical Measurements

Molar conductance of the complexes were measured at room temperature ($30\pm2°$) in DMF (~10^{-3}M solution). Magnetic moment of the complexes were recorded using VSM instrument. IR spectra of the complexes were recorded in the region 400-4000cm^{-1} using a double beam Perkin-Elmer FIIR spectrometer employing KBr disc technique. The electronic spectrum of the complexes was recorded in DMSO using Hitachi UV – visible spectrophotometer in the range 200-1200nm. Cyclic Voltammetry and XRD studies were carried out. TG and DTA studies were carried out with a shimandzu STA-1500 instrument (heating rate 20°C/ minute) in nitrogen atmosphere. Cyclic Voltammetry was carried out with an EG and G instrument model 270/250 research electrochemistry hardware and software using Tetrabutylammonium perchlorate as the supporting electrolyte. XRD measurements were carried out with a Jeol JDX 8030 X-ray diffractometer using CuKα radiation (λ=1.54Å) instrument.

General Preparation of 2-thioxo-6-Methyl-tetrahydro pyrimindin-4(1H)-one (5).

A solution of phenyl ethyl ammine (1.21g), t-Butyl acetoacetate (1.58g) was heated in the presence of O-xylene (5ml) for 1 hr. Then the reaction mixture was poured over crushed ice and separated. The product 3-oxo-N(1)-phenyl butamide was filtered and recrystalized from ethanol. The product (1.025g), Benzaldehyde (0.1g), thiourea (0.38g) dissolved in acetonitrile were reflexed in the presence of CeCl$_3$.7H$_2$O (0.931g) as catalyzed for 6 hrs. The reaction mixture was poured over crushed ice and separated. The product was filtered and recrystalized from ethanol. Yield 50% melting 144°-147°C. (Anal. calc. %) for ligand: C-41.6, H-5.50, N-19.39 Molecular weight 143. Found C-41.6, H-5.56, N-19.44, Molecular weight 144. IR (cm^{-1}) : 3114(s), 3085(s), 2931(s), 1701(s), 1635(s), 1483(sd), 1419(b), 1240(s), 1166(b), 1039(b), 748(w), 696(b), 669(b), 655(s), 511(l).

2.2.6 Preparation of 3-methyl-2,6-diphenyl-tetra hydro thiopyran-4-one (6).

Gaseous H$_2$S was passed into a boiling mixture of 1,4-pentadiene-3-one (40g, 0.29mol) and CH$_3$COONa. 3H$_2$O (40g, 0.29 mol) in 400ml of ethanol for 15 hrs. The reaction mixture was cooled to room temperature and kept at 0°C for 2hrs. The residue was filtered and the alcoholic solution refridgenerated for three days. The white solid that formed was filtered, recrystallised from petroleum ether (60-80°C). Yield: 11g (25%), M.Pt (123-125°C).(Anal. calc. %) for ligand: C-76.57, H-6.37, S-10.35 Molecular weight 279. Found C-76.69, H-6.38, S-11.35, Molecular weight 282. IR (cm^{-1}) : 3158(s), 3052(s), 2925(s), 1701(s), 1629(s), 1492(sd), 1448(b), 1226(s), 1101(s), 1078(s), 1000(s), 933(b), 811(b), 740(w), 586(b), 516(b).

Nickel (II) complexes with ligands (1-2)

Synthesis and characterization of Nickel (II) complexes with the ligands of (1-2) are described in this chapter. Although extensive work has been carried out on the synthesis and characterization of Ni (II) complexes with different organic macromolecules as ligands, no work has been reported so far on the

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comparative studies of Ni (II) complexes of ligands. In this view, it is worth to study the transition metal ion of Ni

Results and Discussion

All the Ni (II) complexes are non-hygroscopic in nature and pale green in colour. They are insoluble in benzene, carbon tetrachloride, chloroform etc but moderately soluble in methanol, DMF and DMSO. The analytical data and composition of the complexes are presented in Table 1.

Electrical Conductance

Molar conductance values of the different Ni (II) complexes ($10^{-3}\mu$) in DMF are given in Table 2. The values are in the range of 140-187ohm^{-1}cm^{2}mol^{-1}. given in Table2, shows that all the complexes are 1:1 electrolyte behaviour in nature.

Magnetic Behaviour

Magnetic moment values of different Ni (II) complexes with ligands (1-2) are given in Table 3. These are useful in establishing the geometry of the complexes.For an octahedral Ni (II) ion complex, the ground state ^3A_2g is expected to show magnetic moment above the spin only value (2.88BM) due to spin orbital coupling or higher state mixing with the ground state. Magnetic moment (2.98 – 3.40BM) are in accordance with high spin d^8 complex and they are diamagnetic in nature.

The magnetic moment values of Ni (II) complexes with ligands (1-2) are found to be in the range of 2.80 – 3.20 BM. These values are in accordance with high spin d^8 complexes. These observations indicate that Ni (II) complexes are high spin octahedral complexes.

Molar Mass

The molar mass of the Ni(II) complexes were determined by Rast method. The values obtained are in agreement with the calculated ones from the suggested formula of the complexes. The mass values are presented in Table 1.

Electronic Spectra

The electronic spectra of Ni (II) complexes of ligands (1-2) were recorded in solid state. The absorption frequencies are given in Table – 4. The electronic spectra of all the complexes exhibit three bands, one at near IR region. These absorption frequencies are in accordance with those expected for an octahedral geometry.[215,255,289] The absorption bands at *Ca* 8308 – 9718 cm^{-1}(ν_1), 13157 – 15728 cm^{-1}(ν_2), and 23327 – 27411 cm^{-1}(ν_3), are assigned to $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)$ transitions respectively. The ν_3/ν_2 ratios fall within 1.70 -1.78 which also favours an octahedral geometry for these complexes. All these spectral observations coupled with the magnetic data lead to the conclusion that the complexes are spin-free with an octahedral geometry. Using the observed transitions, the different ligand field parameters viz., ligand – field splitting energy (10Dq), Racah inter-electronic repulsion parameter (B) and covalent factor (β) have been calculated and are presented in Table 4. The absorption spectra of some typical Ni (II) complexes are given in figs.1.

The electronic spectra of all the Ni(II) nitrate complexes are similar. They exhibit three major bonds in the regiosn 9750 – 9420cm^{-1}, 15,500 – 14,000cm^{-1} and 26,000 – 23,000cm^{-1} which may be assigned to $^3A_{2g(F)} \rightarrow {}^3T_{2g(F)(\nu1)}$, $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)(\nu2)}$ and $^3A_{2g(F)} \rightarrow {}^3T_{1g(P)(\nu3)}$ transitions respectively[297-300] which are characteristic of distorted octahedral geometry of Nickel (II) complexes. Using these energy values different ligand field parameters like ligand field splitting energy (10Dq), Racah inter-electronic repulsion parameter (B^1) and the covalent factor (β) were calculated and presented in the table.

Calculation of 10Dq, B and β for octahedral Nickel(II) complexes

The value of Δ_0 (10Dq) is obtained directly from the lowest energy transition (ν_1). The following equation is employed to calculate the experimental ^3P energy value, i.e., p of eqn.(1).

$$[6Dqp - 16 (Dq)^2] + [-6Dq-p]E + E^2 \quad =0 \quad \dots\dots\dots\dots\dots\dots\dots\dots(1)$$

The quantity p is equal to 15B for nickel (II) ion, where B is Racah parameter. Racah parameter indicates the magnitude of the inter-electronic repulsion between various levels in the gaseous ion. The quantity B is a constant which enables one to express the energy difference between the levels of highest spin multiplicity in terms of some integer, n times B, i.e., nB. Both n and B vary for different ions and in the case of Ni^{2+}, the energy difference between ^3F and ^3P is 15B. The same term for Ni(II) complex is 15B'. To use equation (1), it is necessary to employ the energy value for $^3T_{1g}$ (P) state. This is the energy observed for the $^3T_{1g}$ (P) transition plus the energy of $^3A_{2g}$ level.

E observed for transition $^3A_{2g} \rightarrow ^3T_{1g}$ (P)

$= $ Energy of $^3T_{1g}$ (P) – energy of $^3A_{2g}$ $\dots\dots\dots\dots\dots\dots\dots\dots\dots$(2)

But E of $^3A_{2g}$ $=$ $-12Dq$ $\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$(3)

Thus E of $^3T_{1g}$ (P) $=$ E for the transition $^3A_{2g} \rightarrow ^3T_{1g}$ (P) $-12Dq$

The calculated E for the transition value $^3A_{2g} \rightarrow ^3T_{1g}$ (P) along with Dq value is employed in eqn. (1) to get p value.

Since P = 15B', now B' = P/15

The convalent factor β is calculated using the following equation (4)

$$\beta = B'/B = B_{complex}/B_{free\ ion} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(4)$$

The splitting energies 10 Dq of Ni (II) complexes are found to be in the range $8308 – 9718 cm^{-1}$. The Racahparameter (B) lies in the range $855 -932 cm^{-1}$ which is well below the B value of free Nickel (II) ion ($1041 cm^{-1}$) indicating that the nickel ion has entered into complex formation. The covalent factor (β) is around 0.89, indicating an appreciable covalent nature of metal – ligand bond in all the complexes.

Infrared Spectra

The IR spectral bands of the ligands and the complexes with their probable assignments are listed in Table –5. The moderately strong bands around $3300 cm^{-1}$ in the IR spectra of the free ligands (1-2) are attributed to the stretching mode of N-H vibration. In the spectra of the complexes, (Figs 2), these bands exhibit a considerable downward shift to $30-50 cm^{-1}$. This spectral observation suggests that the coordination of the ligands to the metal ion takes place through the lone pair of electrons of secondary amine nitrogen atom of the ligands (1-5) moiety. The observed similar decreasing trend of C-N stretching frequency of $N-CH_3$ bond in ligands (1,4,5) and their complexes suggests the coordination involvement of lone pair of electrons from the tertiary amine nitrogen atom of the ligands. The only coordinating centre of the ring nitrogen of the ligands is further evidence by the presence of a new band in the region $420-410 cm^{-1}$ due to M-N bonding. The lone pair of electrons from the ring sulphur hetero atom of the ligands and the benzylidene carbonyl moiety of ligandare the coordinating centre to the metal ion.

A slight change in frequency may be due to a change in conformation of the ring during complexation. The bands at the range of $3651-3363 m^{-1}$ in all the complexes with ligands and medium intensity band in the region $1628 -1600 cm^{-1}$ are attributed to O-H stretching and H-O-H bending vibrations respectively.[226] The above bands indicate the presence of water molecule in nickel (II) complexes. This is also supported by the appearance of a new band in the region $540-507 cm^{-1}$ due to M-O bonding.

The C=O stretching frequency of the piperidin-4-ones (ligands) lie around $1700 cm^{-1}$. This absorption is shifted to higher frequency by about $20-31 cm^{-1}$ in the corresponding complexes. This shift is probably due to
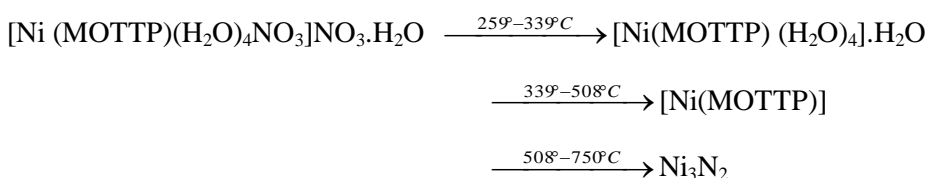
some conformational changes which occur on complexation and not due to carbonyl group participation. The shift of C=O stretching frequency of the ligands in their complexes is found to be only 5-10cm^{-1}. This suggests that the conformational change is larger for piperidin-4-ones containing a NH group than for those containing a NH$_3$ group. This may be due to the difference in the preferential orientation of the nitrogen lone pair of electrons in these two types of piperidin-4-ones. Involvement of nitrogen atom in coordination supported by the presence of new band 425-410cm^{-1} due to ν(M-N) in the free ligand is shited. The sharp band in the region 1720-1680cm^{-1} is assignable to ν (C=O)to lower frequency ($\Delta\nu = 12.52$ cm^{-1}) in the complexes. All these observations confirm the cooridnation of carbonyl oxygen atom to central metal ion. This is further rconfirmed by the appearance of new band in the region 563-510cm^{-1} due to ν (M-O). The presence of water molecules in the complexes is indicated by a sharp band in the region 3473 – 3387cm^{-1} due to O-H stretching and a strong band around 1652 – 1576cm^{-1} due to H-O-H bending vibrations.

Thermal Analysis

The simultanaeous TG –DTA measurements of two nickel (II) complexes were carried out in nitrogen atmosphere and their data are summarized in Table 6. These can be treated as model for all Nickel (II) complexes with ligands (1-2) to characterize them and to study their stability.
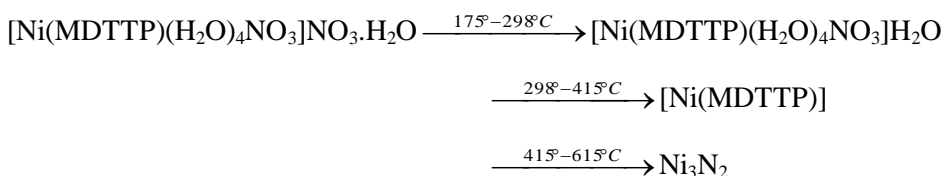
[Ni (MOTTP) (H$_2$O)$_4$ NO$_3$] NO$_3$.H$_2$O Complex

The TG curve of [Ni(MOTTP) (H$_2$O)$_4$ NO$_3$]NO$_3$.H$_2$O shows that the complex is stable upto 220°C and then it undergoes decomposition in three stages. The first decomposition stage takes place in the temperature range 259°-339°C, which corresponds to the removal of coordinated water molecules present in the complex. The dehydration process is followed by the mass loss of 10.61% (Theoretical value 12.01%). The peak temperature is 310°C. In TG curve the second plateau temperature range is 339°-508°C and the corresponding mass loss is 33.08% (theoretical value 34.15%). The second stage endothermic decomposition peak temperature is 460°C in DTA. The third stage of exothermic decomposition ranges from 508°-750°C and the decomposition peak temperature is 427°C in DTA with the mass loss of 85.40% (theoretical value 85.90%). The three stages of decomposition are attributed to the stepwise removal of one nitrate ion, one nitrate ion and water molecules, and organic ligand, resulting in the formation of Ni$_3$N$_2$ as the product. The decomposition scheme of [Ni (MOTTP) (H$_2$O)$_4$NO$_3$].NO$_3$. H$_2$O is given below as a representative example.

[Ni (MOTTP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O $\xrightarrow{259°-339°C}$ [Ni(MOTTP) (H$_2$O)$_4$].H$_2$O

$\xrightarrow{339°-508°C}$ [Ni(MOTTP)]

$\xrightarrow{508°-750°C}$ Ni$_3$N$_2$

The same argument has to be applied in the composition derivation of the complexes of Ni (II) ion with ligand 6 and is given as follows:

[Ni (MDTTP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O

[Ni(MDTTP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O $\xrightarrow{175°-298°C}$ [Ni(MDTTP)(H$_2$O)$_4$NO$_3$]H$_2$O

$\xrightarrow{298°-415°C}$ [Ni(MDTTP)]

$\xrightarrow{415°-615°C}$ Ni$_3$N$_2$

The thermal analysis of the complex of Ni (II) ions with ligands (1) & (2) has been carried out to supplement the infrared spectral data and percentage composition of the complexes. Considering the temperatures at which the dehydration processes take place and the way by which they proceed, one can determine whether water molecule is coordinated or not. In the present investigation, both the complexes show three stages of mass loss with two endothermic and one exothermic reactions. The two model complexes lose water molecules at above 200°C and such high temperature dehydration is in support of the presence of coordinated water molecules in the compound. IR studies also indicate the presence of water molecules in coordination sphere. The first and the second arrests in TG curve of theses complexes show a mass loss

corresponding to five water molecules. The DTA curves of Nickel (II) complexes show two sharp endothermic peaks at 250°C and 380°C. It is thus inferred from the thermal studies that five molecules of water are coordinated to the metal ion. The TGA & DTA of Ni complexes are given in figs – 3.

Cyclic Voltammeteric Studies

The electrochemical behaviours of the Ni(II) complexes and the ligands (1-2) have been investigated by cyclic voltammetric studies, and the results are listed in Table 6 comparison of the peak potentials of the ligands (1-2) and the Ni complex reveals that the metal based one – electron reduction process Ni(II) – Ni(I) occurs in the complex.[311] The separation of the peak potentials of the peaks obtained in the forward and reverse scan indicates the quasi – reversible nature of the electrode process in the Ni(II) complexes. However, in the reverse scan the Ni(II) complex exhibits an anodic peak at 0.56V. This peak is attributed to the one electron oxidation of Ni (II) i.eNi(II) – Ni(III).

X-ray (Powder) Diffraction Study

The X-ray (powder) diffraction photograph was recorded for the Ni complex with ligands (1-2). For example [Ni(MDDP)(H$_2$O)$_4$NO$_3$]NO$_3$.H$_2$O photograph reveals 23 reflections with maximum reflection at 13.00 (2θ) with the spacing of 6.80Å. All the lines in the powder photograph were indexed based on Ito's method.[232] The Ni (II) complexes crystalises in a triclinic lattice. The agreement between observed and computed Q$_{hkl}$ (within 1%) is displayed in Tables 8. The direct cell dimensions calculated from the reciprocal cell dimensions are collected in Table 9.

The molecules is non-centrosymmertric and it is a neutral monomer in the Ni(II) is octahedrally coordinated by two each of crystallographically independent N-coordinated ligands.

The NH, NCH$_3$ groups are quasilinear with 101.1° & 116.7° bonded to the Ni(II) ion through an angle of 189.5° & 165.3° respectively. Interestingly the respective N atoms of the ligands is cis –located whereas the same are trans-positioned in the reported[271]Ni(II) complexes.

The following probable structure has been assigned to the nickel complexes.
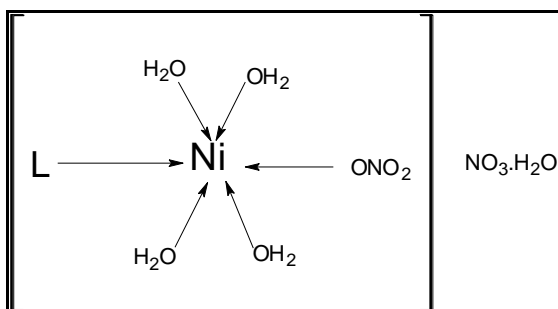
Antimicrobial studies

In this work and many previous reports, the coordination of ligands to metal improves Antibacterial and antifungal activity. The overtones concept and tweedys chelation theory were used for explanation of increased activity of the complexes respect to parent ligands. As mentioned earlier, the in-built spiro carbocylic or heterocylic systems in a ring increases the biological potency, with the systems having smaller rings. On this basis, the synthesized compounds were evaluated for their in-vitro antibacterial and antifungal activities.

The evaluations were carried out using "paper disc diffusion method" for antibacterial activity and the "Turbidity method" for antifungal activity. All the synthesized compounds (1-8) were evaluated for their in-vitro antibacterial activity against the pathogenic micro-organisms, Escherichia coli (gram-positive) and Staphylococcus aureus (gram-negative) using paper disc diffusion method. Sterilized 10mm whatman No.1 paper discs were taken, impregnated with 0.1ml of the sample solutions (200μg in DMF) and placed in the petridish containing 25-30ml of nutrient agar inoculated with 18-24hrs test culture. Incubation was carried out

at 37°C for 24hrs and the zone of inhibition was measured in mm. All the experiments were done in triplicate. Phenol was taken as standard.

Antifungal activity of the compounds were determined in-vitro against Aspergillus Niger adopting the turbidity method. In this method, 0.1ml of the sample solutions (200µg in DMF) in 5ml sterilized fungi medium were treated with 3-4 drops of 48hrs old culture in a test tube. The test tubes were then shaken well and incubated for 48 hrs at 37°C. The extent of inhibition was determined by measuring the decrease in turbidity interms of % transmission at 660µ. Salicyclic acid was taken as standard.Antibacterial and antifungal activities of all the compounds in-vitro against the pathogenic micro-organisms Escherichia coli (gram activity) with solvent control: DMF (positive), staphylococcus aureus (gram-negative) and Asperigillus Niger fungal are given in Fig.4.

Table – 1Analytical Data of Ni (II) Complexes with Ligands (1-2)

Complex	Carbon % Found (Cal)	Hydrogen % Found (Cal)	Nitrogen% Found (Cal)	Sulphur % Found (Cal)	Metal Ni % Found (Cal)	M. Wt Found (Cal)	M.Pt (°C)
1	14.65 (14.40)	4.56 (4.32)	13.70 (13.44)	8.02 (7.68)	14.71 (14.08)	416.80 (416.69)	261-263
2	39.05 (38.94)	5.15 (5.05)	5.15 (5.05)	5.79 (5.77)	10.69 (10.58)	554.97 (554.69)	280

Table – 2 Molar Conductance of Ni(II) Complexes with Ligands (1-2) $(ohm^{-1}cm^{-2}mol^{-1})$

Complex	Molar Conductance
[Ni (MOTTP) $(H_2O)_4NO_3$]NO_3.H_2O	173
[Ni (MDTTP) $(H_2O)_4NO_3$]NO_3.H_2O	175

Table – 3Magnetic Moment of Ni (II) Complexes with Ligands (1-2)

Complex	Magnetic Moment (µeff)
[Ni (MOTTP) $(H_2O)_4NO_3$]NO_3.H_2O	3.30BM
[Ni (MDTTP) $(H_2O)_4NO_3$]NO_3.H_2O	3.40BM

Table – 4 Electronic Spectra of Ni(II) Complexes with Ligands (1-2) in cm^{-1}

Complex	$^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$	$^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$	$^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$	v_3/v_2	10Dq	B	β
1	8750	12150	25719	2.12	8750	923	0.89
2	9010	15540	24509	1.58	9010	855	0.82

TABLE – 5 Important IR bands (in cm^{-1}) of Ni(II) complexes with ligands (1-2)

Complex	$\gamma_{C=O}$	$\gamma^*_{C=O}$	γ_{N-H}	γ^*_{N-H}	γ_{C-S-C}	γ^*_{C-S-C}	γ^*_{M-N}	γ^*_{M-O}	γ^*_{O-H}	γ^*_{N-C}	γ^*_{H-O-H}
1	1739	1731	3340	3361	-	-	830	528	3550	1113	1659
2	1701	1701	-	-	669	669	-	518	3261	-	1598

Table – 6 Thermal Analysis Data of Ni (II) Complexes with MOTTP and MDTTP Ligands

Complex	DTA Peak Temp °c	Thermogravimetry		
		Temperature range °c	Mass loss %	
			Observed	Calculated
[Ni (MOTTP) (H₂O)₄NO₃]NO₃.H₂O	252.19(+)	259-339	10.61	12.01
	377.16(-)	339-508	33.08	34.15
	381.46(+)	508-750	85.40	85.99
[Ni (MDTTP) (H₂O)₄NO₃]NO₃.H₂O	145(+)	175-298	12.97	13.1
	258(+)			
	343(+)	298-415	56.01	58.09
	155(-)			
	294(-)	415-615	97.97	97.99

Table 7 Cyclic voltammetric data of ligands (1-2) and Nickel (II) Complex

Compounds	E_{PC} (V)	E_{Pa} (V)	ΔE_P (V)
MOTTP	1.62	-8.16	2.9
MDTTP	1.57	-7.85	2.8
Nickel (II) Complex	-0.69	-0.40	1.22

Table 8 X-ray (Powder) Diffraction data for complex [Ni(MODDP)(H₂O)₄NO₃]NO₃.H₂O

d	2θ	$Q_{obs} = 1/d^2$	d-spacing [Å]	Rel. Int. [%]	Q_{cal}	Index (h k l)
11.1676	41.80	0.2007	7.92321	4.21	0.004460	Q_{100}
12.3530	993.62	0.1171	7.16541	100.00	0.005045	Q_{010}
22.9919	41.06	0.2676	3.86826	4.13	0.006120	Q_{001}
26.3730	182.59	0.2676	3.37950	18.38	0.007251	Q_{101}
27.3123	295.29	0.1840	3.26537	29.72	0.010809	Q_{111}
33.3886	29.69	0.2175	2.68372	2.99	0.015486	Q_{101}
41.7305	6.56	0.5353	2.16451	0.66	0.020662	Q_{102}
49.4736	16.65	0.4896	1.84084	1.68	0.035702	Q_{301}
50.3914	22.23	0.2040	1.81394	2.24	0.037592	Q_{122}

Table 9 X-ray (Powder) Diffraction data for complex [Ni(MDTTP)(H₂O)₄NO₃]NO₃.H₂O

D	2θ	$Q_{obs} = 1/d^2$	d-spacing [Å]	Rel. Int. [%]	Q_{cal}	Index (h k l)
13.6152	407.70	0.1171	6.50386	20.49	0.002475	Q_{100}
18.1398	1338.93	0.1338	4.89052	67.30	0.004092	Q_{010}
20.3515	37.60	0.2007	4.36376	1.89	0.006300	Q_{001}
22.6736	628.09	0.1338	3.92182	31.57	0.007051	Q_{101}
23.6411	71.25	0.2007	3.76347	3.58	0.010839	Q_{111}
27.2457	1989.59	0.1338	3.27321	100.00	0.015486	Q_{101}
31.8684	571.50	0.1338	2.80818	28.72	0.019662	Q_{102}
36.5403	233.22	0.1338	2.45914	11.72	0.031755	Q_{301}
37.3796	131.02	0.1338	2.40584	6.59	0.031547	Q_{122}
40.5265	23.15	0.2676	2.22599	1.16	0.033193	Q_{310}
41.3077	128.23	0.1338	2.18568	6.45	0.014572	Q_{102}
43.6117	31.46	0.1673	2.07541	1.58	0.033256	Q_{001}
46.1609	48.63	0.2448	1.96493	2.44	0.004258	Q_{010}

Table 10 Crystal Parameters of [Ni(MDTTP)(H$_2$O)$_4$NO$_3$](NO$_3$)$_2$.H$_2$O

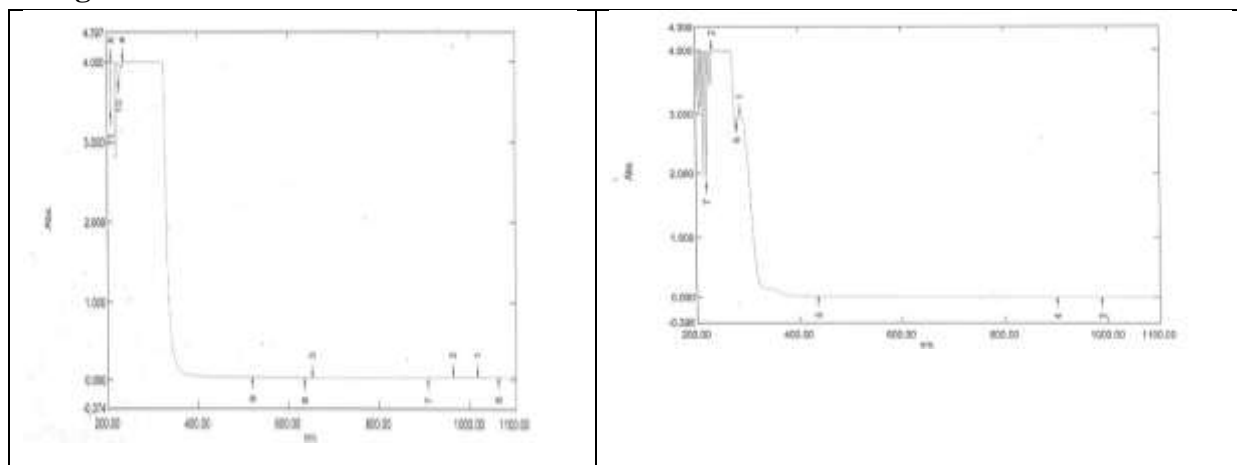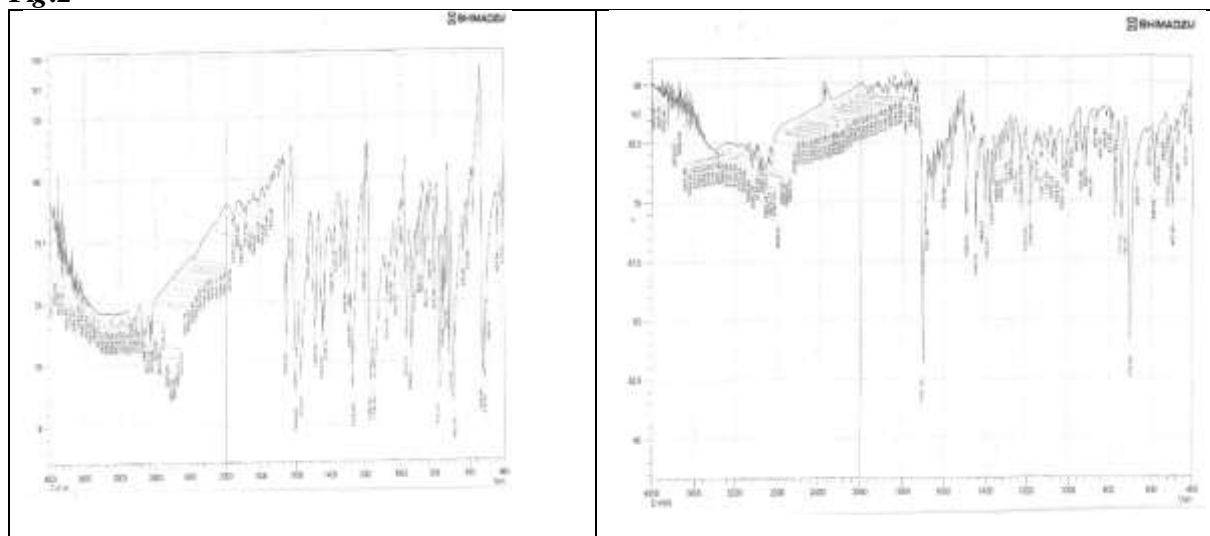| Cell length (Å)	Angular parameters (°)	Cell Volume (Å)^3
a = 15.77	α = 101.1	
b = 12.82	β = 116.7	3275.13
c = 14.58	γ = 107.0	

Uv fig .1

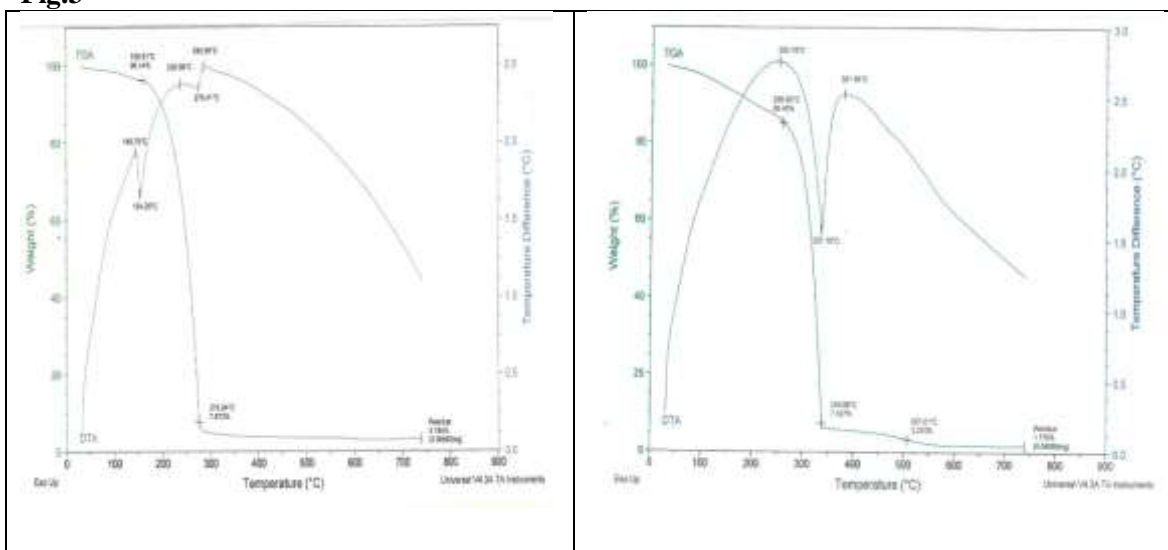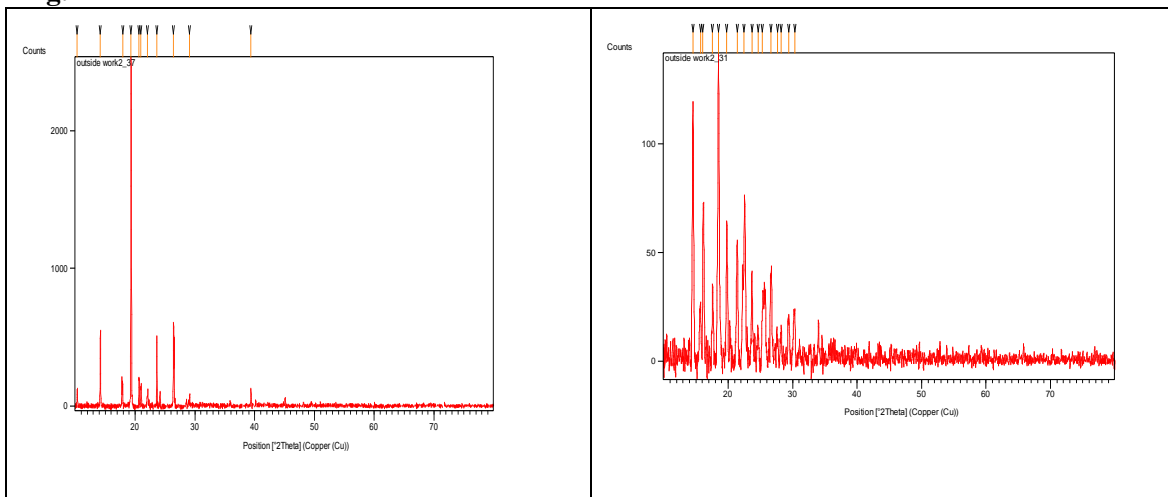
Fig.2

Fig.3

Fig.4

Fig –5a Antibacterial activity of compounds Against *Bacillus subtilis*
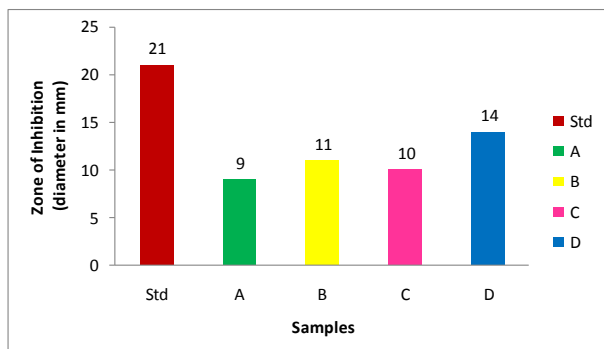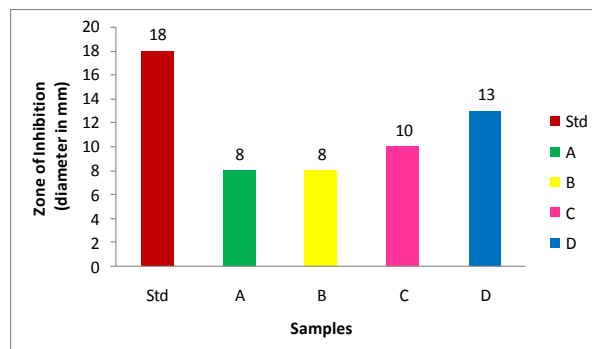
Fig.5b Antibacterial activity of compounds against *Micrococcus luteus*

All the studies of Nickel(II) complexes with various ligands (1-2) lead to the following conclusions.

1. The complexes are 1:1 electrolytes.
2. IR spectral and thermal studies confirm that the complexes contain four coordinated water molecules.
3. Magnetic moments and electronic spectra indicate that Nickel (II) complexes are spin-free with octahedral geometry.
4. One nitrate ion is coordinated with metal ion and the other one is anionic in nature.
5. All the ligands(1) are found to coordinate only through ring hetero atom, whereas the ligand (2) through benzylidene carbonyl moety, thereby indicating the unidentate nature of the ligands.
6. The spectral evidences reveal that these ligands coordinate through chair conformation with slight conformational change.
7. The cyclic voltammetric studies reveal that all the Ni(II) complexes are attributed to one electron oxidation easily i.e. Ni(II)-Ni(III).
8. XRD shows that all the Ni(II) complexes crystalise in triclinic lattice.

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