



ORIGINAL ARTICLE

Spectral and Magnetic Properties of Nickel(II) Divalent Transition Metal Complexes of Mannich Bases of Heterocycles

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ABSTRACT

In the present work some Mannich base nickel(II) complexes of nicotinamide/p-aminosalicylic acid with 2-thienylglyoxal were synthesized by reduction of Schiff base and were characterised with the help of elemental analysis and various advance spectroscopic techniques like IR spectra, NMR spectra, Mass spectra, Magnetic measurements and electronic spectral studies. All complexes shown magnetic moments corresponding to the spin free values for Ni(II) complexes. Compounds were found having octahedral geometry.

Key words: Spectral and Magnetic Properties, Nickel(II), Divalent Transition Metal Complexes

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INTRODUCTION

In the present work *Mannich* base were obtained from the reduction of *Schiff* base synthesized by reaction of 2-thienyl glyoxal and nicotinamide/ p-amino salicylic acid. The importance of nicotinamide is well established in the pharmaceutical chemistry. Moreover, nicotinamide moiety, which has well known biological significance, is a constituent of vitamin B complex. p-Amino salicylic acid and nicotinamide are well known drugs used abundantly in treatment of tuberculosis. The scope as well as significance of coordination compounds of *Mannich* Bases in biological systems and their therapeutic value is well recognized. It has been found that these complexes have a wide range of applications in analgesic, anti-inflammatory activities^{42,23}, antimicrobial activities^{20,21,28,33,45}, potential pesticides³², possible central nervous system stimulant activity¹⁹ potential anticonvulsant agents^{16,46}, influenza neuraminidase inhibitor²⁰ etc. Some *Mannich* bases are known as enzyme inhibitors³⁷ and catalysts¹⁴. *Mannich* bases can also be used in thermally stable fuel composition⁹, as ashless dispersants in engine oils, engine oil additives^{2,18} and as anticorrosives¹⁵.

EXPERIMENTAL WORK

All the *Mannich* bases and their metal complexes were prepared using chemicals of A.R. grade among which solids were used as such and liquids were filtered and distilled.^{6,7,13}

SYNTHESIS OF MANNICH BASE:

Preparation of *Mannich* bases is a multistep process. First of all 2-acetyl thiophene was synthesized by reported method². After distillations of 2-Acetyl thiophene, 2-thienyl

glyoxal was prepared by Kipnis and Ornfelt²⁴ method. Then 2- Thienyl glyoxal is prepared, by stirring a mixture of 32 ml dioxane, 1.1 ml water and 5.55 gm SeO₂ and then heated at 55°C, treated with 2-acetyl thiophene and reflux for additional 4 hrs. Contents were allowed to cool at room temperature to obtain a dark brown product which was (in liquid form) then filtered, distilled, washed with ethanol and dried over CaCl₂.

The Mannich Base (MB₁) TGNA was synthesized by reduction of Schiff Base obtained by reaction of 2- Thienyl Glyoxal and Nicotinamide.

(a) Synthesis of Schiff Base(SB₁) C₁₂H₈O₂N₂S:

Schiff Base was synthesized by mixing 2-thienyl glyoxal with nicotinamide (in equimolar ratio) by constant stirring and refluxed for 3-3½ hrs. Chocolate brown solid was obtained after drying in air. Recrystallisation was carried out by acetone.

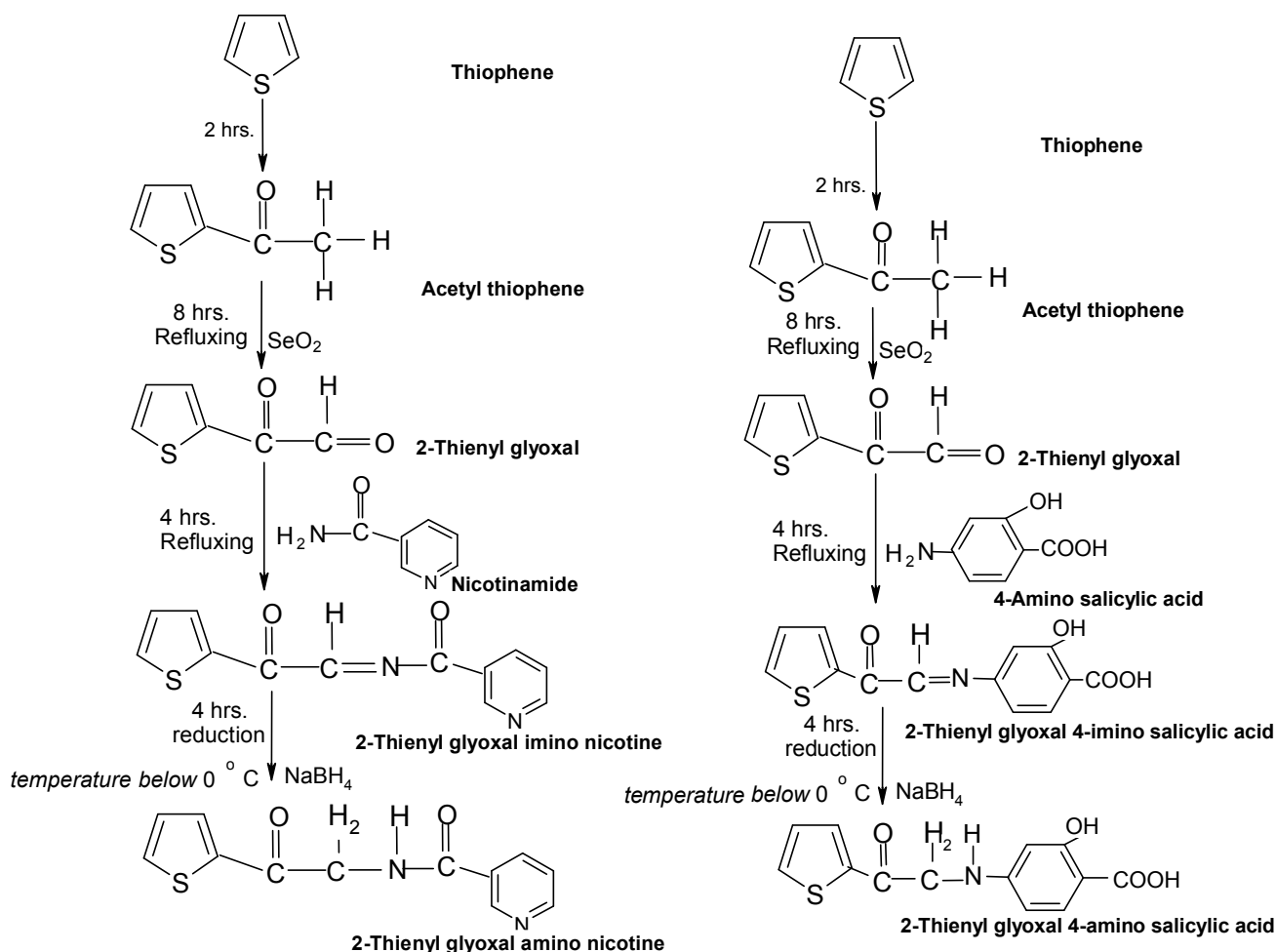
(b) Reduction of Schiff Base to Mannich Base(MB₁) C₁₂H₁₀O₂N₂S [TGNA]:

A solution of Schiff base is chilled to below 0°C and solid NaBH₄ was added with stirring. Finally a blackish brown solid was obtained after drying in air.

The Mannich Base (MB₂) TGASA was synthesized by reduction of Schiff Base obtained by reaction of 2- Thienyl Glyoxal and 4-Amino Salicylic Acid:-

(a) Synthesis of Schiff Base (SB₂) C₁₃H₉O₄NS:

An equimolar amount of 2-thienyl glyoxal and 4-amino salicylic acid was mixed with constant stirring and refluxed for 3-3½ hrs. Dark purple-brown crystals were obtained after drying in air, recrystallised by acetone.



Mannich Base

Mannich Base

(b) Reduction of Schiff base to Mannich Base C₁₃H₁₁O₄NS [TGASA]:

Compound is dissolved and then chilled up to below 0°C before solid NaBH₄ is added to it and is allowed to reach at room temperature slowly. A solid dark chocolate-brown solid is obtained after drying in air.

A stepwise schematic representation for synthesis of *Mannich* base is given in the following section.

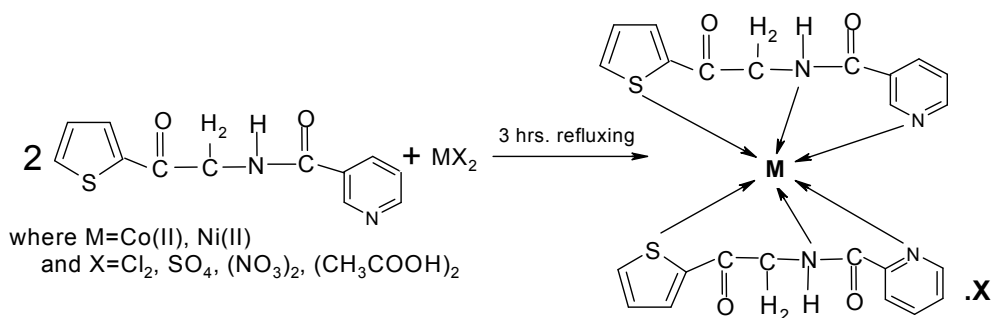
(a) Synthesis of *Mannich* Base 2-TGNA; C₁₂H₁₀O₂N₂S:

(b) Synthesis of *Mannich* Base 2-TGASA; C₁₃H₁₁O₄NS:

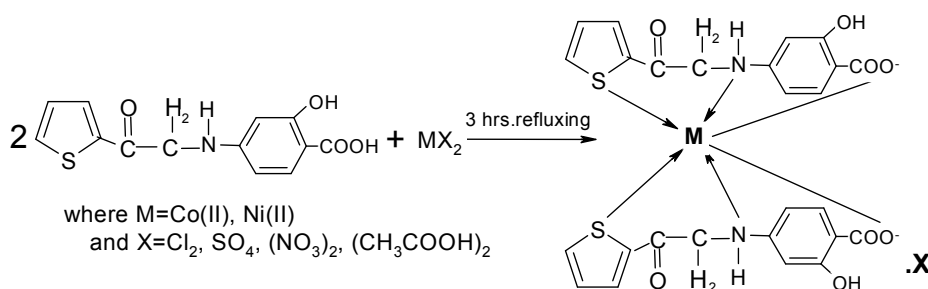
(c) Synthesis of Nickel(II) Complexes:

The reactions of two newly synthesized ligands viz. 2TGNA and 2TGASA were carried out with different nickel(II) salts viz. chloride, sulphate, nitrate and acetate in acetone, ethanol or aqueous medium. Ligand and metal salt were mixed in 2:1:: ligand : metal molar ratio before stirring for 15-20 min. Resulting solution is refluxed for additional 3-3½ hrs and dried in air which have been isolated as:- i) Ni(C₁₂H₁₀O₂N₂S)₂.Cl₂; (ii) Ni(C₁₂H₁₀O₂N₂S)₂.SO₄; (iii) Ni(C₁₂H₁₀O₂N₂S)₂.(NO₃)₂; (iv) Ni(C₁₂H₁₀O₂N₂S)₂.(CH₃COO)₂; (v) Ni(C₁₃H₁₁O₄NS)₂.Cl₂; (vi) Ni(C₁₃H₁₁O₄NS)₂. SO₄; (vii) Ni(C₁₃H₁₁O₄NS)₂. (NO₃)₂; (viii) Ni(C₁₃H₁₁O₄NS)₂. (CH₃COO)₂.

Preparation of metal complexes of 2-TGNA (MB¹):-



Preparation of metal complexes of 2-TGASA (MB²):-



PHYSICAL MEASUREMENTS

Infra red spectra of the ligands and their metal complexes were recorded in FT-IR region using KBr pallets on Perkin Elemer and Shimadzu 8201PC at R.S.I.C, C.D.R.I, Lucknow and also in the Department of Chemistry, St. Johns College, Agra. The NMR spectra of all the ligands were recorded at Torrent Pharmaceuticals Ltd., Gandhinagar (Gujarat) using DMF/DMSO as solvents. The mass spectra of the ligands were recorded in the region 40-350 MHz at RSIC, CDRI, Lucknow. Magnetic susceptibility measurements of the prepared complexes were carried out at room temperature on EG & G model 155 VSM at R.S.I.C., IIT Chennai. The electronic spectra of all the complexes in solution (DMF/DMSO) were

recorded in Elico SL 171 Spectrophotometer at room temperature in the Department of Chemistry, R.B.S. College, Agra.

RESULTS AND DISCUSSION

The analytical data of all the complexes indicating 1:2::metal : ligand stoichiometry is presented in table given below, these solid and greenish brown colored complexes have high melting points and are soluble in general solvents. It is that electronic spectroscopy is a powerful method for investigating transition metal complexes. Additional and complimentary information can be provided by magnetic measurements. Because of partially filled d-orbital of nickel atom, magnetic properties can be expected, depending on oxidation state, electronic configuration and coordination number of central metal ion.

1. INFRARED SPECTRAL STUDIES:

In the present work infrared spectroscopy is used to elucidate tentative structure of metallochelates and donor sites in *Mannich* base ligands by the comparison between infrared spectral data of ligands and its complexes, listed in the table 3.

Infrared Spectra of *Mannich* Base (C₁₂H₁₀O₂N₂S):

MB1- The infrared spectrum (KBr) of the newly synthesized Mannich Base exhibit bands at ~3365, 1619 and 1310-1320 cm⁻¹ (νN-H_{str} and C-N vibration of secondary amine), 1650 and 1680cm⁻¹ (C=O ketonic), ~1255, 828 and 702 cm⁻¹ (2-substituted thiophene), ~1127cm⁻¹ (C-N-C)^{10,34,49}, indicative of presence of mentioned functional groups in the molecule.

It is already known that any shifting in the above-mentioned position, in the infrared spectrum of the metal complexes of this ligand concludes the participation of electron donor atom of that group in formation of metallochelates^{11,39,41}.

Ni(C₁₂H₁₀O₂N₂S)₂Cl₂, Ni(C₁₂H₁₀O₂N₂S)₂SO₄, Ni(C₁₂H₁₀O₂N₂S)₂ (NO₃)₂, Ni(C₁₂H₁₀O₂N₂S)₂ (CH₃COO)₂ The infrared spectral band obtained in ligand is shifted towards higher region and is now obtained at 3300-3400 cm⁻¹ indicating the involvement of this group in chelation. A peak at 1676-1678 cm⁻¹ is almost having same position as in ligand, suggesting, carbonyl group is not in coordination. νC-N-C and νC-S-C are now appeared nearly at 1100-1170 and 800-900 cm⁻¹ indicating the involvement of active atoms of these groups. New peaks nearly at 400 and 500 cm⁻¹ suggest the presence of two metal-nitrogen bonds and frequency at 323 cm⁻¹ is assignable to metal-sulphur bond.

The above discussion concludes that the *Mannich* base C₁₂H₁₀O₂N₂S is tridentate in behaviour, having *NNS* donor set.

Infrared Spectral studies of *Mannich* base (C₁₃H₁₁O₄NS):

Infrared spectra of C₁₃H₁₁O₄NS confirmed the structural features. The infrared bands at ~3430 cm⁻¹ (-OH), 3344 cm⁻¹, ~1424 and 1131 cm⁻¹ (ν_{as}NH of amide group, νN-H bend and C-H vib.), ~3382 (νCOOH), ~1592 cm⁻¹ (νC=O), ~825 and 708 cm⁻¹ (2- substituted thiophene ring) confirms^{8,22,26,31,49} the presence of above groups in the molecule^{10,48,27}.

Ni(C₁₃H₁₁O₄NS)₂Cl₂, Ni(C₁₃H₁₁O₄NS)₂SO₄, Ni(C₁₃H₁₁O₄NS)₂ (NO₃)₂, Ni(C₁₃H₁₁O₄NS)₂ (CH₃COO)₂:-

Broad and almost undisturbed band at 3430-3432 cm⁻¹ indicates the presence of free phenolic -OH group in the complex molecule. The CH₂-NH band frequency at 3344 cm⁻¹ in ligand is now disappeared and may be reappeared/shifted at nearly 3420-3430 cm⁻¹ at overlapped with the peak belongs to phenolic -OH group. This may also be a cause of broadening in phenolic OH frequency, or it may be shifted towards lower region 2924 cm⁻¹. Although it may not be the only cause of broadening but it is not an ignorable fact.

Acetate frequency band is disappeared and a new band appeared at 1362-83, 1144-1161 cm^{-1} , indicates the participation of oxygen, which belongs to deprotonated acetate group in complex formation.

Band at 809 cm^{-1} (lower shift of $\sim 16 \text{ cm}^{-1}$) assignable to C-S-C frequency clearly indicate the involvement of sulphur atom in coordination. Some new bands at 430 cm^{-1} , 370 cm^{-1} and 305 cm^{-1} assignable to metal-oxygen, metal-nitrogen and metal-sulphur bonds indicate the presence of chelating environment around $\text{Ni}(\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS})_2\text{Cl}_2$ atoms.

$\nu\text{C-S-C}$ is disappeared and new band is appeared at 310 cm^{-1} assignable to $\nu\text{M-S}$ indicate the participation of thienyl sulphur in chelation. The spectrum also exhibits three new bands at 450 cm^{-1} and 380 cm^{-1} indicates the presence of metal-oxygen and metal-nitrogen band in $\text{Ni}(\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS})_2\text{SO}_4$ molecule.

A frequency with 20 cm^{-1} lower shift at 805 cm^{-1} indicates the coordination through thienyl sulphur in this molecule. Band frequencies at 465 cm^{-1} , 378 cm^{-1} and 305 cm^{-1} indicates the presence of νMO , $\nu\text{M-N}$ and $\nu\text{M-S}$ bond in $\text{Ni}(\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS})_2(\text{NO}_3)_2$ nickel(II) heterochelate.

$\nu\text{C-S-C}$ is disappeared and a new bond appeared at 935 cm^{-1} indicative of participation of active sulphur atom of this group in chelation. Presence of metal-sulphur bond frequency further provides support of this.

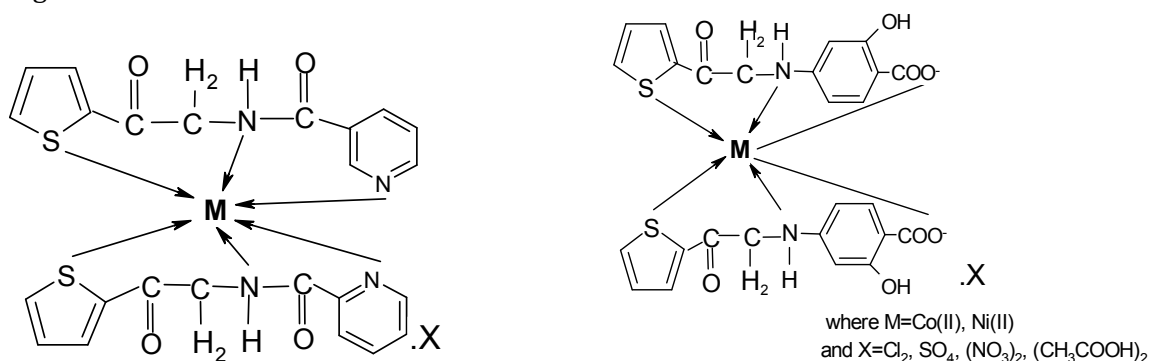
Presence of new bonds at 468 cm^{-1} , 372 cm^{-1} and 309 cm^{-1} indicates the presence of metal-oxygen, metal-nitrogen and metal-sulphur bonds in $\text{Ni}(\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS})_2(\text{CH}_3\text{COO})_2$ molecule.

In all the complexes of this series $\nu\text{M-N}$ bond is usually sharp and strong and the $\nu\text{M-O}$ bond is usually broad and strong since a large dipole moment change is involve in the vibration of the $\nu\text{M-O}$ bond in comparison to that of the M-N bond¹¹. Hence it is expected that the $\nu\text{M-O}$ bond should occur at a higher frequency then the $\nu\text{M-N}$ bond^{11,39}. Although some authers^{3,25} still assign $\nu\text{M-N} > \nu\text{M-O}$ erroneously, it is now generally believed that the $\nu\text{M-O}$ bond occur at higher frequency then the $\nu\text{M-N}$ bond as per expectations⁴⁰.

The above discussions reveal that the *Mannich* base ligand ($\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}$) is tridentate in nature and have three donor sites (*ONS* donor set) in it.

On the basis of above discussed infrared absorptiometric data [table 3] the tentative structures for metalochelates of Mannich base ligands $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ and $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}$ are as follows:-

Metalochelates of Mannich base ligands $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ and Metalochelates of Mannich base ligands $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}$.



2. NUCLEAR MAGNETIC RESONANCE STUDIES:

MB1- The ^1H NMR spectrum of a representative compounds have signals at $\delta 6.956$ (triplet, 3H, thiophene ring), $\delta 2.547$ (doublet, 2H, CH_2 proton), $\delta 7.502$ (triplet, 3H, NH-CH_2 protons), $\delta 7.619$ (singlet, CONH proton) and $\delta 8.709$ (doublet, 2H, 2,6 positions of pyridine ring further confirms the structure of this Mannich Base.

MB2- The NMR spectral signals at δ 2.512 (doublet, 2H, CH₂ proton), δ 7.14 (triplet, 3H, aromatic protons)^{17,36,47}, δ 6.902 (triplet, 3H, thiophene ring)¹, δ 7.840 (triplet, 3H, NHCH₂ protons), δ 8.53 (Singlet, H, Ar-OH)³⁵ and δ 12.8 (singlet, H, COOH)⁴⁴ in ppm further confirms the structure. Data is tabulated in Table 1.

3. MASS SPECTRSCOPY:

MB1 : Elemental analysis

Elements	C	H	N	S
% found	58.4	4.7	10.9	13.8
% calculated	58.52	4.09	11.37	13.02

The Mass spectra of this ligand exhibit characteristic molecular ion peaks. The important peaks observed in mass spectra of this ligand are m/e 248, 168, 125, 111, 83, 79 corresponding to C₁₂H₁₀O₂N₂S, C₇H₆O₂NS, C₆H₅OS, C₅H₃S, C₅H₅N etc. This spectra also aid in characterization of ligand.

MB2 : Elements

Elements	C	H	N	S
% found	56.4	4.2	5.1	11.62
% calculated	56.31	4.00	5.05	11.56

The bar graph in mass spectra of the ligand also helped in structure elucidation, as it exhibits m/e values; 278, 216, 167, 125, 113, 85 and 77 assignable to C₁₃H₁₁O₄NS, C₁₂H₉ONS, C₆H₅OS, C₅H₃OS, C₄H₃S and C₆H₅ molecular ion. Data is listed in table 2.

4. MAGNETOCHEMISTRY:

The magnetic features of nickel(II) complexes have been studied extensively started with the work of Schlapp and Penney³⁸. Magnetically, octahedral nickel(II) complexes have relatively simple behavior. From both d-orbital splitting and energy level diagrams it follows that they should have two unpaired electrons and this is found always to be the case, the magnetic moments ranging from 2.9 to 3.4 B.M. depending on the magnitude of orbital contribution. All newly synthesized nickel(II) complexes of *Mannich* base exhibits magnetic moments in the range of 2.85-3.2 B.M., values shown in magnetic susceptibility table 4(a) and 4(b). The observed magnetic moment values are in good agreement with the complexes having ²A_{2g} or ³B_{1g} ground term. These values shown orbital contribution expected for hexa-coordinated Nickel(II) ions. Slightly higher values are probably due to distortion from the pure octahedral to tetragonal symmetry. The spin free behaviour of these complexes is common in d⁸ configuration because of *Jahn Teller* effect.

5. ELECTRONIC SPECTRAL STUDIES:

The present observed electronic graphs are gicm⁻¹ⁿ and the spectral data is tabulated in table 5(a) and 5(b). The electronic spectra of all the complexes exhibits three transitions, assigned confidently to ³A_{2g}→³T_{2g}(F) (ν₁)(8200-8700), ³A_{2g}→³T_{1g}(F) (ν₂)(16225-17800) and ³A_{2g}→³T_{1g}(P) (ν₃)(25500-26530), respectively are in good agreement of octahedral geometry⁴⁴. Ratio ν₂/ ν₁ is nearly 1.6 which is considered as identification of octahedral geometry.

The classical Hamiltonian scrambles the DQ and DT parameters. Dq is only a measure of equatorial field, while DQ is a global quantity measuring the totally symmetric contribution to the field, i.e. the average global field strength. The ratio of DT/ DQ gives the amount of distortion. Calculated values (table) indicates that the structure of the present complexes lies somewhere between square planer and octahedral structure. Nearly all the calculated parameters are in good agreement^{4,12,29,30,43} with the previously reported tetragonally distorted octahedral compounds of d⁸ Nickel(II) ion. All ligand field parameters viz. 10 Dq and B were calculated using Koning's numerical method. Some other parameters such as C, F², F⁴, β₃₅, ν₂/ν₁, Dq/B are suggesting an octahedral

environment around the nickel(II) heterochelates of mannich base $C_{12}H_{10}O_2N_2S$ and $C_{13}H_{11}O_4NS$ and provides a sort of distorted octahedron in which two groups along the z-axis are at larger distance from the central nickel(II) ion, then the four groups along the x and y axis. These calculated values were further supported by Tanabe-Sugano diagram treatment⁴³ of electronic spectra of Ni complexes.

Table 1: NMR Spectral Data of Mannich Base

$C_{12}H_{10}O_2N_2S$					$C_{13}H_{11}O_4NS$				
S. No.	Chemical Shift	Peak Position	No. of Protons	Group Assigned	S. No	Chemical Shift	Peak Position	No. of Protons	Group Assigned
1.	2.547	Doublet	2H	CH ₂	1	2.512	Doublet	2H	CH ₂
2.	6.956	Triplet	3H	Thiophene	2	6.902	Triplet	3H	Thiophene
3.	7.502	Triplet	3H	NH-CH ₂	3	7.14	Triplet	3H	Aromatic
4.	7.619	Singlet	H	CO-NH	4	7.28	Triplet	3H	NH-CH ₂
5.	8.709	Doublet	2H	2,6 position, pyridine	5	7.84	Singlet	H	CO-NH
					6	8.53	Singlet	H	Ar-OH
					7	12.8	Singlet	H	-COOH

Table 2: Tabular Representation of Mass Spectra of Mannich Base

$C_{12}H_{10}O_2N_2S$				$C_{13}H_{11}O_4NS$			
M/z	Relative Abundance(%)	M/z	Relative Abundance(%)	M/z	Relative Abundance(%)	M/z	Relative Abundance(%)
75	65.3	150	38.8	71	93.2	125	13.6
83	55.1	168	100.0	77	84.7	140	32.2
96	18.4	185	12.2	83	52.5	152	100.0
97	69.4	196	14.3	84	20.3	167	47.5
111	28.6	212	29.4	95	18.6	216	15.3
125	18.4	248	16.3	96	10.2	256	15.2
				111	20.3	278	27.1

Table 3: Infrared Spectral Data of Mannich Base and Its Complexes

Derived From 2-Thienyl Glyoxal and Nicotinamide $C_{12}H_{10}O_2N_2S$			S. No	Ligand/Complexes 2-TGNA	Ligand modes (cm ⁻¹)				Coordination modes (cm ⁻¹)	
S. N	Frequency found (cm ⁻¹)	Group Assigned			ν_{CH_2NH}	$\nu_{C=O}$	ν_{C-N-C}	ν_{C-S-C}	ν_{M-N}	ν_{M-S}
1	~3365	$\nu_{N-H_{str}}$	1	$C_{12}H_{10}O_2N_2S$	3365	1680	1127	828	-	-
2	1619 and 1310-1320	C-N vibration	2	$Ni(C_{12}H_{10}O_2N_2S)_2Cl_2$	3392	1677	1150	880	450,400	323
3	~1680, 1650	>C=O	3	$Ni(C_{12}H_{10}O_2N_2S)_2SO_4$	3390	1676	1147	787	489,435	320
4	1255, 828 and 702	2-substituted thiophene	4	$Ni(C_{12}H_{10}O_2N_2S)_2(NO_3)_2$	3400	1678	1170	930	495,418	315
5	1127	C-N-C	5	$Ni(C_{12}H_{10}O_2N_2S)_2(CH_3COO)_2$	3338	1678	1102	854	479,432	330
2-Thienyl Glyoxal and P-Amino Salicylic Acid $C_{13}H_{11}O_4NS$			S. No	Ligand/Complexes 2-TGASA	Ligand modes (cm ⁻¹)				Coordination modes (cm ⁻¹)	
S. N.	Frequency found (cm ⁻¹)	Group Assigned			ν_{OH}	ν_{CH_2NH}	ν_{COOH} [ν_{as} and $\nu_{s COO}$]	$\nu_{C=O}$	ν_{C-S-C}	ν_{M-O}
1	~3344	$\nu_{N-H_{as}}$	1	$C_{13}H_{11}O_4NS$	3430	3344	3382	1592	828	-
2	1424 and 1131	N-H bend and C-N vibration	2	$Ni(C_{13}H_{11}O_4NS)_2Cl_2$	3432	-	1380,1161	1592	809	430
3	3430	ν_{OH}	3	$Ni(C_{13}H_{11}O_4NS)_2SO_4$	3430	-	1362,1144	1590	-	450
4	3382	ν_{COOH}	4	$Ni(C_{13}H_{11}O_4NS)_2(NO_3)_2$	3431	-	1381,1160	1590	805	465
5	1592	>C=O	5	$Ni(C_{13}H_{11}O_4NS)_2CH_3COO)_2$	3431	-	1383,1159	1590	935	468
6	828 and 708	2-substituted thiophene								

Table 4(a): Physical Properties, Analytical Data and Magnetic Moment Values of Metal Complexes of Mannich Base (C₁₂H₁₀O₂N₂S)

S.No	Metal Complexes	M.P. (°C)	Formula Weight	Color	Percentages of Elements Found/Calculated						(B.M.)
					C	H	N	S	M	Cl	
	C ₁₂ H ₁₀ O ₂ N ₂ S	112	246.29	Choc. Brown	58.50 58.52	4.12 4.09	11.40 11.37	12.99 13.03	-	-	-
1	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ Cl ₂	202-204	622.18	Reddish brown	46.21 46.33	3.18 3.24	8.95 9.01	10.28 10.31	9.39 9.43	11.36 11.40	3.21
2	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ SO ₄	215-217	647.34	Pale brown	44.46 44.53	3.06 3.11	8.60 8.66	14.83 14.86	9.02 9.07	-	3.20
3	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ (NO ₃) ₂	180-183	675.28	Dark brown	42.55 42.69	2.94 2.99	12.40 12.45	9.46 9.50	8.65 8.69	-	2.95
4	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ (CH ₃ COO) ₂	211-213	669.36	Pale brown	50.13 50.24	3.87 3.92	8.34 8.37	9.55 9.59	8.72 8.77	-	2.90

Table 4(b): Physical Properties, Analytical Data and Magnetic Moment Values of Metal Complexes of Mannich Base (C₁₃H₁₁O₄NS)

S. N	Metal Complexes	M.P. (°C)	Formula Weight	Color	Percentages of Elements (Found/Calculated)						(B.M.)
					C	H	N	S	M	Cl	
	C ₁₃ H ₁₁ O ₄ NS	110	277.3	Dark brown	56.28 56.31	3.96 4.00	5.01 5.05	11.52 11.56	-	-	-
1	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ Cl ₂	217-219	684.20	Pale brown	45.60 45.64	3.20 3.24	4.06 4.09	9.34 9.37	8.54 8.58	10.3 10.36	3.15
2	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ SO ₄	198-200	709.36	Dark brown	43.97 44.02	3.10 3.13	3.91 3.95	13.52 13.56	8.24 8.27	-	2.85
3	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ (NO ₃) ₂	216-218	737.30	Dark brown	42.31 42.36	2.98 3.01	7.56 7.60	8.67 8.70	7.93 7.96	-	3.10
4	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ (CH ₃ COO) ₂	275-277	731.38	Pale brown	49.25 49.27	3.82 3.86	3.80 3.83	8.73 8.77	8.00 8.03	-	3.05

Table 5(a): Electronic Spectral Data- Ligand Field Spectral Data (5000-30000cm⁻¹) of Ni(II) Complexes

S.N.	Complexes	³ B _{1g}	³ B _{1g}	³ B _{1g}	³ A _{2g} (F)	³ A _{2g} (F)	10 Dq	B
		↓ ³ B _{2g} (vB)	↓ ³ E _g (vE)	↓ E _g (Sh)	↓ ³ T _{1g} (F) v ₂	↓ ³ T _{2g} (P) v ₃		
1	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ .Cl ₂	8290	10220	14340	16225	25500	10220	737.67
2	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ .SO ₄	8210	10520	14500	16730	25720	10520	726.00
3	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ .(NO ₃) ₂	8520	10580	14130	16600	26460	10580	755.00
4	Ni(C ₁₂ H ₁₀ O ₂ N ₂ S) ₂ .(CH ₃ COO) ₂	8350	10680	14500	17800	25900	10680	777.00
5	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ .Cl ₂	8400	10540	14470	16780	26500	10540	777.00
6	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ .SO ₄	8550	10900	14640	17350	26300	10900	730.00
7	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ .(NO ₃) ₂	8380	10620	14600	16810	26400	10620	757.00
8	Ni(C ₁₃ H ₁₁ O ₄ NS) ₂ .(CH ₃ COO) ₂	8700	10660	14450	16820	26530	10860	758.00

Table 5(b): Calculated Electronic Spectral Parameters (cm⁻¹) for Ni(II) Complexes

S. N.	Parameter	Complexes of MB 1(L ₁)				Complexes of MB 2(L ₂)			
		Ni(L ₁) ₂ Cl ₂	Ni(L ₁) ₂ SO ₄	Ni(L ₁) ₂ (NO ₃) ₂	Ni(L ₁) ₂ (CH ₃ COO) ₂	Ni(L ₂) ₂ Cl ₂	Ni(L ₂) ₂ SO ₄	Ni(L ₂) ₂ (NO ₃) ₂	Ni(L ₂) ₂ (CH ₃ COO) ₂
1	Dq ^{XY}	1022	1052	1058	1068	1054	1090	1062	1066
2	Dq ^Z	636	590	646	602	262	620	614	674
3	Dt	220.57	264	235	266	245	268.57	256	224
4	Ds	360.12	426.67	460.71	439	436	507.6	421.67	441.67
5	-Ds	2520.80	2986.68	3225	3072	3052	3553	2952	3092
6	DQ	22794	22574	23426	22959	23096	23509	23041	23921
7	-DT	2990	3579	3191	3610	3315	3641	3470	3036
8	DQ ^L	19256	18339	19650	18688	19174	19201	18935	20328
9	DQ ^Z	29869	31042	30978	31501	30942	32124	31253	31107
10	DQ ^A	15718	14105	15874	14417	15251	14893	14829	16736
11	DQ ^E	26331	26808	2720	27230	27019	27816	27147	27514
12	-DT/DQ	0.13	0.16	0.14	0.16	0.14	0.16	0.15	0.13
13	dσ	954	1135	1133	1158	1113	1261	1113	1082
14	dπ	11.25	20.00	103	-	43	86	7.50	103
15	Δ ₁	22.49	39.99	205	15.02	85	180	15	205
16	Δ ₂	9577	9750	9893	9903	9827	10117	8622	10007
17	Δ ₃	2543	3027	3020	3087	2967	3373	2967	2887
18	Dq ^E	957.67	975	989	990	983	1012	987	1001
19	Dt/Ds	0.61	0.62	0.51	0.61	0.60	0.53	0.61	0.51

REFERENCES

1. Abraham R.J., Fisher J. and Loftus P.; "Introduction to NMR Spectroscopy", 2nd ed., Wiley, New York, (1989).
2. Ahmadi M.R., Gray J. A. and Sengers H. P. M.; Chevron Oronite Tech. B. V. ;C. A., 265564v; 136(17) (2002).
3. Balakrishnan K. and Khadar A.M.A.; J. Indian Council Chem., 304, 390 (1991).
4. Ballhausen C.J.; Kgl. Danske Videnskab, Selskab, Mat-Fys. Medd., 29(8), (1955)
5. Barnes M.d., Bhagavatula L., DeMattei J., Gupta A., Hill D.R., Manna S., Mclaughlin M. A., Nichols P., Premchandran R., Rasmussen M.W., Tian Z. and Steven J.; Tetrahedron: Asymmetry, 14(22), 3541, Nov(2003).
6. Cotton F.A., Wilkinson G., Murillo C.A. and Bochmann M.; "Advanced Inorganic Chemistry", 6th ed., 837, John Willey, India (1992).
7. De. A.K.; "A Textbook of Inorganic Chemistry", 7th ed., 692, Willey, India (1992).
8. Dyer J.R.; "Applications of Absorption Spectroscopy of Organic Compounds" 10th Ed., 22, Prentice Hall, India (1997).
9. Eckert G.W. and Love D. (Texaco Inc.) U.S.; C.A., 70, 39551(a) (1969).
10. Ewing G.W.; "Instrumental Methods of Chemical Analysis" 5th Ed., McGraw Hill, New York (1985)
11. Feraro J. R.; "Low Frequency Vibrations of Inorganic and Co-ordination Compounds", 90, 229, Plenum Press, New York, (1971).
12. Figgis B.N. In Comprehensive Chemistry; Wilkinson G., Gillard R.D., Mc. Cleverty J.A., Edi.; Pergmon, New York (1987).
13. Finar I.L.; "Organic Chemistry", 6th ed., ELBS Longmann, 1, 375 (1973).
14. Fonseca M. H., Eibler E., Zabel M. and König B.; Inorganica Chimica Acta, 352,136 (2003).
15. Gao L., Zhang D., Jiang K., Zhou G. and Li H.; Fushi Yu Fanghu, 2001, 22(8), 353, 345(2002); C. A., 136(17), 264510n (2002).
16. Gul H.I., Calis U. and Vepsalainen J.; Arzneim-Forsh/Drugs Res., 52, (2002).
17. Henold K.H.; Chem. Commun., 1340 (1970).
18. Houser K.R.(Chevron Oronite comp.) U.S.A.; C. A., 136(17), 2655634 (2002).
19. Ibrahim M.A and Omar N.M.; J .Pharm Sci., UAR 6, 211 (1965); C. A., 68, 871004 (1968).
20. Joshi S. and Khosla N.; Bioorganic and Med. Chem. Letters, 13(21), 3747 (2003).
21. Joshi S., Khosla N. and Tiwari P.; Bioinorg. and Med. Chem., 12(3), 571, Feb (2004).

22. Kalsi P.S.; "Spectroscopy of Organic Compound", 5th ed., 60, New Age, India (2002).
23. Kasture A.V., Wadodkar S.G. and Jain K.P.; J. Indian Chem. Soc., 65 (1988).
24. Kipnis F. and Ornfelt; J. Am. Chem. Soc., 68, 273 (1946).
25. Korthi S.B., Kulkarni V.H. and Patil B.R.; Orient J. Chem., 13, 49 (1997).
26. Krikland J.J.; Anal. Chem., 27, 1537 (1955).
27. Kumar A., Jha A.K., Mazumdar N., Yadav S.N. and Mishra L.K.; J. Indian Chem. Soc., 74, 485 (1997).
28. Lal B., Gund V.G., Bhise N. B and Ganopadhyay A. K.; Bioinorg. and Med. Chem., 12(7),1751, Apr.(2004).
29. Lever A.B.P.; "Inorganic Electronic Spectroscopy", 2nd ed., 507, Elsevier, New York (1984).
30. Lever A.B.P.; London G. and Mc Carthy P.J.; can. J. Chem., 55, 3172 (1977).
31. Mohan J.; "Organic Analytical Chemistry", Narosa, India (2003).
32. Nath J. P., Dash M. , Satrusallya S.C. And Mahapatra G. N.; Indian J. Chem., 20 B, 606 (1981).
33. Patel M.M. and Patel H. R.; J. Indian Chem. Soc., 73, 313, (1996).
34. Pietrzyk D. J. and Frank C.W.; "Analytical Chemistry" 2nd Ed., Academic Press, New York (1979).
35. Popovici I. Comanita E., Roman G. and Comanita B.; Acta Chim. Solv., 46(3), 413 (1999).
36. Poulder W.W.; "Nuclear Magnetic Resonance", Wiley, New York (1987).
37. Riechell A., Burr S.K. and Mortain S. F.; Tetrahedron, 58(32), 6323, Aug(2002).
38. Schlapp R. and Penny W. G.; Phys. Rev., 42, 666, (1932).
39. Shyamal A.; J. Indian Counc. Chem., 20(1), 71 (2003).
40. Shyamal A.; J. Indian Counc. Chem., 20(1), 71 (2003).
41. Silverstein R.M. and Webster F.X.; "Spectrometric Identification of Organic Compounds" 6th Ed., Johnwiley, New York (1998).
42. Suleyman H., Gul H.I. and Asoglu M. ; Pharmacological Research, 47(6), 471 (2003).
43. Tanabe Y. and Sugano S.; J. Phys. Soc., Japan, 9, 766 (1954).
44. Udipi R.H., Kushnoor A. and bhat A.R.; J. Indian Chem. Soc., 76, 461 (1999).
45. Udipi, R. H., Kushnoor A. and Bhat A. R.; J. Indian Chem Soc., 76, 461 (1999).
46. Vashistha S.C., Zello G. A., Nienaber K.H., Balzarine J., DeClercq E., Stables J.P. and Dimmock J. R.; Euro. J. Med. Chem., 39(1), 27 (2004).
47. Webster F.X. and Silverstein R.M.; Aldrichimica Acta., 18(3), 58 (1985).
48. Willard H.H., Merritt L.L., Dean J.A. and Settle F.A. ; "Instrumental Method of Analysis", 6th Ed., C.B.S., India (1986).
49. Williams D.H. and Fleming I.; "Spectroscopic Methods in Organic Chemistry", 4th Ed., Tata McGraw Hill, India (2003).