

Synthesis and characterization of Ni(II) complexes with ester thiosemicarbazone

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ABSTRACT - Complexes of Ni (II) of general composition $[ML_2X_2]$, $[ML_2X]X$ were prepared with thiosemicarbazones (L^1 , L^2 , L^3 & L^4). These complexes were characterized by elemental analysis, molar conductances measurements, Magnetic moments IR, electronic spectra, and EPR spectral studies. All are the nonelectrolyte in nature therefore these complexes may be formulated $[M(L)_2X_2]$. All the complexes are of high-spin and show octahedral geometry.

Key words - Acetoacetic ester thiosemicarbazone, Isopropyl ester thiosemicarbazone, 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid ester thiosemicarbazone, Biological activity

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The biological and medicinal properties of these ligands and their derivatives have gained much interest. Thiosemicarbazones and their 3d-metal complexes have been found to exhibit anti-fungal[1], anti-bacterial[2], antiviral[3], anti-tubercular[4] and anti carcinogenic activities [5]. The anti-fungal activity of these compounds is due to the presence of toxophyrically important N=C=S moiety[6]. Thiosemicarbazides and their Schiff bases also display anti-tumour [7-8] activity. It is expected that thio ligands will also show variability in structure and bonding in its transition metal complexes. It has been reported that thiosemicarbazide and its complexes with 3d-metal ions show *in vitro* and *in vivo* anti-tumour activity[9].

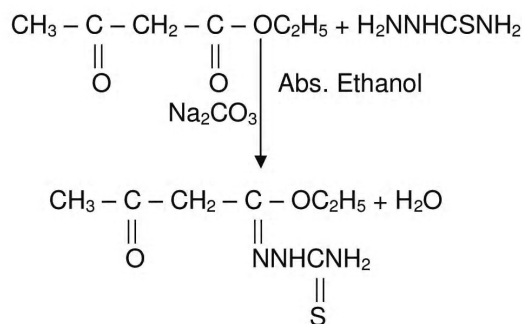
EXPERIMENTAL METHODOLOGY

A.R. Grade chemical and fluka reagents were used in the present study. The solvent were purified before use by processing. Semicarbazide hydrochloride, acetoacetic ester, isopropyl ester, methyl ester of 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid, sodium acetate different metallic salts.

Preparation of ligands (L^1 , L^2 , L^3 and L^4):

Preparation of Acetoacetate ester Thiosemicarbazons (L^1):

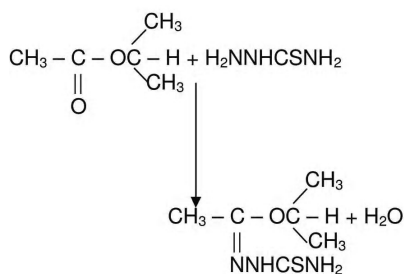
Hot ethanolic solution of thiosemicarbazide (0.01 mol, 0.91 g) and ethanolic solution of acetoacetic ester (0.01 mol, 1.183 ml) were mixed slowly with constant stirring. This mixture was refluxed at 75°C for 3-4 hr. On cooling cream precipitate was formed. It was filtered, recrystallized with cold ethanol and dried under vacuum over P_4O_{10} . The structure of ligand and scheme for synthesis is shown in scheme 1.



Scheme -1

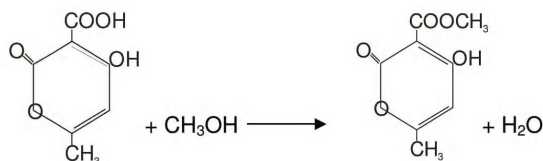
Preparation of isopropyl ester Thiosemicarbazone (L²):

Hot ethanolic solution of Isopropyl acetate (0.01 mol, 0.849 ml) and thiosemicarbazide (0.1 mol, .91g) were mixed slowly with constant stirring. This mixture was refluxed at 80°C for 2 hr. On cooling, white precipitate formed. It was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀. The structure of ligand and scheme for synthesis is shown in scheme 2.

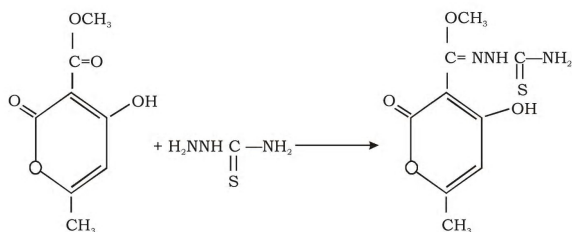
**Scheme -2****Preparation of Thiosemicarbazone of 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid [L³]:**

The starting materials 6-methyl-2H Pyran-2, 4, (3H), dione-3-carboxylic acid and thiosemicarbazide were purchased Fluko reagents. The ligand was prepared in two steps.

Step 1: 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid (0.01 mol, 1.70 g) was refluxed with methanol (0.01 mol, 0.25 ml) in the presence 10 per cent sulphuric acid. Thus, the ester of 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid was formed.



Step 2 : 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid (0.01 mol, 1.84 g) and thiosemicarbazide (0.01 mol, 0.91 g) were refluxed in ethanol for 2 hr at 70-80°C. On cooling light yellow precipitate was formed. It was filtered, recrystallized

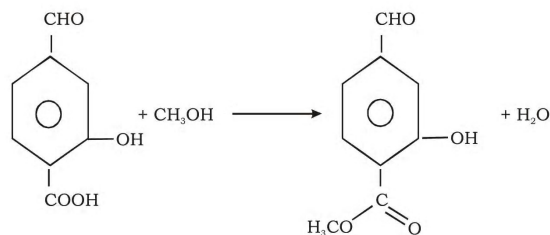
**Scheme -3**

with cold ethanol and dried under vacuum P₄O₁₀. The structure of ligand and scheme for synthesis is shown in scheme 3.

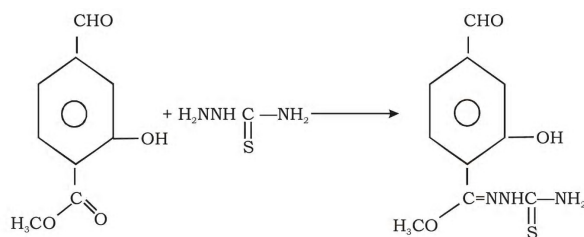
Preparation of 3-Formylmethyl salicylate Thiosemicarbazone (L⁴):

The ligand was prepared in two steps :

Step 1 : The 3-formyl salicylic acid (0.01 mol, 1.66g) was refluxed with methanol in the presence of 10 per cent H₂SO₄ for 2 hr. A light yellow colour precipitate, 3-formyl methyl salicylate was formed.



Step 2 : The 3-formyl methyl salicylate (0.01 mol, 1.80 g) thiosemicarbazide (0.01 mol, 0.91 g) in ethanolic solution were refluxed for 2 hr at 75°C. On cooling, white precipitate was formed. It was filtered washed with cold ethanol and dried under vacuum over P₄O₁₀. The structure of ligand and scheme for synthesis is shown in scheme 4

**Scheme -4****Characterization of ligands:****Elemental analysis:**

The ligands were found to have the composition as shown in Table 1.

Mass spectra [10-14] :

Electron impact mass spectra of the ligands were recorded on TOF MS ES+ Mass spectrometer from University of Delhi.

Mass spectrum is a presentation of the masses of the positively charged fragments (including the molecular ion) versus their relative concentrations. The more intense peak in the spectrum, called the base peak, is assigned a value of 100

Table 1 : Physical and elemental analysis data of ligands

Sr. No.	Elemental formula	Colour	Yield (%)	Melting Point (0°C)	Molecular weight	Elemental analysis found (Calculated)			
						C	H	N	S
1.	C ₇ H ₁₃ N ₃ O ₂ S	Cream	65%	198	203	41.10 (41.37)	6.15 (6.40)	20.50 (20.68)	15.56 (15.76)
2.	C ₆ H ₁₃ N ₃ OS	White	64%	192	175	41.00 (41.14)	7.25 (7.42)	24.00 (24.00)	18.12 (18.28)
3.	C ₉ H ₁₁ N ₃ O ₄ S	Light Yellow	70%	200	259	41.99 (42.02)	4.00 (4.28)	16.00 (16.34)	12.15 (12.45)
4.	C ₁₀ H ₁₇ N ₃ O ₃ S	White	76%	197	259	46.00 (46.33)	6.00 (6.56)	16.00 (16.21)	12.00 (12.35)

per cent and the intensities of other peaks, including the molecular ion peak are reported as percentages of the base peak. The molecular ion peak may some times the base peak. The molecular ion peaks is usually the peak of highest mass number for the isotopic peaks. The intensities of the isotope peaks relative to parent peak can lead to the determination of a molecular formula. The measured isotope peaks are usually slightly higher than the calculated contribution because of incomplete resolution, bimolecular couisions or a contribution from the incident peak of ion impurity of the proposed ligands.

Mass spectrum of the ligands :

The mass spectrum of ligand L¹ shows the molecular ion peak (M⁺) at m/z = 203 amu. The different ions gives the peaks of different mass like 160, 146, 101, 75, 60 and 16. The intensities of these give the idea of stability of ligands

The mass spectrum of Ligand L² shows that molecular ion peak (M⁺) at m/z=175 amu. The other peaks at 160, 148, 101, 75, 60 and 16 amu. Corrosponds to various fragments show the stability of ligand.

The mass spectrum of Ligand L³ shows the molecular ion peak (M⁺) at m/z=259 amu. The other different ions gives peaks of 132, 101, 75, 60 and 16 amu. The intensities of peaks are in correspondance with the abundance of the ions.

The mass spectrum of Ligands L⁴ shows the molcular ion peak (M⁺) at m/z=259 amu. The other different ions give the peaks of different mass numbers like 132, 101, 75, 60 and 16 amu. The intesities of these peaks give the idea of stability of ligand.

I.R. Spectra[15-32] :

In the present study in IR spectra of ligands the bands appeared at 1560-1595 cm⁻¹ and 729-780 cm⁻¹ due to ν(C=N) and ν(C=S) groups, respectively.

L¹ ⇒ Nitrogen atom of ν(C=N) group and oxygen of ν(C=S) group ⇒ Bidentate

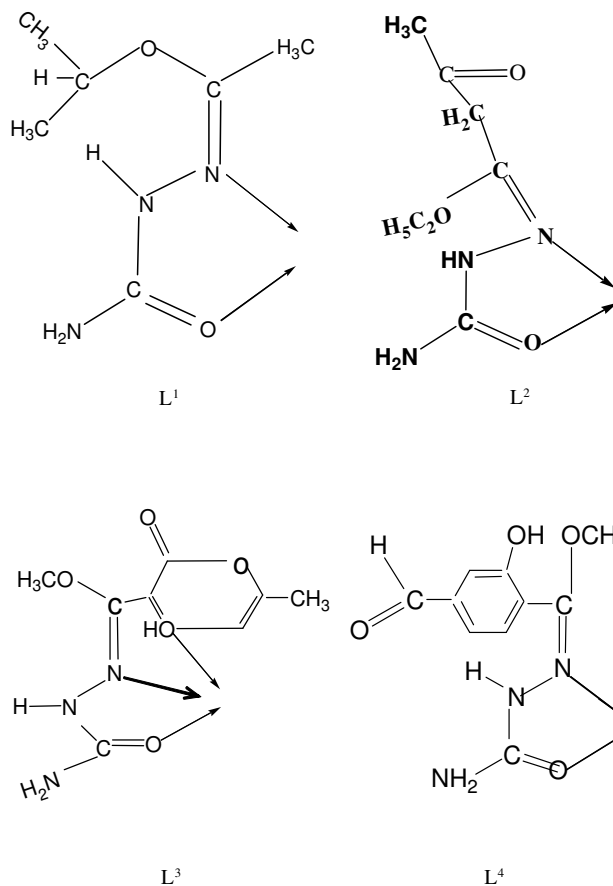
L² ⇒ Nitrogen atom ν(C=N) group and oxygen of ν(C=S) group ⇒ Bidentate

L³ ⇒ Nitrogen atom ν(C=N) group and atom ν(C=S) group and atom of ν(C=O) phenolic oxygen group ⇒ Tridentate

L⁴ ⇒ Nitrogen atom of ν(C=N) group and oxygen atom of ν(C=S) group ⇒ Bidentate

Proposed structure of the ligands :

On the basis of elemental analysis, mass and IR spectra the following structure has been assigned for the ligands.



Preparation of complexes :

All the complexes were prepared by the following method. A hot ethanolic solution of corresponding metal salt (0.05 mol) was mixed with hot ethanolic solution of the corresponding ligand (0.1 mol). The contents were refluxed for about 2-4 hr. On cooling the contents coloured complex was separated out. The complex was filtered washed with 50 per cent ethanol and dried in a vacuum desiccator over P_4O_{10} .

EXPERIMENTAL FINDINGS AND ANALYSIS

On the basis of the elemental analysis (Table 2) the complexes have the composition $M(L_2)X_2$ (where $X=Cl^-, NO_3^-$ and CH_3COO^-). Molar conductance (Table 2) of the complexes with ligand L^1, L^2, L^3 and L^4 indicates the following nature :

Ligands	Metal salts	Nature of complex	Composition
L^1, L^2, L^4	$NiCl_2 \cdot 6H_2O$	Non-electrolyte	$[Ni(L)_2X_2]$
	$Ni(CH_3COO)_2 \cdot 4H_2O$		
	$Ni(NO_3)_2 \cdot 6H_2O$		
L^3	$NiCl_2 \cdot 6H_2O$	1:2 electrolyte	$[Ni(L)_2]X_2$
	$Ni(CH_3COO)_2 \cdot 4H_2O$		
	$Ni(NO_3)_2 \cdot 6H_2O$		

Ligands L^1, L^2 and L^4 act as bidentate manner coordinate through N and S atom. On the other hand L^3 acts as tridentate coordinate through N, S and O atoms.

Magnetic moment:

Magnetic moments of Ni(II) complexes under study lie in the range 2.85-2.96 B.M. corresponding to two unpaired electrons. However, it is difficult to deduce the geometry of the complexes on the basis of the magnetic moments alone. Therefore, the geometry of the complexes were deduced with the help of magnetic moments and spectral studies.

Infrared spectra:

Infrared spectra of the ligands and their mode of coordination have already been discussed in ligand synthesis and characterization.

IR spectra of complexes :

IR spectra of nitrate complex :

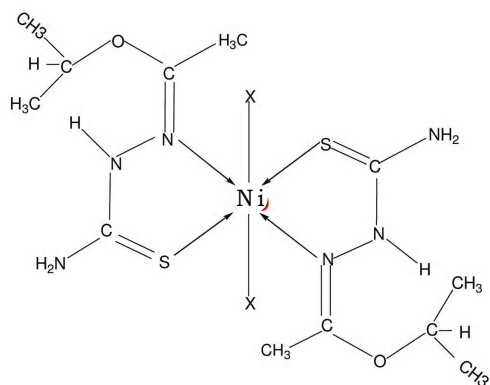
The IR spectra of nitrate complexes with ligands L^1, L^2 and L^4 show bands in the region $1411-1478\text{ cm}^{-1}$ (ν_3) $\nu_a(NO_2)$, $1298-1316\text{ cm}^{-1}$ (ν_1), $\nu_a(NO_2)$ and $899-939\text{ cm}^{-1}$ (ν_2) $\nu(NO)$. This indicates that nitrate group coordinated to central metal as

Table 2 : Elemental Analysis and molar conductance of Ni(II) complexes

Sr. No.	Complex	Colour	M. Point ($^{\circ}C$)	Yield (%)	Molar conductance	Elemental analysis found (Calculated)			
						C	H	N	M
1.	$[Ni(L^1)_2Cl_2]$	Green	272	65	8	31.10	4.56	15.52	10.59
	$NiC_{14}H_{26}N_6O_4S_2Cl_2$					(31.36)	(4.85)	(15.68)	(10.95)
2.	$[Ni(L^1)_2(NO_3)_2]$	Light Green	290	75	5	37.00	5.00	14.21	10.00
	$NiC_{14}H_{26}N_8O_{10}S_2$					(27.07)	(5.14)	(14.41)	(10.07)
3.	$[Ni(L^1)_2(CH_3COO)_2]$	Dark Green	289	65	6	28.21	4.35	19.00	9.56
	$NiC_{18}H_{30}N_6O_8S_2$					(37.07)	(4.41)	(19.02)	(9.96)
4.	$[Ni(L^2)_2Cl_2]$	Shiny Green	282	70	15	30.00	5.41	17.50	12.15
	$NiC_{12}H_{26}N_6O_6S_2Cl_2$					(30.06)	(5.42)	(17.53)	(12.25)
5.	$[Ni(L^2)_2(NO_3)_2]$	Shiny Green	265	69	20	36.15	6.00	15.56	11.00
	$NiC_{12}H_{26}N_8O_{12}S_2$					(36.45)	(6.07)	(15.94)	(11.14)
6.	$[Ni(L^2)_2(CH_3COO)_2]$	Green	270	67	12	26.59	4.56	21.00	11.00
	$NiC_{16}H_{32}N_6O_{10}S_2$					(27.03)	(4.88)	(21.02)	(11.01)
7.	$[Ni(L^3)_2]Cl_2$	Light Green	286	76	185	33.25	3.30	13.00	9.01
	$NiC_{18}H_{22}N_6O_8S_2Cl_2$					(33.55)	(3.41)	(13.04)	(9.11)
8.	$[Ni(L^3)_2(NO_3)_2]$	Light Green	286	68	170	38.10	4.10	12.06	8.25
	$NiC_{18}H_{22}N_8O_{10}S_2Cl_2$					(38.22)	(4.05)	(12.16)	(8.49)
9.	$[Ni(L^3)_2(CH_3COO)_2]$	Green	275	78	165	31.00	3.00	15.90	8.22
	$NiC_{22}H_{28}N_6O_{12}S_2$					(31.00)	(3.15)	(16.07)	(8.42)
10.	$[Ni(L^4)_2Cl_2]$	Shiny Green	288	65	19	37.51	3.26	13.00	9.00
	$NiC_{20}H_{22}N_6O_6S_2Cl_2$					(37.55)	(3.46)	(13.21)	(9.23)
11.	$[Ni(L^4)_2(NO_3)_2]$	Green	280	70	18	42.00	4.00	12.00	8.40
	$NiC_{20}H_{22}N_8O_{12}S_2$					(42.18)	(4.10)	(12.30)	(8.59)
12.	$[Ni(L^4)_2(CH_3COO)_2]$	Shiny Green	292	78	15	34.62	3.11	16.20	8.20
	$NiC_{24}H_{28}N_6O_{10}S_2$					(34.84)	(3.19)	(16.26)	(8.52)

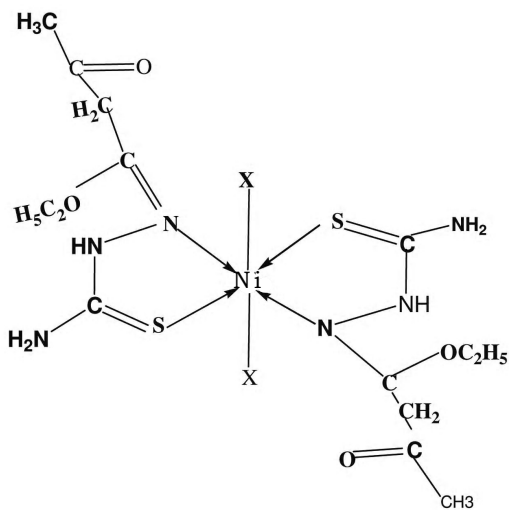
Table 3 : Ligand field parameters and ESR spectral data of Ni (II) complexes

Complex	Dq (cm ⁻¹)	B (cm ⁻¹)	β	LFSE (kJmole ⁻¹)
[Ni(L ¹) ₂ Cl ₂]	1118	407	0.39	160
[Ni(L ²) ₂ Cl ₂]	988	568	0.55	151
[Ni(L ³) ₂ Cl ₂]	933	681	0.65	134
[Ni(L ⁴) ₂ Cl ₂]	956	633	0.61	137
[Ni(L ¹) ₂ (CH ₃ COO) ₂]	1123	359	0.34	161
[Ni(L ²) ₂ (CH ₃ COO) ₂]	968	632	0.61	139
[Ni(L ³) ₂ (CH ₃ COO) ₂]	967	663	0.64	138
[Ni(L ⁴) ₂ (CH ₃ COO) ₂]	935	622	0.60	134
[Ni(L ¹) ₂ (NO ₃) ₂]	975	646	0.62	140
[Ni(L ²) ₂ (NO ₃) ₂]	999	550	0.53	143
[Ni(L ³) ₂ (NO ₃) ₂]	987	563	0.54	142
[Ni(L ⁴) ₂ (NO ₃) ₂]	973	604	0.58	140



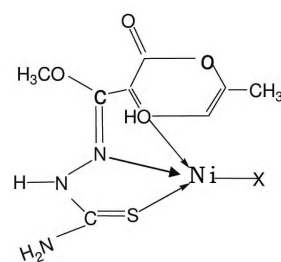
X=Cl⁻, NO₃⁻, CH₃COO⁻

Nickel complexes of isopropyl ester thiosemicarbazone



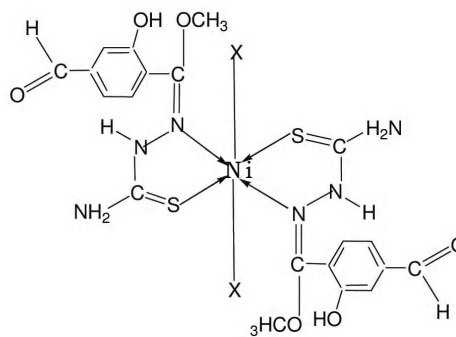
X=Cl⁻, NO₃⁻, CH₃COO⁻

Nickel complexes of acetoacetate ester thiosemicarbazone



X=Cl⁻, NO₃⁻, CH₃COO⁻

Nickel complexes of Methyl ester of 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid thiosemicarbazone



X=Cl⁻, NO₃⁻, CH₃COO⁻

Nickel complexes of 3-Formylmethyl salicylate thiosemicarbazone

unidentate [33-35]. However, nitrate complex of ligand L³ the position of at 1393 cm⁻¹ indicating that nitrate group is uncoordinated.

IR spectra of acetato complexes :

IR spectral bands of acetato complex, L¹, L² and L⁴ show bands in the region 1411-1478 cm⁻¹ (ν₅) ν_a (NO₂), 1298-1316 (ν₁), ν_a (NO₂) and 899-939 cm⁻¹ (ν₂) ν(NO) corresponding to monodentate nature. On the other hand ligands shows IR bands corresponding to uncoordinated acetate group (36).

Electronic spectra :

The electronic spectra of the complexes of Ni(II) metals with L¹, L², L³ and L⁴ show three bands in the range of 9337-11185 cm⁻¹, 13123 -14980 cm⁻¹, 23364-25700 cm⁻¹ (Table 4.2). These bands may be assigned to ³A_{2g} (F) → ³T_{2g} (F) (ν₁), ³A_{2g} (F) → ³T_{1g} (F) (ν₂) and ³A_{2g} (F) → ³T_{1g} (P) (ν₃) transition, respectively. The position of these bands corresponding to an octahedral geometry around the nickel ion.

Ligand field parameters:

The value of b has been calculated with the relation $b = B_{\text{Complex}} / B_{\text{Free ion}}$. The value of b for the nickel (II) complexes, under study, lie in the range 0.34-0.65 (Table 3).

Proposed structure of the complexes :

On the basis of elemental analysis, magnetic moment, molar conductance, IR, electronic and EPR spectral studies an octahedral geometry has been assigned for the complexes with ligand L¹, L², L³ and L⁴ as follows :

Acknowledgement :

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