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CHAPTER 8

STUDIES ON INNER TRANSITION METAL COMPLEXES OF HETEROCYCLIC SCHIFF BASES

Three heterocyclic Schiff bases such as 3-(1-(2-phenylhydrazono)ethyl)pyridine (3PHEP), 2-(1-(pyridine-3-yl)ethylidene)hydrazine carbothioamide (2PEHCT) and 3-((thiophen-2-ylmethylene)amino)benzoic acid (3TMAB) were synthesized and characterized by means of elemental analysis and spectral studies such as FTIR, UV-visible, NMR (^1H and ^{13}C) and Mass spectroscopy. Chelating ability of these Schiff base ligands were proved by synthesizing inner transition metal complexes of La(III), Nd(III) and Sm(III). Elemental (CHN) analysis, FTIR, UV-visible, magnetic moment, estimation of metal and molar conductance studies were used for the characterization of the metal complexes.

This chapter is divided into three sections. Section I deals with synthesis and characterization of the Schiff base ligand 3-(1-(2-phenylhydrazono)ethyl)pyridine (3PHEP) and its inner transition metal complexes. Section II consist of synthesis and characterization of the Schiff base ligand 2-(1-(pyridine-3-yl)ethylidene)hydrazine carbothioamide (2PEHCT) and its inner transition metal complexes. Synthesis and characterization of the Schiff base ligand 3-((thiophen-2-ylmethylene)amino)benzoic acid (3TMAB) and its inner transition metal complexes were discussed in the section III.

Section I

La(III), Nd(III) and Sm(III) complexes of 3-(1-(2-phenylhydrazono)ethyl)pyridine

This section deals with synthesis and characterization of the Schiff base ligand 3-(1-(2-phenylhydrazono)ethyl)pyridine (3PHEP) and its inner transition metal complexes of lanthanum, neodymium and samarium.

Synthesis and characterization of 3PHEP and its inner transition metal complexes

Equimolar amount of ethanolic solution of 3-acetylpyridine and phenylhydrazine hydrochloride was dissolved in ethanol-water (3:1) mixture and refluxed for 4 h. Solution is then evaporated to dryness and cooled slowly. Yellow coloured precipitate formed was filtered and washed with minimum amount of ethanol. Then melting point was determined after recrystallization from ethanol. 81% yield is obtained and melting point is found to be 245⁰C.

Ln(III) nitrate solution was first prepared by digesting Ln₂O₃ (0.01 mol) in con HNO₃ thrice. After digestion and evaporation, the residue is cooled and added 20 ml ethanol. This ethanolic nitrate solution was then refluxed for 3 h, after adding ethanolic solution of 3PHEP (0.02 mol) into it. Then allowed to cool and added dilute ammonia (1:20) dropwise till a turbidity is formed. Magnetically stirred the solution and the precipitate formed was filtered, washed with ethanol and dried over anhydrous calcium chloride.

Elemental analysis

Results of microanalytical, magnetic and conductance data of 3PHEP and its inner transition metal complexes are shown in Table 8.1. Experimental and calculated values are in good agreement. From the data it is clear that 1:1 stoichiometry exist between 3PHEP and metal ions.

FTIR spectral studies

Stretching frequencies corresponding to different bonds in 3PHEP were observed in its IR spectrum. Broad peak at 3265 cm^{-1} corresponds to the N-H stretching frequency. Formation of C=N linkage is proved by the stretching vibration at 1593 cm^{-1} . Also a peak corresponding to $\nu_{\text{C-N}}$ was observed at 1048 cm^{-1} . C=C present in the aromatic rings displayed an emerged spectrum of peaks having range $1540\text{-}1600\text{ cm}^{-1}$. Stretching frequencies in the range $3030\text{-}3100\text{ cm}^{-1}$ corresponds to aromatic C-H bond stretching and in plane deformation of the pyridine ring was shown at 621 cm^{-1} and 667 cm^{-1} .

Lowering of C=N stretching frequency of complexes in comparison to 3PHEP clearly confirmed the coordination between imine nitrogen of ligand and metal. Presence of water molecules in the complexes was shown by the additional peaks in the range $3328\text{-}3426\text{ cm}^{-1}$. Also the peaks observed in the range $1300\text{-}1500\text{ cm}^{-1}$ signified the existence of coordinated nitrate ion in complexes with unidenticity. New peaks in the range $610\text{-}690\text{ cm}^{-1}$ and $530\text{-}550\text{ cm}^{-1}$ are a clear indication of the M-N and M-O bonds formed in the complexes. Characteristic infrared absorption frequencies (cm^{-1}) of 3PHEP and its inner transition metal complexes are given in Table 8.2.

Electronic spectral studies

In the electronic spectra of 3PHEP two peaks were observed. Peak at 29239 cm^{-1} corresponds to $n \rightarrow \pi^*$ transition and the peak at 32679 cm^{-1} corresponds to $\pi \rightarrow \pi^*$ transition. On comparing the electronic spectra of the complexes with that of ligand it is observed that there is bathochromic shift for the absorption bands in the case of the complexes, which clearly indicates that the Schiff base ligand is coordinated to metal ion.

NMR spectral studies

Nine non-equivalent protons were observed in the proton NMR spectrum of 3PHEP. Methyl protons displayed a singlet at 2.3 δ . Weak and broad singlet at 9.8 δ corresponds to the proton present in the NH group of phenylhydrazine portion. Protons present in the benzenoid and pyridine ring exhibited signals in the range 6.7-7.3 δ and 8.7-9.0 δ respectively.

Eleven chemically different carbon atoms present in 3PHEP showed 11 distinct signals in the ^{13}C NMR spectrum. Methyl carbon displayed a peak at 12.53 ppm. Peak at 137.99 ppm corresponds to the carbon atom of azomethine group. Quaternary carbon atom present in the pyridine ring and benzenoid ring displayed a signal at 134.88 ppm and 145.07 ppm respectively. Remaining carbon atoms of both ring showed signals in the range 113-140 ppm.

Mass spectral studies

Molecular ion peak was appeared at m/z 211 in the mass spectrum of 3PHEP, which is also appeared to be as the base peak, reflects the stability of the ligand molecule. In addition to M peak, M+1 peak is observed at m/z 212 in the intensity ratio 100:14 which confirms the presence of thirteen carbon atoms in the ligand molecule. The fragments $[\text{C}_5\text{H}_4\text{N}]^+$ and $[\text{C}_6\text{H}_6\text{N}]^+$ displayed signals at m/z 78 and 92 respectively. These fragments have the relative natural abundance of 56 and 55 respectively. Secondary fragments such as $[\text{C}_4\text{H}_3]^+$ and $[\text{C}_5\text{H}_5]^+$ formed from the pyridine fragment showed signal at m/z 51 and 65 respectively.

Magnetic moment studies

Geometry prediction of the complexes is possible by magnetic moment measurement. La^{3+} ($4f^0$) with zero unpaired electron is found to be diamagnetic whereas neodymium and samarium complexes are found to be paramagnetic. Sm^{3+} ion has an odd

electronic configuration, $[\text{Xe}]4f^5$ labelled as Kramer's ion and exhibited μ_{eff} 1.72 BM as expected. Neodymium ion which has 3 unpaired electron exhibited magnetic moment value 4.09 BM. Thus octahedral geometry is assigned for all the complexes.

Molar conductance studies

Molar conductance of all the complexes was studied in DMSO. The value of molar conductance was found to be in between $2\text{-}5 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. This indicates that outside the coordination sphere, no counter ions were present and thus possess non-electrolytic nature.

Table 8.1 Microanalytical, magnetic and conductance data of 3PHEP and its inner transition metal complexes

Parameter	3PHEP (L)	*Complex		
		La(III)	Nd(III)	Sm(III)
Colour	Yellow	brown	brown	brown
Yield	82	70	61	66
Molecular weight	211	554	559	565
Melting point ($^{\circ}\text{C}$)	245	>300	>300	>300
M% Found	-	24.98	26.82	25.88
(Cald.)	-	(25.09)	(25.76)	(26.55)
C% Found	72.44	29.01	26.99	28.12
(Cald.)	(73.92)	(28.15)	(27.90)	(27.61)
H% Found	5.99	2.18	2.97	3.01
(Cald.)	(6.16)	(2.70)	(2.68)	(2.65)
N% Found	19.15	16.04	14.84	14.27
(Cald.)	(19.90)	(15.16)	(15.02)	(14.86)
μ_{eff} (BM)	-	Diamagnetic	4.09	1.72
Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	-	5	2	3
Geometry	-	Octahedral	Octahedral	Octahedral

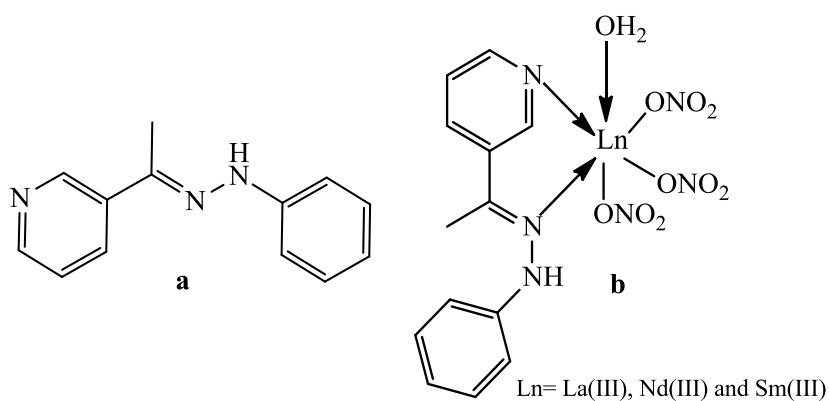
* $[\text{LnL}(\text{NO}_3)_3(\text{H}_2\text{O})]$ where Ln=La(III), Nd(III) and Sm(III)

Based on the physicochemical data, octahedral geometry was assigned to all these chelates where the ligand 3PHEP is behaving as zerovalent bidentate with NN donor sites. Structures of the ligand 3PHEP and its inner transition metal complexes are represented in Fig 8.1.

Table 8.2 Characteristic infrared absorption frequencies (cm^{-1}) of 3PHEP and its inner transition metal complexes

Assignment	3PHEP	*Complex		
	(L)	La(III)	Nd(III)	Sm(III)
$\nu_{\text{H}_2\text{O}}$	-	3426	3328	3410
ν_{NH}	3265	3228	3228	3227
$\nu_{\text{C}=\text{N}}$	1593	1573	1570	1584
$\nu_{\text{C}=\text{C}}$	1540	1404	1393	1503
ν_{NO_3}	-	1394, 1427	1388, 1456	1391, 1449
$\nu_{\text{C}-\text{N}}$	1048	1033	1048	1013
In plane bending	941	927	913	903
Out of plane bending	856	844	856	864
$\nu_{\text{M}-\text{N}}$	-	612	667	683
$\nu_{\text{M}-\text{O}}$	-	538	543	534

* $[\text{LnL}(\text{NO}_3)_3(\text{H}_2\text{O})]$ where Ln=La(III), Nd(III) and Sm(III)

**Fig. 8.1** Structures of a) ligand 3PHEP and b) its inner transition metal complexes

Section II

La(III), Nd(III) and Sm(III) complexes of 2-(1-(pyridine-3-yl)ethylidene)hydrazine carbothioamide

Synthesis and characterization of the Schiff base ligand 2-(1-(pyridine-3-yl)ethylidene)hydrazine carbothioamide (2PEHCT) and its of inner transition metal complexes are explained in this section.

Synthesis and characterization of 2PEHCT and its inner transition metal complexes

3-acetylpyridine and thiosemicarbazide in the ratio 1:1 in ethanol were mixed and refluxed for 3 h. After evaporation to dryness the solution was allowed to cool slowly. Pale yellow coloured precipitate formed was filtered and washed with minimum amount of ethanol. Recrystallized from ethanol and melting point was determined. Yield of 2PEHCT was found to be 79% and it melts at 205⁰C.

Ln₂O₃ (0.01 mol) was decomposed with con HNO₃ thrice and heated to prepare Ln(III) nitrate. Concentrated, cooled and added 20 ml ethanol. Ethanolic solution of 2PEHCT (0.02 mol) was added to this ethanolic nitrate solution and refluxed for 3 h. Dilute ammonia was added dropwise in the ratio 1:20 till a turbidity is formed after cooling the ethanolic mixture. Then stirred the solution magnetically and the precipitate formed was filtered, washed with ethanol and dried over anhydrous calcium chloride.

Elemental analysis

Percentage of C, H and N as well as the metal content were estimated by microanalytical methods. The results of microanalytical, magnetic and conductance data of 2PEHCT and its inner transition metal complexes are shown in Table 8.3. There is a good correlation between observed and calculated values of elemental analysis. 1:1 stiochiometry exist between metal and ligand in all complexes.

FTIR spectral studies

IR spectrum of 2PEHCT consists of characteristic stretching frequencies corresponding to various bonds. Peak observed at 1612 cm^{-1} is due to the presence of azomethine group. Stretching frequency due to NH vibration was identified at 3201 cm^{-1} as a medium band. Terminal amino group exhibited symmetrical and asymmetric vibrations and the corresponding peaks were observed at 3246 cm^{-1} and 3385 cm^{-1} . C=S vibration was identified at 880 cm^{-1} . A very weak band at 2466 cm^{-1} is a clear evidence for the existence of tautomeric form of the ligand, with thiol moiety.

In complexes the stretching frequencies of the azomethine group were found to be lowered due to its involvement in complexation. Additional bands in the range $3424\text{-}3474\text{ cm}^{-1}$ and $1313\text{-}1477\text{ cm}^{-1}$ implies the coordination of water and nitrate molecules in the complexes respectively. Appearance of M-N and M-S bands in the spectrum of complexes is very much in favor to the coordination of N and S atom to the metal. Characteristic infrared absorption frequencies (cm^{-1}) of 2PEHCT and its inner transition metal complexes are given in Table 8.4.

Electronic spectral studies

In the electronic spectra of 2PEHCT two peaks were observed. The peak at 31347 cm^{-1} corresponds to $n \rightarrow \pi^*$ transition and the adsorption frequency at 31948 cm^{-1} implies $\pi \rightarrow \pi^*$ transition. In the case of complexes these peaks are found to shift to higher wavelength. This is a clear proof for the formation of complexes.

NMR spectral studies

In the proton NMR spectrum of 2PEHCT eight distinct signals were observed. The signal at $2.3\ \delta$ is due to methyl protons. Protons in the terminal NH_2 of the thiosemicarbazide moiety exhibited a broad peak at $3.4\ \delta$. A singlet observed at $8.1\ \delta$ was assigned to NH proton present in the thiosemicarbazide part. SH proton displayed a

peak at 10.3 δ . This is due to the existence of tautomeric structure of the molecule.

Protons in the pyridine ring exhibited signals in the range 7.4-9.2 δ .

Table 8.3 Microanalytical, magnetic and conductance data of 2PEHCT and its inner transition metal complexes

Parameter	2PEHCT (L'H)	*Complex		
		La(III)	Nd(III)	Sm(III)
Colour	Pale yellow	Cream	Grey	Off white
Yield	70%	65%	68%	59%
Molecular weight	194	492	497	503
Melting point ($^{\circ}\text{C}$)	205	>300	220	235
M% Found	-	27.95	29.13	28.98
(Cald.)	-	(28.19)	(28.92)	(29.76)
C% Found	48.55	19.26	18.89	19.58
(Cald.)	(49.49)	(19.51)	(19.31)	(19.08)
H% Found	4.99	2.45	3.25	3.09
(Cald.)	(5.15)	(2.64)	(2.61)	(2.58)
N% Found	29.22	18.35	15.86	17.28
(Cald.)	(28.9)	(17.07)	(16.90)	(16.69)
μ_{eff} (BM)	-	Diamagnetic	3.51	1.40
Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	-	3	40	5
Geometry	-	Octahedral	Octahedral	Octahedral

*[LnL'(NO₃)₂(H₂O)₂] where Ln=La(III), Nd(III) and Sm(III)

¹³C NMR spectrum of 2PEHCT consists of eight signals corresponding to eight chemically distinct carbon atoms. Methyl carbon exhibited its signal at 13.72 ppm. The signal at 145.55 ppm is due to azomethine carbon. Quaternary carbon present in the pyridine ring displayed a signal at 133.23 ppm. The other carbon atoms of the pyridine ring appeared at 149.67 ppm, 123.23 ppm, 133.94 pmm and 147.74 ppm. Signal at 179.08 ppm is assigned to the carbon atom present in the thiosemicarbazone moiety.

Magnetic moment studies

Information's concerning the geometry of the complexes was obtained from the magnetic moment measurement. Magnetic moment values of Nd(III) and Sm(III)

complexes are found to be 3.51 BM and 1.40 BM respectively, whereas La(III) complex is diamagnetic. Octahedral geometry is assigned for all complexes.

Molar conductance studies

Molar conductance measurement was done for all complexes and is given in Table 8.3. Molar conductance values of the complexes are in the range of 3-40 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. These values suggest non-electrolytic behaviour and absence of counter ions outside the coordination sphere of metal chelates.

On the basis of spectral, elemental and magnetic data, octahedral geometry with 1:1 stoichiometry between ligand and metal is assigned to all the Ln complexes. 2PEHCT behaved monovalent bidentate ligand with NS donor sites. Structures of the ligand 2PEHCT and its inner transition metal complexes are represented in Fig 8.2.

Table 8.4 Characteristic infrared absorption frequencies (cm^{-1}) of 2PEHCT and its inner transition metal complexes

Assignment	2PEHCT (L H)	*Complex		
		La(III)	Nd(III)	Sm(III)
$\nu_{\text{H}_2\text{O}}$	-	3424	3430	3474
ν_{NH}	3264	3211	3249	3267
$\nu_{\text{C=N}}$	1612	1574	1609	1604
$\nu_{\text{C=C}}$	1508, 1583	1498, 1543	1470, 1528	1503, 1588
ν_{NO_3}	-	1416, 1313	1414, 1313	1477, 1414
$\nu_{\text{C-S}}$	1132	1113	1089	1089
In plane bending	1012	980	973	973
Out of plane bending	701	722	761	701
$\nu_{\text{M-N}}$	-	601	642	622
$\nu_{\text{M-O}}$	-	548	581	504
$\nu_{\text{M-S}}$	-	473	481	486

*[LnL'(NO₃)₂(H₂O)₂] where Ln=La(III), Nd(III) and Sm(III)

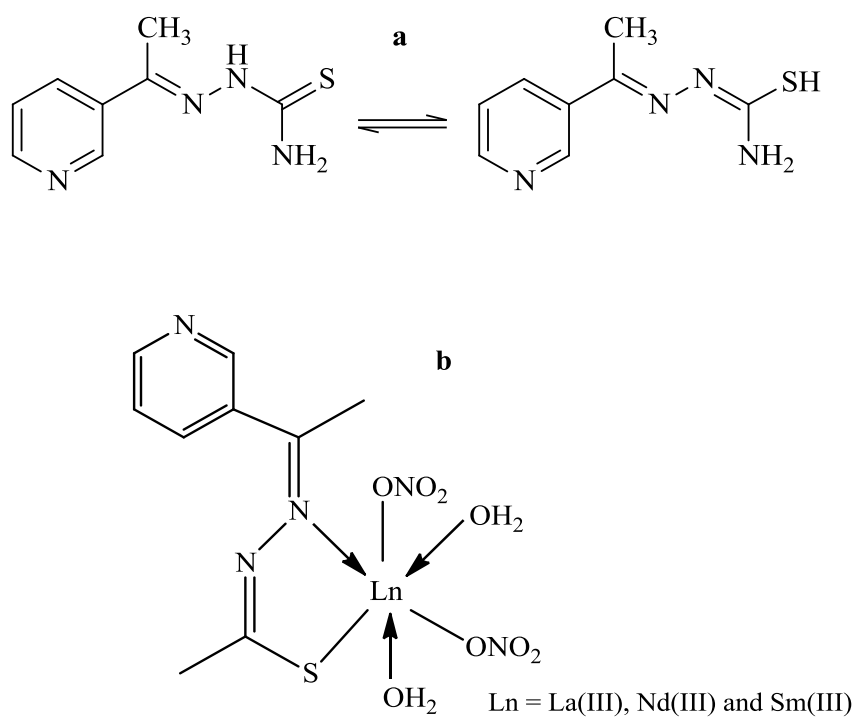


Fig. 8.2 Structures of a) ligand 2PEHCT and b) its inner transition metal complexes

Section III

La(III), Nd(III) and Sm(III) complexes of 3-((thiophen-2-ylmethylene)amino)benzoic acid

This section deals with synthesis and characterization of the Schiff base ligand 3-((thiophen-2-ylmethylene)amino)benzoic acid (3TMAB) and its inner transition metal complexes

Synthesis and characterization of 3TMAB and its inner transition metal complexes

Ethanol solution of thiophene-2-carbaldehyde was added to solution of 3-aminobenzoic acid in ethanol and refluxed for 3 h. Solution was then evaporated and cooled to obtain pale yellow coloured precipitate, which was filtered and washed with minimum amount of ethanol. Recrystallization from ethanol resulted in 82% yield of the product. Melting point was found to be 136⁰C

Nitrate solution of lanthanide ions were prepared by heating 0.01 mol of its oxides (Ln₂O₃) in con HNO₃. Volume of the solution is then reduced, cooled and 20 ml ethanol was added. Then the solution was refluxed for 3 h after adding 0.02 mol of 3TMAB dissolved in ethanol. Resulting mixture is then cooled and added dilute ammonia (1:20) drop wise till a turbidity is formed. Precipitate was formed when the solution is magnetically stirred, which was filtered, washed with ethanol and dried over anhydrous calcium chloride.

Elemental analysis

The stoichiometry present between metal and ligand is obtained from elemental analysis data. Results of elemental analysis are shown in Table 8.5. From the data it is clear that 1:1 stoichiometry exist between metal and ligand.

FTIR spectral studies

In the IR spectrum of 3TMAB the peak observed at 1612 cm^{-1} is due to the presence of azomethine group. A scalloped band is obtained for OH group at 3000 cm^{-1} . A signal at 1689 cm^{-1} corresponds to the asymmetric stretching vibration of COO group. A signal at 1292 cm^{-1} was assignable to $\nu_{\text{C-O}}$. In plane deformation was observed at 1197 cm^{-1} and out of plane deformation was observed at 717 and 914 cm^{-1} . Stretching frequency due to sp^2 hybridized C-H bond was shown at 3062 cm^{-1} .

In complexes the involvement of azomethine group in coordination with metal was confirmed by the shift of its stretching frequency to lower value. Also the asymmetric stretching vibration of COO group is also shifted, which indicates coordination of carboxylate group to the metal. The presence of new signal around 1450 cm^{-1} and 3400 cm^{-1} in complexes confirmed the presence of coordinated nitrate and water molecule. Also the appearance of stretching frequencies corresponding to M-O and M-N confirmed the formation of complex. Characteristic infrared absorption frequencies (cm^{-1}) of 3TMAB and its inner transition metal complexes are given in Table 8.6.

Electronic spectral studies

Two separate peaks observed at 32154 cm^{-1} and 39062 cm^{-1} in the electronic spectra of 3TMAB correspond to $\text{n} \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. In the case of complexes bathochromic shift was occurred for these bands which are a clear evidence for the complex formation.

NMR spectral studies

In the proton NMR spectra of 3TMAB, signal at $12.9\ \delta$ correspond to the proton present in the COOH group. A broad signal at $3.2\ \delta$ was assignable to the proton in azomethine carbon. Protons of the aromatic ring and thiophene ring showed signal in the range $7.7\text{-}8.8\ \delta$ and $7.1\text{-}7.7\ \delta$ respectively.

^{13}C NMR spectrum of 3TMAB displayed 12 peaks corresponding to 12 chemically distinct carbon atoms. Azomethine carbon displayed a peak at 154.99 ppm. Carbon atom of carboxyl group showed a peak at 167.03 ppm. Peaks due to protons of the benzene ring and thiophene ring were appeared in the range 129-151 ppm and 120-129 ppm respectively.

Magnetic moment studies

Idea about the geometry of the complexes was obtained from the magnetic moment measurement. Magnetic moment values of Nd(III) and Sm(III) complexes are found to be 3.73 BM and 1.51 BM respectively, whereas La(III) complex is diamagnetic. Octahedral geometry is assigned for all complexes.

Table 8.5 Microanalytical, magnetic and conductance data of 3TMAB and its inner transition metal complexes

Parameter	3TMAB (L'H)	*Complex		
		La(III)	Nd(III)	Sm(III)
Colour	Pale yellow	Pale brown	Dark brown	Light brown
Yield	70%	62%	58%	52%
Molecular weight (MW)	231	529	534	540
Melting point ($^{\circ}\text{C}$)	136	>300	220	245
M% Found	-	25.98	26.01	27.25
(Cald.)	-	(26.28)	(26.97)	(27.78)
C% Found	63.84	27.11	27.01	25.95
(Cald.)	(62.34)	(27.22)	(26.96)	(26.66)
H% Found	3.81	2.68	2.38	2.18
(Cald.)	(3.90)	(2.26)	(2.24)	(2.22)
N% Found	7.04	8.01	7.48	8.08
(Cald.)	(6.06)	(7.94)	(7.86)	(7.77)
μ_{eff} (BM)	-	Diamagnetic	3.73	1.51
Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	-	15	49	41
Geometry	-	Octahedral	Octahedral	Octahedral

*[LnL''(NO₃)₂(H₂O)₂] where Ln=La(III), Nd(III) and Sm(III)

Molar conductance studies

Molar conductance measurement was done for all complexes and is given in Table 8.5. The molar conductance value of the complexes is in the range of 15-50 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These values suggest non-electrolytic behaviour and absence of counter ions outside the coordination sphere of metal chelates.

Table 8.6 Characteristic infrared absorption frequencies (cm^{-1}) of 3TMAB and its inner transition metal complexes

Assignment	3TMAB (L'H)	*Complex		
		La(III)	Nd(III)	Sm(III)
$\nu_{\text{H}_2\text{O}}$		3382	3393	3427
ν_{COO} (asym)	1689	1615	1614	1614
$\nu_{\text{C=N}}$	1579	1565	1570	1561
ν_{COO} (sym)	1524	1515	1521	1510
ν_{NO_3}	-	1501, 1403	1498, 1394	1492, 1394
$\nu_{\text{C-O}}$	1292	1291	1291	1291
In plane bending	1197	1188	1039	1039
Out of plane bending	914, 717	893, 752	901, 814	901, 814
$\nu_{\text{M-N}}$	-	682	673	673
$\nu_{\text{M-O}}$	-	423	492	498

*[LnL'(NO₃)₂(H₂O)₂] where Ln=La(III), Nd(III) and Sm(III)

From the characterization data the ligand 3TMAB coordinates with metal through NO donor sites and acted as monovalent bidentate ligand. Also it was noticed that 1:1 stoichiometry exist between all metal and ligand and possess octahedral geometry. Structure of the ligand 3TMAB and its inner transition metal complexes are represented in Fig 8.3.

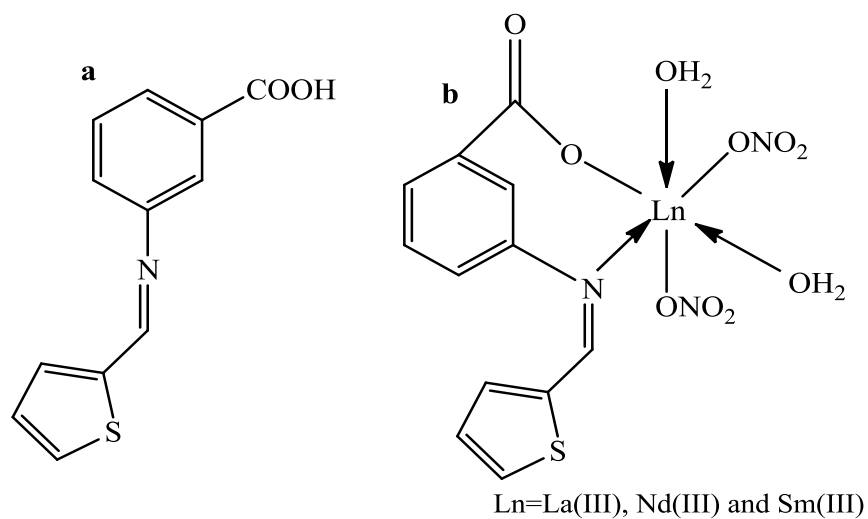


Fig. 8.3 Structures of a) ligand 3TMAB and b) its inner transition metal complexes

SUMMARY

Synthesized three heterocyclic Schiff bases derived from 3-acetylpyridine and thiophene-2-carbaldehyde such as 3-(1-(2-phenylhydrazono)ethyl)pyridine (3PHEP), 2-(1-(pyridine-3-yl)ethylidene)hydrazine carbothioamide (2PEHCT) and 3-((thiophen-2-ylmethylene)amino)benzoic acid (3TMAB) and their characterization were done by CHN analysis, spectral studies such as FTIR, UV-visible, NMR (^1H and ^{13}C) and mass spectroscopy. The inner transition metal complexes of these heterocyclic Schiff bases were synthesized to check their chelating ability. The complexes were also subjected to characterization by means of elemental (CHN) analysis, FTIR, UV, magnetic moment, estimation of metal and molar conductance measurements and structures were formulated.

Chelating ability of the heterocyclic Schiff bases 3PHEP, 2PEHCT and 3TMAB was explored by synthesizing inner transition metal complexes with metal ions of Lanthanum, Neodymium and Samarium. It was observed that 1:1 stoichiometry exists between metal and ligand in the case of all complexes. Ligand 3PHEP acted as zerovalent bidentate ligand and coordinates through azomethine nitrogen and the nitrogen atom present in the pyridine ring while the other two, 2PEHCT and 3TMAB were behaved as monovalent bidentate ligands but their coordination sites are different. 2PEHCT coordinates through azomethine nitrogen and sulphur atom where as in 3TMAB azomethine nitrogen and oxygen of the carboxylate group are the coordination sites.

On the basis of physicochemical data, octahedral geometry was assigned to La(III), Nd(III) and Sm(III) complexes of all these ligands. Diamagnetic behaviour was found for La(III) complexes, whereas Nd(III) and Sm(III) complexes are paramagnetic

as expected. Molar conductance data suggested that all the complexes are non-electrolytic in nature.

Presence of coordinated water molecules in all the chelates is evident by the appearance of additional broad peaks at almost 3400 cm^{-1} in the FTIR spectra. Nitrate ions with unidentate nature are present in all the complexes. Based on physicochemical data the general structure $[\text{LnL}(\text{NO}_3)_3(\text{H}_2\text{O})]$ is assigned to lanthanide complexes derived from Schiff base, 3PHEP while the lanthanide chelates derived from 2PEHCT and 3TMAB possess the general formula $[\text{LnL}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$.

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