



Synthesis and Physico-chemical studies of Ni(II) and Zn(II) Complexes with Schiff bases of Thiophene-2-thiohydrazide

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ABSTRACT

The complexes of Nickel(II) and Zinc(II) with Schiff bases of thiophene-2-thiohydrazide of compositions $[M(LH)_2]$ [$M=Ni^{2+}$ or Zn^{2+} and $LH=$ Acetone-thiophene-2-thiohydrazone (Hactth), Acetylacetone-thiophene-2-thiohydrazone (Hacactth), Benzaldehyde-thiophene-2-thio-hydrazone (Hbentth), Furfural thiophene-2-thiohydrazone (Hffth)]; $[ML_2]$, $[ML(H_2O)] \cdot nH_2O$ ($n=0$ or 2); $[ML(NH_3)]$ and $[ML(Py)]$; [$M=Ni^{2+}$ or Zn^{2+} and $LH_2=$ Salicylaldehyde-thiophene-2-thiohydrazone (H_2Salth), 2-hydroxyacetophenone thiophene-2-thiohydrazone (H_2aptth)] have been prepared and characterized by elemental analysis, spectral (UV-Vis, IR, 1H NMR) Studies, electrical conductance values, thermogravimetric analysis and magnetic Susceptibility measurements at room temperature. Some of the ligands as well as their Ni(II) and Zn(II) complexes exhibit appreciable antifungal activity.

Keyword: Schiff's base, Thiohydrazones, Spectral studies, Thermogravimetric analysis, Antifungal activity.

INTRODUCTION

Thiohydrazides and thiohydrazones are one of the most Studied ligands owing to their flexibility of binding sites to metal ions, broad range of biological activity and various commercial applications like, wear inhibiting additives in lubricants, vulcanization accelerators for rubber, specific analytical reagents etc¹⁻⁶. We have already reported the complexes of a number of metal ions with various thiohydrazides and their Schiff bases⁷⁻⁸. Many other workers⁹⁻¹⁰ have also synthesised and characterized the complexes of these ligands using different metals, but little

work has been carried out on the complexes of Schiff bases of biologically active thiophene-2-thiohydrazide. The capability of thiohydrazones to coordinate to metal ions is due to the delocalization of electron density over the chelate ring. Keeping in view, '2+' as the most prolific oxidation state of Nickel & Zinc which is also easily accessible for complex formation, very alluring stereochemistry of Ni(II) complexes, involvement of both these elements in several biological processes and immense utility of their complexes¹¹⁻¹⁴, we report here the preparation, characterization, thermal and biological studies of complexes of Ni(II) and Zn(II) with thiophene-



2-thiohydrazones derived from acetone (Hactth), acetylacetone (Hacactth); benzaldehyde(Hbentth), Salicylaldehyde (H₂Salth); 2-hydroxyacetophenone (H₂apth) and furural (Hftth).

EXPERIMENTAL

All the reagents were of E.Merck (AR grade) and the solvents were purified by standard methods and dried before use. The magnetic susceptibility was determined at room temperature by Gouy method. IR Spectra were recorded as KBr Pellets or nujol mull in the range 400-4000 cm⁻¹ on Perkin. Elmer FTIR-Spectrometer. The electronic absorption Spectra of the complexes and ligands were recorded in the range of 220-900 nm in ethanol, dioxane or CCl₄ at RSIC Chandigarh, CDRI-Lucknow as well as in the P.G.Deptt. of Chemistry, B.R.A.B.U. Muzaffarpur. ¹HNMR Spectra were recorded from CDRI. Lucknow.

Sulphur was estimated gravimetrically as BaSO₄. The metal ions were estimated by standard methods¹⁵.

Thiophene-2-thiohydrazide (tthH) was prepared by the same procedure as adopted in the case of furan-2-thiohydrazide by published method¹⁶. Thiophen-2-thiohydrazones were prepared by refluxing 0.025mol of appropriate aldehyde or ketone with methanolic solution (60 mL) of thiophene-2-thiohydrazide (0.025mol; 3.95g). On cooling, the thiohydrazones, separated were filtered washed with cold methanol and recrystallised from hot methanol or hot benzene. The reactions in the process are given below.

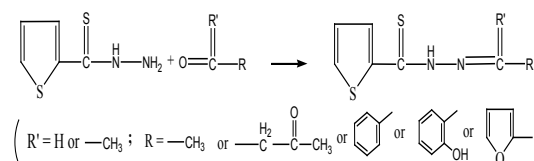


Table 1: Analytical data of prepared ligands are summarised

Ligands	Colour	m.p.(°C)	Analysis % Found (Calc)			
			Carbon	Hydrogen	Nitrogen	Sulphur
Thiophene-2-thiohydrazide (Htth)	Flaky white	146	37.35 (37.97)	3.68 (3.80)	17.59 (17.72)	40.46 (40.51)
Acetone-thiophene-2-thiohydrazone(Hactth)	White	156	48.17 (48.48)	4.83 (5.05)	13.96 (14.14)	32.13 (32.32)
Acetylacetone-thiophene-2-thiohydrazone (Hacactth)	White	165	49.84 (50.0)	4.79 (5.0)	11.41 (11.66)	26.52 (26.66)
Benzaldehyde-thiophene-2-thiohydrazone(Hbentth)	Cream	169	58.31 (58.53)	3.87 (4.06)	11.17 (11.38)	25.88 (26.01)
Salicylaldehyde- thiophene-2-thiohydrazone (H ₂ Salth)	Cream	176	54.77 (54.96)	3.67 (3.81)	10.48 (10.68)	24.28 (24.42)
2-Hydroxy acetophenone-thiophene-2-thiohydrazone (H ₂ apth)	Light cream	179	56.31 (56.52)	4.17 (4.34)	9.02 (10.14)	23.03 (23.18)
Furfural-thiophene-2-thiohydrazone (Hftth)	Cream	171	50.62 (50.84)	3.21 (3.38)	11.67 (11.86)	26.96 (27.11)

Preparation of complexes

[ML₂], (M=Ni²⁺ or Zn²⁺; LH=Hactth; Hacactth, Hbentth, Hftth) and

[M(LH)₂], (LH₂=H₂Salth, H₂apth)

An aqueous solution (40-50 mL) of the metal chloride (0.005mol) was added slowly with stirring to a hot ethanolic solution (40-50 mL) of appropriate ligand (0.005 mol), and refluxed for 0.5 to 1 h, when metal complexes separated gradually. In a few Zn(II), the complexes separated on adding equal volume of water. On, cooling, the products were collected on filter paper, washed with aqueous

ethanol and dried over CaCl₂ and finally in air over at 60-70°C.

[ML(H₂O)].nH₂O (M=Ni²⁺ or Zn²⁺; LH₂=H₂Salth, H₂apth; n=2 or 0)

An aqueous solution (40-50 mL) of the appropriate metal acetate (0.0015mol) was treated with a hot ethanolic solution of ligand (.0015mol) and refluxed for 1-2 h and PH was maintained at ≈ 7-8 by adding aqueous solution of sodium acetate. The solid products were collected on a filter paper, washed with aqueous ethanol, dried over CaCl₂ and finally in an air oven (60-70°C).

[ML(NH₃)₃], (M=Ni²⁺ or Zn²⁺; LH₂=H₂Salth; H₂apth)

By carrying out similar reactions as above in the presence of 15% NH_4OH solution ($\text{pH}\approx 9$), yielded complexes of composition $[\text{ML}(\text{NH}_3)_2]$, which was collected on a filter paper, washed with ethanol and dried as above.

$[\text{ML}(\text{Py})_2]$ ($[\text{ML}_2]$, ($\text{M}=\text{Ni}^{2+}$ or Zn^{2+} ; $\text{LH}_2=\text{H}_2\text{Saltth}$; H_2apth)

An aqueous Solution (50 mL) of metal chloride (0.0015mol) was treated with pyridine (3-4 mL) and the resulting solution was treated with hot ethanolic solution (50 mL) of appropriate ligand (0.0015mol) and refluxed for 1-2 h, when mixed ligand complexes separated out. The solid products were washed with aqueous ethanol and dried over $\text{KOH}+\text{CaCl}_2$.

The analytical results and physical data of complexes are recorded in Table 2, the UV-Vis results are given in Table 3.

RESULTS & DISCUSSION

The analytical data recorded in Table 2, are fully consistent with the formulation of

complexes. Thermogravimetric analysis show that, the complexes are stable below 180-200°C, some complexes melt after 200°C but majority of them start decomposing slowly above 210-220°C. the complexes are non-hygroscopic and insoluble in water, Sparingly soluble in methanol, ethanol but highly soluble in DMF, DMSO and dioxane. The negligible molar conductivities in DMF ($5-10 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) suggest that the complexes are non electrolytes. Except $[\text{Ni}(\text{Saltth})\cdot(\text{H}_2\text{O})]$ and $[\text{Ni}(\text{apth})\text{H}_2\text{O}]$, which are feebly paramagnetic, the other complexes are diamagnetic. A minor paramagnetism of these two complexes can be attributed to partial population of a spin-triplet state close to idealised ground state $^1\text{A}_{1g}$ for D_{4h} symmetry¹⁸. The diamagnetism of all other Ni(II) complexes indicate their square planar geometry¹⁸.

The preference for tetrahedral stereochemistry for complexes of d^{10} electronic system and observed metal ligand stereochemistry¹⁹ indicate tetrahedral structure for the Zn(II) complexes which were found diamagnetic.

Table 2: Analytical and physical data of complexes

Complexes	Colour	Analysis%, found (Cal)				μ_{eff} (B.M.)	ΔM ($\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$)
		Metal	Carbon	Nitrogen	Sulphu		
$[\text{Ni}(\text{actth})_2]$	Brown	12.78 (12.88)	42.37 (42.66)	12.26 (12.44)	28.22 (28.44)	Dia	5
$[\text{Zn}(\text{actth})_2]$	Light yellow	14.04 (14.22)	41.72 (42.01)	11.96 (12.25)	28.17 (28.00)	Dia	6
$[\text{Ni}(\text{acactth})_2]$	Reddish brown	10.62 (10.86)	44.71 (44.94)	10.27 (10.48)	23.19 (23.40)	Dia	6
$[\text{Zn}(\text{acactth})_2]$	Yellow	11.82 (12.01)	44.16 (44.36)	10.18 (10.35)	23.42 (23.65)	Dia	7
$[\text{Ni}(\text{bentth})_2]$	Orange red	10.35 (10.62)	43.76 (43.95)	12.04 (12.28)	23.25 (23.44)	Dia	5
$[\text{Zn}(\text{bentth})_2]$	Orange yellow	11.63 (11.75)	43.23 (43.39)	9.89 (10.12)	23.25 (23.14)	Dia	5
$[\text{Ni}(\text{HSaltth})_2]$	Reddish brown	9.84 (10.03)	41.31 (41.52)	9.49 (9.68)	21.97 (22.14)	Dia	5
$[\text{Zn}(\text{HSaltth})_2]$	Yellow	10.93 (11.11)	40.87 (41.02)	9.38 (9.57)	21.72 (21.88)	Dia	7
$[\text{Ni}(\text{Hapth})_2]$	Brick red	9.33 (9.57)	51.24 (51.48)	9.07 (9.24)	20.95 (21.12)	Dia	6
$[\text{Zn}(\text{Hapth})_2]$	Yellow	10.41 (10.60)	50.65 (50.89)	9.05 (9.13)	20.68 (20.88)	Dia	7
$[\text{Ni}(\text{ftth})_2]$	Brown	10.74 (11.02)	45.38 (45.62)	10.51 (10.64)	24.13 (24.33)	Dia	5
$[\text{Zn}(\text{ftth})_2]$	Yellow	11.91 (12.19)	44.82 (45.02)	10.35 (10.50)	23.87 (24.01)	Dia	6
$[\text{Ni}(\text{Saltth})(\text{H}_2\text{O})]$	Brown	16.97 (17.26)	42.62 (42.85)	8.19 (8.33)	18.82 (19.04)	0.62	5
$[\text{Ni}(\text{apth})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$	Brick red	14.87 (15.02)	40.22 (40.41)	7.03 (7.25)	16.24 (16.58)	0.65	6
$[\text{Zn}(\text{Saltth})(\text{H}_2\text{O})]$	cream	18.71 (18.95)	41.74 (41.98)	7.02 (8.16)	18.49 (18.65)	Dia	7
$[\text{Zn}(\text{apth})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$	Light Yellow	16.21 (16.53)	39.33 (39.69)	6.95 (7.12)	16.07 (16.28)	Dia	5
$[\text{Ni}(\text{Saltth})(\text{NH}_3)]$	Red	17.14 (17.31)	42.81 (42.98)	12.32 (12.53)	18.87 (19.10)	Dia	5
$[\text{Ni}(\text{apth})(\text{NH}_3)]$	Reddish brown	16.45 (16.61)	44.38 (44.69)	11.83 (12.03)	18.08 (18.33)	Dia	5
$[\text{Zn}(\text{Saltth})(\text{NH}_3)]$	yellow	18.77 (19.00)	41.82 (42.10)	11.98 (12.28)	18.53 (18.71)	Dia	5
$[\text{Zn}(\text{apth})(\text{NH}_3)]$	Yellow	18.05 (18.25)	43.64 (43.82)	11.57 (11.79)	17.83 (17.97)	Dia	5
$[\text{Ni}(\text{Saltth})\text{Py}]$	Red	14.47 (14.60)	36.03 (36.27)	10.34 (10.57)	15.91 (16.12)	Dia	5
$[\text{Ni}(\text{apth})\text{Py}]$	Reddish brown	13.93 (14.11)	37.76 (37.95)	9.94 (10.21)	15.29 (15.57)	Dia	6
$[\text{Zn}(\text{Saltth})\text{Py}]$	Light Yellow	15.88 (16.08)	35.45 (35.64)	10.24 (10.39)	15.67 (15.84)	Dia	5
$[\text{Zn}(\text{apth})\text{Py}]$	yellow	15.32 (15.55)	37.06 (37.32)	9.88 (10.04)	15.17 (15.31)	Dia	6

Table 3: Electronic reflectance band position in nm

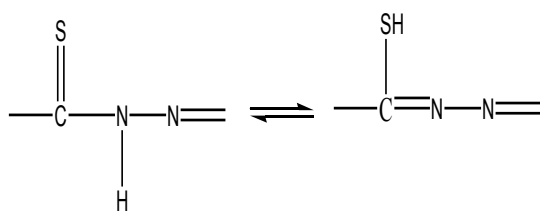
Complexes	Electronic band positions in nm.	Assignments
[Ni(actth) ₂]	360sbr, 375br, 440sh	$\pi - \pi^*$, C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(acacth) ₂]	375sbr, 445m, 560m	$\pi - \pi^*$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$
[Ni(bentth) ₂]	380br, 450m, 495m	$\pi - \pi^*$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$
[Ni(HSaltth) ₂]	390br, 450m	$\pi - \pi^*$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(Hapth) ₂]	250s, 305br, 365br, 460sh	$\pi - \pi^*$, n- π^* , C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(ftth) ₂]	262s, 317br, 450sh	$\pi - \pi^*$, n- π^* , ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(Saltth)(H ₂ O)]	270s, 380sbr, 465sh, 580br	$\pi - \pi^*$, n- π^* , ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$
[Ni(Saltth)(NH ₃)]	260s, 325br, 450sh	$\pi - \pi^*$, C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(apth)(NH ₃)]	262s, 321br, 455sh	$\pi - \pi^*$, C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$
[Ni(Saltth)Py]	235s, 305s, 465sh, 500m	$\pi - \pi^*$, C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$
[Ni(apth)Py]	240s, 310s, 472sh, 505m	$\pi - \pi^*$, C-T, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$

Electronic Spectral Studies

The solid reflectance spectra of Ni(II) complexes below 400nm display strong absorption attributable to charge transfer band or ligand absorptions. A weak band or shoulder in the regions 420-480nm and 500-600nm are assignable to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively in a planar arrangement of ligand molecules around Ni(II) atom in D_{4h} symmetry^{8,20-21}. The thioamide bands of ligands observed in the regions ≈ 475 nm suffers blue Shift in the complexes due to thioenolisation²¹⁻²⁴ and broadens considerably probably due to the overlap of ligand to metal charge transfer transitions.

IR Spectral Studies

The absence of any band in the region 2500-2600 cm⁻¹ due to ν (SH) shows that all the ligands exist in the thioketo form, which is also supported by ¹HNMR studies. The IR absorption bands of ν_{NH} in the region 3200-3400 cm⁻¹ of the free ligands disappear in complexes, which indicates that the ligands are deprotonated in complexes. The thioamide band IV of the free ligands (865-935 cm⁻¹) which has major contribution from $\nu_{C=S}$ vibration is observed at 705 \pm 20 cm⁻¹ in their complexes, indicating the coordination through the deprotonated thiol sulphur atom⁷⁻⁸.



Along with this the $\nu_{C=N}$ band of agomethine group of ligand (1625 \pm 5 cm⁻¹) is observed at lower frequency by 15-10 cm⁻¹ as strong band in

the complexes, which indicates coordination of azomethine group. This is further substantiated by the appearance of azine chromophores 22 (>C=N—N=C<) around 1605-1600 cm⁻¹ in the complexes. A broad band at 2950-3150 cm⁻¹ for bis ligated complexes of thiophene-2-thiohydrazones of salicylaldehyde and 2-hydroxyacetophenone having composition [M(LH)₂] (M=Ni²⁺, or Zn²⁺, LH₂=H₂Saltth; H₂apth) is absent in their monoligated complexes of compositions [ML(H₂O)]; [ML(NH₃)] and [MLPy], which indicates that phenolic OH of salicylaldehyde (or 2-hydroxy acetophenone) part is retained in bis-chelates and involved in hydrogen bonding while deprotonated and coordinated to metal in monoligated complexes. The hydrated complexes [ML(H₂O)] (M=Ni²⁺, or Zn²⁺, LH₂=H₂Saltth; H₂apth) display a broad band near 3350 cm⁻¹ attributed to water molecules. The rocking band of H₂O is not observed for coordinated water which indicates lattice nature of H₂O in the complexes²³. Drastic condition required to dehydrate these complexes also favor a structure containing coordinated water molecule in these complexes.

The coordination of NH₃ in the complexes of composition [ML(NH₃)] (M=Ni²⁺, or Zn²⁺, LH₂=H₂Saltth; H₂apth) is indicated by the appearance of bands as 3300-3100, 1590, 1280, and 850 cm⁻¹ assignable to ν NH₃, δ NH₃ and ρ NH₃ respectively. In the pyridine complexes of composition [ML(Py)] (M=Ni²⁺, or Zn²⁺, LH₂=H₂Saltth; H₂apth) the pyridine ring $\nu_{C=N}$ band is observed at 1595 \pm cm⁻¹ in the complexes. The pyridine ring breathing mode of vibrations observed at 1020 \pm 5 cm⁻¹ are attributed to coordinated nature of pyridine molecule²⁴.

The bis ligated complexes of acetone and acetylacetone of composition [ML₂] (M=Ni²⁺, or Zn²⁺,

LH=Hactth; Hacactth), display vibrations between 1680-1720 cm^{-1} indicating that carbonyl oxygen is completely free and uncoordinated in complexes. In far infrared region all the complexes display a number of bands at 460-410, 400-380, 360-320 cm^{-1} which are tentatively assigned to M-O, M-N and M-S stretching vibrations^{21,25-26} respectively.

So it is found that in slightly alkaline medium (PH \approx 9) the ligands, salicylaldehyde thiophene-2-thiohydrazone (H_2saltth) and 2-hydroxyacetophenone thiophene-2-thiohydrazone (H_2apth) react with Ni(II) or Zn(II) salt giving rise to monoligated complexes of composition $[\text{ML}(\text{H}_2\text{O})]$, $[\text{ML}(\text{NH}_3)]$ & $[\text{ML}(\text{PY})]$, thus behaving in a dibasic tridentate fashion and bonding takes place through O, N and S-atoms. In neutral or feebly alkaline conditions these ligands and other ligands also found to act in a bidentate monobasic way bonding through azomethine N-atom and sulphur atom (via thioenolisation) keeping the phenolic -OH free.

¹HNMR studies

The signals due to -NH proton $\delta(\approx 11.8)$ ppm and phenolic -OH proton $\delta(\approx 12.4)$ ppm of ligands (H_2Saltth) and (H_2apth) disappear in its monoligated complexes of composition $[\text{ML}(\text{H}_2\text{O})]$, $[\text{ML}(\text{NH}_3)]$ & $[\text{ML}(\text{Py})]$, which shows the dibasic tridentate nature of these ligands in complexes, bonding through O, N & S atoms²⁷⁻²⁸. In the neutral bis chelates signals due to -NH proton $\delta(11-12)$ ppm of ligands disappear

in complexes, which suggests thioenolisation & coordination through deprotonated thiol sulphur atom. In neutral bis chelates of (H_2Saltth) & (H_2apth), the signals due to phenolic -OH appearing in the range $\delta(\approx 12.4)$ ppm remains unaffected in complexes and its downfield shift than normal phenolic -OH, shows H-bonding. The chemical shift of thiophene ring protons $\delta(7.1-7.3)$ ppm of ligands undergo slight downfield shift $\delta(7.2-7.5)$ on complexation.

Biological Studies

Monoligated pyridine complex of salicylaldehyde thiophene-2-thiohydrazone $[\text{M}(\text{Saltth})(\text{Py})]$ and bis ligated complexes of furfural thiophene-2-thiohydrazone $[\text{M}(\text{ftth})_2]$; (M=Ni²⁺, or Zn²⁺) have also been tested for antifungal activity. The screening of all the complexes were carried out against two fungal species viz. *Aspergillus niger* and *Rhizopus* at three concentrations. Viz 25, 50 and 100 $\mu\text{g mL}^{-1}$. All the complexes are found to be active and show a higher percentage of inhibition at lower concentrations. The complexes are found biologically more active than ligands.

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