



SYNTHESIS, SPECTRAL CHARACTERIZATION, THERMAL AND BIOLOGICAL STUDIES OF MONONUCLEAR CR(III), MN(III), FE(III), VO(IV) AND UO₂(VI) COMPLEXES DERIVED FROM THIOCARBOHYDRAZONE LIGAND

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ABSTRACT New metal complexes of ML type, where M= Cr(III), Mn(III), Fe(III), VO(IV) and UO₂(VI) was synthesized by using thioicarbohydrazone (LH₂) derived from thioicarbohydrazide and 5-bromo-2-hydroxyacetophenone. Newly synthesized complexes were characterized by elemental analysis, IR, ¹H NMR, mass spectra, molar conductance, magnetic measurements, ESR and TG analysis. The data of molar conductance indicated the non-electrolyte nature for all synthesized metal complexes. The spectroscopic data pointed out the behavior of the ligand towards metal ions from which the coordination number of complexes exhibited to be five and six. The parameters summarized from the ESR spectra of VO(IV) complex confirmed the proposed structure. The thermogravimetric analysis for complexes suggests the absence of water molecule in or out of the coordination sphere. From the change in weight with respect to temperature, activation energy, free energy and order of reaction of complexes was calculated. The thioicarbohydrazone ligand shows lower antibacterial activity than the complexes.

KEYWORDS : Thioicarbohydrazone, Mononuclear complexes, Electronic Spectra, antibacterial activity.

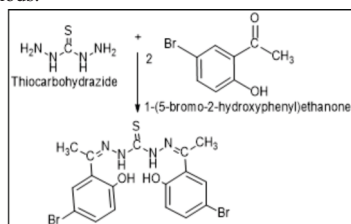
1. INTRODUCTION

The coordination chemistry of complexes of thioicarbohydrazone ligand is a fascinating area, which has attracted the attention of inorganic chemists [1]. Over the past few years, physicochemical and chemotherapeutic properties of acyclic Schiff base complexes derived from thioicarbohydrazone ligands have become progressively more significant. The additional hydrazine moiety in thioicarbohydrazone results the ligand of significant metal-bonding modes, structural diversities and promising biological implications [2]. Metal complexes of ligand containing ONS donors have antibacterial [3], anticancer [4], antifungal [5] and antitumor activity [6] wherefore it is highly prudent to synthesize and characterize Schiff base metal complexes derived from thioicarbohydrazone. The present work is dealing with the preparation of Cr(III), Mn(III), Fe(III), VO(IV) and UO₂(VI) metal complexes with the ligand(LH₂) derived from thioicarbohydrazide and 5-bromo-2-hydroxyacetophenone in 1:1 metal to ligand ratio. Here we report the coordination behavior of the ligand towards transition metal ions by various spectral techniques. The thermal study indicates the presence of coordinated and non-coordinated water molecules and predicts the thermal stability of the synthesized compounds.

2. EXPERIMENTAL

2.1. Materials:

The chloride salts of Cr(III) and Fe(III) while acetate salts of Mn(III) and UO₂(VI) were used while the synthesis of the complexes. The VO(VI) complex was synthesized by the reaction of vanadyl acetylacetonate with ligand. All the chemicals and reagents used in this work were of analytical grade (Aldrich), used without further purification. The solvents were of analytical grade and purified by standard methods.



Scheme 1: Synthesis of the Schiff base ligand(LH₂).

2.2. Measurements:

The elemental analyses (C, H, N and S) were performed at Sophisticated Analytical Instrument Facility, Chandigarh. The IR spectra of the compounds were recorded in the 4000-400 cm⁻¹ region in KBr disks. FT-IR instrument used during research work was of Perkin-Elmer spectrophotometer (L1280032). The electronic spectra (DMF) of the ligand and complexes were recorded on a Shimadzu (UV-1800 Series) UV/Vis spectrophotometer in the region 200-800 nm. Room temperature molar conductance of the complexes (DMF) was recorded

on the Equip-Tronic conductivity meter at a conc. of 10⁻³ M. ¹H NMR spectrum of the ligand was recorded in DMSO-d₆ solution on a Bruker 300-FT-NMR spectrophotometer. ESR spectra (RT and LNT) were recorded on a JES - FA200 ESR Spectrometer at IIT, Mumbai. The magnetic susceptibility of complexes were recorded at room temperature by the Gouy method. Thermal analysis results of the complexes were obtained at a rate of 10°C per minute on a Rijaku-Thermo plus EVO2 thermomodilometer.

2.3. Synthesis of the thioicarbohydrazone ligand LH₂:

Thioicarbohydrazide and 5-bromo-2-hydroxyacetophenone were prepared by reported methods [7]-[8]. The mixture of thioicarbohydrazide (0.01 mole, 0.91g) and 5-bromo-2-hydroxyacetophenone (0.02mol, 4.30g) in absolute ethanol (20 mL) was refluxed for 2 h (Scheme 1). The reaction mixture then allowed for cooling to room temperature for half an hour. A yellow precipitate was formed, which was filtered, washed with cold distilled water, and dried under vacuum. (yield 73%).

2.4. Synthesis of the metal complexes:

An ethanolic solution of the ligand LH₂ (0.002 mol) was added to an ethanolic solution of respective Cr(III)chloride, Mn(III)acetate, Fe(III)chloride, VO(VI)acetylacetonate, and UO₂(VI)acetate separately. The resulting mixture was heated at reflux for about 4 h on a water bath. The solid product obtained on cooling was filtered, washed thoroughly with ethanol and finally with petroleum ether. Finally dried and stored in vacuum over fused calcium chloride (yield 70-73%).

2.5. Antibacterial activity:

In the disc diffusion test sterile Whatman filter paper disc were impregnated with 20µl of different samples. The culture of each of the respective *E. coli*, *K. pneumoniae*, *S. aureus* and *S. epidermis* was spread on the surface of sterile Mueller Hinton Agar plates. The impregnated discs with respective samples were then placed on the inoculated surface of the agar plates. The agar plates were incubated at 37°C for 24hr. Antibacterial activity of each sample against the test species measured by growth free "zone of inhibition" near the respective spots as per the reported method [9]. The assay was performed in triplicate.

3. RESULTS AND DISCUSSION:

Scheme 1 shows the condensation of thioicarbohydrazide and 1-(5-Bromo-2-hydroxyphenyl)ethanone (1:2) in ethanol yields the Schiff base ligand (LH₂). All the complexes derived from LH₂ are colored and non-hygroscopic solids and are stable in air. They are insoluble in water, but soluble in coordinating solvents like DMF and DMSO. The molar conductance values of the complexes in DMF (10⁻³M) are very low (3-10 Ω⁻¹ cm²mol⁻¹) indicating their non-electrolytic nature. The analytical and physical data of the ligand and its complexes is given in Table 1. The analytical data of all the complexes suggested 1:1 (metal: ligand) stoichiometry. The FAB mass spectra of the ligand and the complexes were recorded. All the spectra exhibited parent peaks due to

molecular ions (M+). The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with the m/z values. The molecular ion peaks obtained were as follows: m/z 501 (ligand), 609 (Cr(III) complex), 655 (Mn(III) complex) 552 (Fe(III) complex) 563 (VO(IV) complex) and 796 (UO₂(VI) complex). These data are in good agreement with the proposed molecular formula for these complexes. In addition to the molecular ion peaks, the spectra exhibited different peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity suggested the stability of the fragments. In the spectra of Cr(III) and Fe(III) complexes isotopic peaks of Cl were also observed.

3.1. ¹H NMR spectrum of ligand:

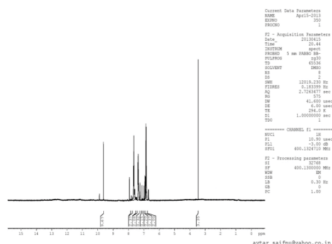


Figure 1: ¹H NMR spectrum of LH₂ Ligand.

The ¹H NMR spectrum of ligand shows signals at 9.86 ppm corresponding to proton of phenolic OH. The signals observed at 9.67 ppm and 3.35 ppm may be due to the NH, and (6H) methyl protons respectively. The aromatic protons showed signals in the range 6.8-

7.99 ppm as shown in Figure 1.

3.2. Infrared Spectra:

To study the binding modes of ligand toward metal ion, IR spectral data of the ligand was compared with those of respective metal complexes (Table 2). The IR spectrum of the ligand exhibit the most characteristic bands at 3267, 2726, 1643 1281 and 1135 cm⁻¹ νN-H, νO-H (intramolecular H-bonded), νC=N (azomethine), νC-O (phenolic) and νC=S (thioamide) respectively. The data of the ligand suggest that the free ligand exist in thioketo form. The disappearance of νO-H band in the spectra of all the complexes indicated the involvement of both the hydroxyl Oxygen in coordination to the metal ion via deprotonation. This is further supported by shift of the νC-O (phenolic) to lower frequency by 12-43 cm⁻¹ and appearance of new bands in the range 566-624 cm⁻¹ due to ν(M-O) bands in the spectra of complexes. The νC=N band of the ligand is shifted to lower frequency by 15-53 cm⁻¹ in all the spectra of all complexes indicating coordination of azomethine Nitrogen of the ligand to the metal ion [10]. An additional band in the spectra of all complexes, in between 459 and 549 cm⁻¹ and was assigned to ν(M-N), also support the coordination of azomethine Nitrogen to the metal ions. The frequencies for ν(C=S) in all the compounds remain unchanged or not shifted to higher frequencies suggesting nonparticipation of the (C=S) group in coordination [11]. The presence of lattice and/or coordinated water is indicated by broad bands in the range 3400–3360 cm⁻¹, which is further confirmed by thermal analyses. A band at 910 cm⁻¹ in the spectrum of the UO₂(VI) complex is assignable to ν_{asym}(O=U=O) of the trans O=U=O. The force constant calculated by the method of Mc Glynn *et al* and the bond length by Jones' relation was found to be 6.665/A³ and 1.7321 Å³ respectively [12]-[14]. The spectrum of VO(IV) complex exhibits an additional band at 981 cm⁻¹ corresponding ν(V=O).

Table – 1 Analytical and physical data for LH₂ ligand and its metal complexes

No.	Compound	Color	M. P. (°C)	Yield (%)	%Found (calcd.)					Molecular Mass
					M %	C %	N %	H %	S %	
1	LH ₂	Yellow	226	72	-	40.80(40.82)	11.18(11.20)	3.21(3.22)	6.40(6.41)	501
2	[Cr(L) Cl (H ₂ O)]	Green	270	72	8.56(8.61)	32.78(33.82)	9.31(9.28)	2.63(2.67)	5.29(5.31)	604
3	[Mn(L) OAc].2H ₂ O	Pale brown	285	73	8.44(8.48)	35.20(35.21)	8.66(8.64)	3.23(3.27)	4.93(4.95)	649
4	[Fe(L)Cl(H ₂ O)].2H ₂ O	Dark brown	276	71	8.70(8.68)	31.66(31.73)	8.72(8.71)	3.10(3.13)	4.97(4.98)	644
5	[VO(L)]	Green	281	73	8.99(9.01)	36.10(36.13)	9.94(9.91)	2.45(2.50)	5.66(5.67)	566
6	[UO ₂ (L)].H ₂ O	Orange	276	70	30.24(30.27)	25.95(25.97)	7.10(7.13)	2.02(2.05)	4.05(4.08)	787

Table – 2 Infrared frequencies (cm⁻¹) of the ligand LH₂ and its metal complexes

Compound	H bonded-OH stretching	ν(N-H)	Coordinated water (OH)	ν(C=N)	ν(C-O) phenolic	ν(C=S)	ν(M-O)	ν(M-N)
LH ₂	2726	3267	-	1643	1281	1135	-	-
[Cr(L) Cl (H ₂ O)]	-	3181	3400	1618	1246	1142	566	459
[Mn(L) OAc].2H ₂ O	-	3190	-	1628	1269	1137	562	454
[Fe(L)Cl(H ₂ O)].2H ₂ O	-	3247	3360	1616	1255	1136	583	436
[VO(L)]	-	3231	-	1598	1265	1157	590	466
[UO ₂ (L)].H ₂ O	-	3255	-	1590	1238	1143	624	549

3.3. Electronic absorption spectra and magnetic moments:

Electronic spectra of the ligand and its complexes were recorded in DMF. The shifting of the absorption bands after coordination was observed from the comparative study of absorption bands of synthesized complexes with ligand as depicted in Table 3. The electronic spectra of Cr(III) complex showed bands in the region 750, 550 and 360 nm assigned to the ⁴B_{1g} → ⁴B_{2g}, ⁴B_{1g} → ⁴A_{2g} and ⁴B_{1g} → ⁴E_g transitions indicating octahedral geometry. The magnetic moment for this complex was found to be 4.42 B.M. supported octahedral geometry [15]. The electronic spectra of the Mn(III) complex exhibits bands at 700, 610, 515 and 400 due to ³B₁ → ³A₁, ³B₁ → ³B₁, ³B₁ → ³E, and LMCT. The effective magnetic moment of the Mn(III) complex was found to be 4.93 B.M., which is in good agreement with a high spin d⁴ system [16]. This Mn(III) spectrum resembles to those reported five coordinated complexes having square pyramidal geometry [17]. The electronic spectrum of the Fe(III) complex showed three absorption bands at 765, 620 and 465 nm may be assigned to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴T_{2g} and ⁶A_{1g} → ⁴E_g transitions, respectively, which are well characteristic of the octahedral geometry for the complex. The magnetic moment of the Fe(III) complex was 5.61 B.M., which indicates a d⁵ sp³ hybridization [18]-[19]. The electronic spectrum of oxovanadium complex reflects two bands at 510 and 715 assignable to ³B₂ → ³E and ¹B₂ → ³A₁ suggesting a square-pyramidal configuration [20] with the effective magnetic moment of 1.80 B.M.

thermogravimetric analysis, support the proposed geometry of this complex to be square pyramidal. The electronic spectra of the UO₂(VI) complex showed first absorption bands at 520 nm, which may be attributed to electronic transitions from the apical Oxygen's to f-orbitals of the Uranium(VI) ion or due to a charge transfer transition from the ligand to the Uranium(VI) ion [21]-[22].

3.4. ESR Spectra:

ESR spectrum of VO(IV) complex was recorded in the solid-state at 298 K and in solution (DMF) as shown in Figure 2. The spectrum gives a typical eight-line pattern due to the interaction of the unpaired electron with a nucleus spin of ⁵¹V [I = 7/2], shows that the single vanadium is present in the complex i.e. it is a monomer. In LNT spectrum, first set due to the parallel feature and the other set due to perpendicular feature results into sixteen line hyperfine splitting. Thus, the compound shows well-resolved axial anisotropy with g_{||} < g_⊥ and A_{||} > A_⊥ relationship, characteristic of an axially compressed d_{xy} configuration for unpaired electron. The calculated parameters of A (Hyperfine contents calculated from solution sample) and g are found to be in agreement with the values generally observed for the oxovanadium complex with square pyramidal geometry with C_{4v} symmetry [23]-[25]. The g_{av} values determined from the spectra are nearer to the spin only value. Some variation in value may be due to the spin-orbit coupling. The ESR spectral data of VO(IV) complex is depicted in Table 4.

ESR spectra, magnetic susceptibility values as well as the

Table – 3 Electronic and magnetic data LH₂ and its metal complexes

Compound	ν (nm)	Assignments	μ_{eff} (BM)	Proposed Geometry	Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
LH ₂	215 350	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
[Cr(L)Cl(H ₂ O)]	750 550 360	${}^4B_{1g} \rightarrow {}^4B_{2g}$ ${}^4B_{1g} \rightarrow {}^4A_{2g}$ ${}^4B_{1g} \rightarrow {}^4E_g$	4.42	Octahedral	7.18
[Mn(L)OAc].2H ₂ O	700 610 515 400	${}^5B_1 \rightarrow {}^5A_1$ ${}^5B_1 \rightarrow {}^5B_1$ ${}^5B_1 \rightarrow {}^5E$ LMCT	4.93	Square Pyramidal	6.92
[Fe(L)Cl(H ₂ O)].2H ₂ O	765 620 465	${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ ${}^6A_{1g} \rightarrow {}^4E_g$	5.61	Octahedral	8.56
[VO(L)]	510 715	${}^1B_2 \rightarrow {}^2E$ ${}^1B_2 \rightarrow {}^2A_1$	1.80	Square Pyramidal	5.10
[UO ₂ (L)].H ₂ O	520	CT	Diamagnetic	Octahedral	3.14

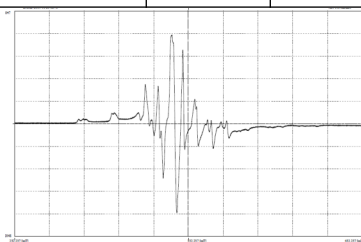


Figure 2 : ESR spectra of VO(IV) complex (LNT)

3.5. Thermal analysis:

Thermal decomposition of metal complexes is an important study as it provides useful information about the thermal stability of complexes as well as the coordination ability of water whether it is inside the coordination sphere or outside. The half decomposition temperature, Entropy Change (ΔS), Free Energy Change (ΔF) and Frequency Factor (Z) of compounds were calculated by employing Freemann Caroll and Sharp Wentworth method [26]-[28]. The thermal curves of ligand and complexes were obtained with heating rate $10^\circ \text{C min}^{-1}$ are given in fig. 3, while the kinetic parameters are assigned in Table 5. The ligand shows two-step decomposition pattern with the lowest half decomposition temperature. The Cr(III), Fe(III) VO(IV), and UO₂(VI) complexes indicate a two-stage decomposition pattern whereas Mn(III) complex shows a three-stage decomposition pattern. The UO₂(VI) complex shows the elimination of one lattice water molecules while Mn(III) and Fe(III) complexes show the elimination of two lattice water molecules respectively up to 120°C indicates the presence of non-coordinated water molecules in the complexes. On the other hand, Cr(III) and Fe(III) complexes exhibit loss of one water molecule between $120-220^\circ \text{C}$ which indicates the presence of coordinated water molecules in the complexes. [% wt. loss, obs./

calcd.] Mn(III):5.59/5.80; Fe(III):5.94/5.59 and UO₂(VI):2.17/2.28 for lattice water and Cr(III):2.70/2.98; Fe(III): 2.85/2.79 for coordinated water. In the TG curve of VO(IV) complex, no weight loss up to 220°C indicates the absence of any water molecule in the complex. Further weight loss was observed above 440°C , which may be due to the thermal degradation of the free part of the ligand along with some other side chain present in the complexes. A gradual weight loss observed above 440°C , due to the degradation of the actual coordination part of the ligand and TG curves attain a horizontal level above 580°C suggesting the formation respective stable metal oxides. From the half decomposition temperature, the relative thermal stability of the compounds is found to be UO₂(VI) > VO(IV) > Mn(III) > Cr(III) > Fe(III) > Lh₂.

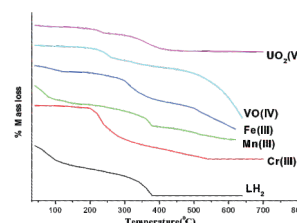


Figure 3 : Thermal graph of LH₂ and metal complexes.

Table – 4 ESR parameters of powder VO(IV) Complex.

Complex	$g_{ }$	g_{\perp}	$ g $	Hyperfine contents $\times 10^{-4} \text{ cm}^{-1}$		
				$A_{ }$	A_{\perp}	$ A $
VO RT (Powder)	1.927	1.957	1.947	166.96	61.69	96.69
VO LNT (DMF)	1.935	1.960	1.951			

Table – 5 Thermal analysis data of metal complexes

Compound	Half Decomposition Temp ($^\circ \text{C}$)	Ea (kJ/mole ⁻¹)		Entropy change ΔS (J/mol/K)	ΔF (kJ/mol)	Frequen-cy factor Z (S^{-1})	Apparent entropy change S^* (kJ)	Order of Reaction (n)
		FC	SW					
LH ₂	160	11.41	10.91	-363.05	110.01	167	-23.72	0.97
[Cr(L) Cl (H ₂ O)]	425	26.82	25.69	-281.27	98.96	155	-24.77	0.93
[Mn(L) OAc].2H ₂ O	440	15.22	14.95	-295.55	98.95	197	-24.56	0.91
[Fe(L)Cl(H ₂ O)].2H ₂ O	390	18.66	18.32	-291.88	88.45	152	-24.70	0.97
[VO(L)]	465	20.37	19.51	-358.23	108.56	117	-25.06	0.98
[UO ₂ (L)].H ₂ O	480	15.81	16.71	-306.72	92.95	168	-24.81	0.97

Table – 6 Antibacterial activity of the ligand LH₂ and its metal complexes

No.	Compound	<i>E. coli</i>	<i>S. aureus</i>	<i>S. epidermis</i>	<i>K. pneumoniae</i>
1	LH ₂	S10	S11	S08	S06
2	[Cr(L)Cl(H ₂ O)]	S16	S21	S17	S13
3	[Mn(L)(OAc)].2H ₂ O	R	S10	S10	S11
4	[Fe(L)Cl(H ₂ O)].2H ₂ O	S10	S11	R	S10
5	[VO(L)]	S03	R	R	S06
6	[UO ₂ (L)].H ₂ O	R	R	S16	S10

3.6. Antibacterial Activity:

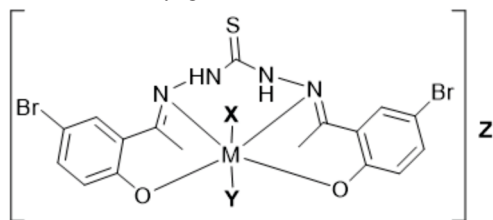
The thiocarbohydrazone ligand and its transition metal complexes were screened for antibacterial activity against *E. Coli* (ATCC 14948),

S. aureus (ATCC 33591), *S. epidermis* (MTCC 3086), and *K. pneumoniae* (MTCC 4030). Study shows the lower activity of ligand against *K. pneumoniae*. Activities of compound 5 were comparatively less. The mean inhibition zone of the bacteria growth in mm shows that the complexes are more active than their thiocarbohydrazone ligand. The compound 2 show almost high to moderate bactericidal (sensitive) nature against all the bacterial strains. Moderate activities of compounds 3, 4 and 6 were noticeable as shown in Table 6.

4. CONCLUSIONS

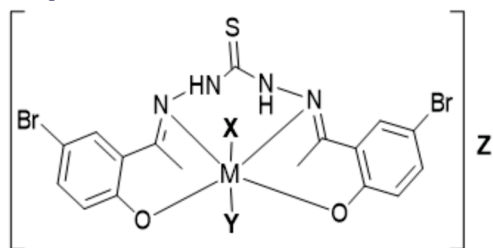
The thiocarbohydrazone ligand coordinates with the metal center (1:1 mole ratio) as a dibasic tetradentate ligand through azomethine Nitrogen atoms and deprotonated phenolic Oxygen atoms in synthesized metal complexes. Analytical data, IR, electronic spectra

and magnetic susceptibility data reveal octahedral geometry for all the complexes except Mn(III) & VO(IV) complexes exhibit square pyramidal geometry. The absence of a coordinated water molecule was observed in the thermogram of both Mn(III) & VO(IV) complexes. The calculated spin Hamiltonian parameters from the spectra of [VOL] confirmed its square pyramidal geometry. The activation energy calculated by the Freemann-Caroll and Sharp-Wentworth methods is in good agreement with each other. The probable structures are shown below, Fig. 4-5. The ligand, as well as some metal complexes, showed good antibacterial activity against selected kinds of bacteria.



M=Cr(III), X=Cl, Y= H₂O and Z= nill.
 M=Mn(III), X=OAc, Y= nill and Z= 2. H₂O.
 M=Fe(III), X=Cl, Y= H₂O and Z= 2. H₂O

Figure 4 : The probable structure for Cr(III), Mn(III) and Fe(III) metal complexes.



M=VO(IV), X= =O, Y=Z= Nill.
 M=UO₂(VI), X=Y= =O Z=H₂O.

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