



Synthesis, Characterization and Antimicrobial Studies of Oxo Vanadium (IV & V) Complexes with Semi and Thiosemicarbazones of Furan-2-Carbaldehyde and Pyrrole-2-carbaldehyde

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Authors' contributions

This work was done in equal collaboration between both authors. Author SKS designed the work, did the synthesis part and then after both authors shared the remaining part of the work equally. Both authors wrote, read and approved the final manuscript.

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ABSTRACT

Oxovanadium (IV & V) complexes were synthesized from semi- and thiosemicarbazones (L₁, HL₂, HL₃ and H₂L₄) derived from furan-2-carbaldehyde (L₁, HL₂) and pyrrole-2-carbaldehyde (HL₃, H₂L₄). The solid isolated complexes were characterized through elemental analysis, UV-Visible spectra, I.R spectra, ¹H NMR spectra, mass spectra, magnetic susceptibilities and molar conductance measurements. The isolated complexes except [VO(L₂)(OH)₂].H₂O are paramagnetic in nature and having square pyramidal geometry. Molar conductance values justify the proposed structure with their electrolytic nature. The electronic spectra of these complexes are interpreted by using the Vanquickenborne and MacGlynn ordering $xy < xz, yz < x^2 - y^2 < z^2$. The only oxovanadium(V) complex [VO(L₂)(OH)₂].H₂O was synthesized from an alkaline solution of the ligand L₂ in aqueous-ethanol and was found to be diamagnetic and distorted octahedral in geometry. The cyclic voltammetric

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studies of the complexes in DMSO were studied to explore the redox behavior of complexes. The free ligands and some of its complexes showed considerable biological activities as antibacterial and as well as possessing antifungal properties.

Keywords: Semicarbazones; thiosemicarbazones; oxovanadium (IV & V); cyclic voltammetry; antibacterial activity; antifungal activity.

1. INTRODUCTION

Semicarbazones and thiosemicarbazones as free ligands and as well as of different metal complexes are of much interest, because of their biological interest. It has been observed that such type of complexes were found to be active as anti tuberculosis and leprosy, small pox, antitumor activity, and as anticancer drug [1-9]. This has triggered the synthetic inorganic chemists to explore the more possibilities and its effective use to resolve the various biological problems. Besides it is found that thiosemicarbazones are of much useful in stabilizing both higher and lower oxidation states of transition metal ions [7-9]. Vanadium plays a prominent role as one of the most bioactive transition metal ion.

The present work is in continuation of our work with oxovanadium (IV&V) complexes with different semi and thiosemicarbazones. In the present work oxovanadium (iv&v) complexes were synthesized from semi- and thiosemicarbazones (L_1 , HL_2 , HL_3 and H_2L_4 , see Fig. 1.) derived from furan-2-carbaldehyde and pyrrole-2-carbaldehyde. The most remarkable area of observation that thiosemicarbazones can play both thione-thiol form in solution in which chelation behavior is different. In the present work we have also evaluated the antibacterial activities towards some gram positive and gram negative bacteria of ligands and newly synthesized complexes of it. Antifungal activities were also studied.

2. EXPERIMENTAL

All chemicals used are of AR grade. Furan-2-carbaldehyde and pyrrole-2-carbaldehyde were purchased from Aldrich. $VOCl_2 \cdot 2H_2O$ and $VOSO_4 \cdot 5H_2O$ were used of AR grade. The solvents were used after distillation where required. Vanadium was estimated gravimetrically as its vanadate form, after decomposing the complex with few drops of concentrated nitric acid [10].

2.1 Instrumentation

Magnetic susceptibilities of dried sample were measured in Gouy balance at room temperature. Mercury tetrathiocyanatocobaltate (II), $Hg[Co(CNS)_4]$, was used as calibrant.

Infrared spectra of the pure sample were measured from CDRI, Lucknow, India.

Mass Spectra was recorded by using Electro-ionization technique.

Melting Point determination was carried out in the laboratory in a sulphuric acid bath.

Cyclic Voltammetry was performed with BAS 100B Electrochemical Analyzer. The equipment for measurements in anhydrous DMSO consists of a platinum disk electrode (1.2 mm dia) and a platinum wire as an auxiliary electrode. The reference electrode particularly employed was $Ag/AgCl$.

Molar conductance of the approximately 10^{-3} M DMSO solutions of the complexes was carried on using a Philips conductivity bridge at room temperature (ca.25°C).

1H NMR spectra was recorded in DMSO solution of the free ligands and as well as of complexes and data's are expressed in ppm. It is recorded at room temperature using Tetramethyl silane as reference.

2.2 Synthesis

The ligands L_1 , HL_2 , HL_3 and H_2L_4 (see Fig. 1.) were synthesized by refluxing Furan-2-carbaldehyde/Pyrrole-2-carbaldehyde with semicarbazide or thiosemicarbazide in 1:1 molar stoichiometry in EtOH/ H_2O (85:15) for about 3-4 hours on water bath, thereafter the volume was reduced to half of its original volume and finally kept in a desiccator. The solid crystalline compound was filtered, recrystallized from EtOH and finally dried in a desiccator.

2.2.1 Ligand

L₁- Furan-2-carbaldehyde semicarbazone:

(C₆H₇N₃O₂) Greyish white, yield 68%, m.p. 193-196°C. Anal.Calcd.% C, 47.06; H,4.57; N, 27.45; Found. C, 47.03; H, 4.59; N, 27.47 . IR (cm⁻¹): 1585 (HC=N), 1632 (C=O), 3321-3243 (-NH) .ESI MS: m/z 153 (M⁺).¹ H NMR (DMSO-d₆): δ (ppm):, 7.30 (s,CH=N), 10.90 (s, NH).

HL₂-Furan-2-carbaldehyde thiosemicarbazone:

(C₆H₇SN₃O) Yellowish white, yield 72%, m.p. 213°C. Anal.Calcd.% C, 42.60; H,4.14; N, 24.85; Found. C, 42.63; H, 4.1; N, 24.87. IR (cm⁻¹): 1590 (HC=N),783 (C=S), 3325-3100 (-NH) ESI MS: m/z 169 (M⁺).¹H NMR(DMSO-d₆): δ (ppm):, 7.70 (s,CH=N), 10.70 (s, NH).

HL₃-Pyrrole-2-carbaldehyde semicarbazone:

(C₆H₈N₄O) off white, yield 71%, m.p. 217-218°C. Anal.Calcd.% C, 47.37; H, 5.26; N, 36.84; Found. C, 47.34; H, 5.27; N, 36.82. IR(cm⁻¹): 1585 (HC=N) , 1630 (C=O), 3375-3150 (-NH). ESI MS: m/z 152 (M⁺).¹H NMR (DMSO-d₆): δ (ppm):, 7.80 (s, CH=N), 11.13 (s, NH).

H₂L₄-Pyrrole-2-carbaldehyde thiosemicarbazone:

(C₆H₈N₄S)Grey, yield 78%. m.p. 218-220°C. Anal.Calcd.% C, 42.86; H, 4.76; N, 33.33; Found. C, 42.89; H, 4.73; N, 33.35. IR(cm⁻¹): 1575 (HC=N), 825 (C=S) ,3435-3100 (-NH) . ESI MS: m/z 168 (M⁺).¹ H NMR (DMSO-d₆): δ (ppm):, 7.30 (s,CH=N), 10.90 (s, NH).

2.2.2 Complexes

[VO(L₁)(Cl)]Cl was synthesized by refluxing the Ligand (L₁) and VOCl₂.2H₂O in stoichiometric amounts in aqueous-ethanol for about 2-3 hours, filtered and kept in a dessicator in vacuo. The crystallized yellowish green complex obtained was recrystallized in ethanol and dried. Anal. Calcd. % C, 24.74; H, 2.41; N, 14.43; V, 17.53. Found. C, 24.72; H, 2.43; N, 14.46; V,17.55. IR(cm⁻¹): 1555(HC=N) 1620 (C=O) 3325-3115 (-NH) 343 (V-Cl). μ_{eff} = 1.73 B.M. ESI MS: m/z 291 (M⁺).¹H NMR (DMSO-d₆): δ (ppm):, 7.65 (s, CH=N), 10.72 (s, NH).

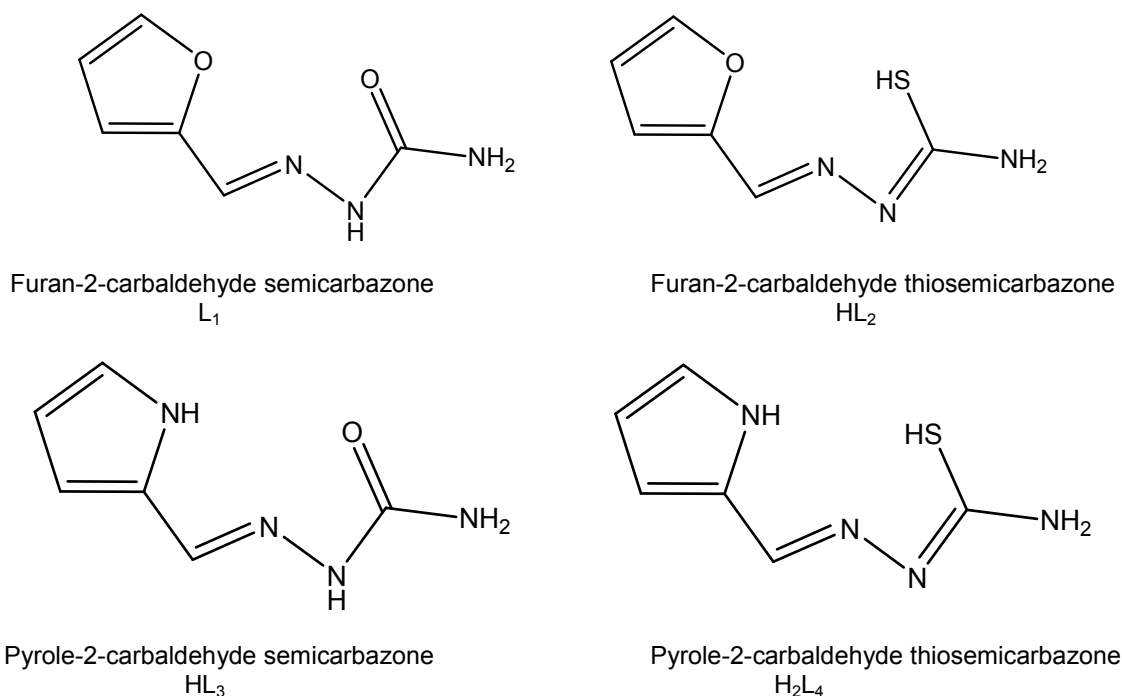


Fig. 1. Structure of ligands (L₁ to H₂L₄)

[VO(L₁)(H₂O)]SO₄ was synthesized by refluxing the ligand furan-2-carbaldehyde semicarbazone(L₁) and VOSO₄·5H₂O in aqueous-ethanol for about 2-3 hours. Yellowish brown crystalline precipitate was obtained from the filtrate. It was recrystallized and dried in desiccator. Anal. Calcd. % C, 21.56; H, 2.69; N, 12.57; V, 15.27. Found. C, 21.57; H, 2.71; N, 12.59; V, 15.25. IR(cm⁻¹): 1565(HC=N) 1625 (C=O) 3375-3125 (-NH) $\mu_{\text{eff}} = 1.73$ B.M. ESI MS: m/z 334 (M⁺). ¹H NMR (DMSO-d₆): δ (ppm):, 7.58 (s, CH=N), 10.68 (s, NH).

[VO(L₂)(Cl)]·H₂O was synthesized by refluxing the stoichiometric amount of ligand furan-2-carbaldehyde thiosemicarbazone with VOCl₂·2H₂O as above. Anal. Calcd. % C, 24.96; H, 2.77; N, 14.56; V, 17.68. Found. C, 24.99; H, 2.78; N, 14.58; V, 17.71. IR(cm⁻¹): 1567(HC=N) 719(C-S) 3298 (-NH₂) 342(V-Cl) 369(V-S). $\mu_{\text{eff}} = 1.74$ B.M. ESI MS: m/z 288 (M⁺). ¹H NMR (DMSO-d₆): δ (ppm): 7.79 (s, CH=N), -(NH).

[VO(L₂)(OH)₂]·H₂O The ligand HL₂ was dissolved in aqueous-ethanol with ca. equimolar amount of sodium hydroxide. The resulting solution was mixed with stoichiometric amount of VOCl₂·2H₂O and sodium acetate in ethanol. The mixture was refluxed for 3 hours and filtered. The brownish green precipitate was obtained on standing. This was filtered, washed with aqueous-alcohol and dried. Anal. Calcd. % C, 25.09; H, 3.48; N, 14.63; V, 17.77. Found. C, 25.11; H, 3.49; N, 14.65; V, 17.75. IR(cm⁻¹): 1559(HC=N) 718 (C-S) 3295 (-NH₂) 378(V-S) Complex is diamagnetic. ESI MS: m/z 287 (M⁺). ¹H NMR (DMSO-d₆): δ (ppm):, 7.50 (s, CH=N), -(NH).

[VO(L₃)(Cl)]·H₂O was synthesized by refluxing the stoichiometric amount of ligand pyrrole-2-carbaldehyde semicarbazone with VOCl₂·2H₂O in aqueous-ethanol for about 3 hours. The isolated complex was filtered and dried in air. Anal. Calcd. % C, 26.52; H, 3.31; N, 20.63; V, 18.78. Found. C, 26.54; H, 3.30; N, 20.65; V, 18.76. IR(cm⁻¹): 1560(HC=N) 1690 (C=O) 3325-3100 (-NH) 345(V-Cl). $\mu_{\text{eff}} = 1.73$ B.M. ESI MS: m/z 271 (M⁺). ¹H NMR (DMSO-d₆): δ (ppm) , 7.85 (s, CH=N), 11.2 (s, NH).

[VO(L₄)(H₂O)] was synthesized by similar way as mentioned in the synthesis of [VO(L₃)(Cl)]·H₂O by refluxing with pyrrole-2-carbaldehyde thiosemicarbazone ligand(H₂L₄). Anal. Calcd. % C, 28.69; H, 3.19; N, 22.31; V, 20.32. Found. C, 28.72; H, 3.22; N, 22.34; V, 20.35. IR(cm⁻¹): 1553(HC=N) 762 (C-S) 3415-3115 (-NH) 375(V-

S). $\mu_{\text{eff}} = 1.75$ B.M. ESI MS: m/z 251 (M⁺). ¹H NMR (DMSO-d₆): δ (ppm):, 7.69 (s, CH=N), -(NH).

3. RESULTS AND DISCUSSION

The isolated complexes are colored and sufficiently stable in atmospheric conditions for handling. The elemental analyses support the formulation of isolated complexes. The complexes are soluble in ethanol on heating on water bath. They are also completely soluble in DMSO or pyridine. The formulations and final structures were established besides elemental analysis through results of IR spectral data, electronic spectra, ¹H NMR spectra, mass spectra, magnetic susceptibilities and molar conductance data.

3.1 Electronic Spectra

The electronic spectra of the complexes are mentioned in Table 1. Mainly three spectral bands are observed in the region 12,500-27,500 cm⁻¹. The low energy band is comparatively broad in comparison to two high energy bands. The electronic spectra of oxovanadium (IV) complexes are thoroughly discussed in many places [11-16] and are found to be the assignments of spectral bands are not clear, mostly explained in terms of C_{4v} and in some cases as C_{2v} symmetry. In C_{4v} symmetry the three transitions are expected theoretically, d_{xy}→d_{xz}, d_{yz}; d_{xy}→d_{x²-y²}; and d_{xy}→d_{z²} for d¹ oxovanadium (IV) ion [17]. The lowering of symmetry from C_{4v} to C_{2v} has the effect of removing degeneracy in the d-orbitals and thus four transitions are expected, following the order of Vanquickenborne and MacGlynn [16] of the energy level of the oxovanadium(IV) complexes. The first band of the present complexes around 13,000 cm⁻¹ is assigned to an unresolved band resulting from d_{xy}→d_{xz}, d_{yz}; transition. In pyridine the two components with close intensities as shown in Table 1. On comparison of this band with that of [VO(acac)₂] and [VO(Sal-L-alanine)(H₂O)] [18] supports this assignment. Another band around 17,500 cm⁻¹ is attributed to d_{xy}→d_{x²-y²} transition. The high-energy shift of the second band and low-energy shift of the first band agrees with the results noted for several oxovanadium(IV) complexes [18]. High-energy band at 26,500 cm⁻¹ due to d_{xy}→d_{z²} transition may be considered as charge transfer and intra ligand transitions. The complex [VO(L₂)(OH)₂]·H₂O in which no d-d bands were observed, because of 3d⁰ configuration [19]. In

this case the electronic spectra show a broad (but intense) adsorption band at about $17,500\text{ cm}^{-1}$. This may be due to ligand \rightarrow metal charge transfer transition. It is worth mentioning that charge transfer should be appropriate for oxovanadium(V) complexes and in addition the diamagnetism of the present complex is good agreement of pentavalent vanadium.

3.2 Magnetic Susceptibilities

Magnetic moments of oxovanadium(IV) complexes were measured at room temperature and the values are in the range of $1.71 - 1.79\text{ B.M}$, which correspond to a single electron d^1 system of square pyramidal geometry. Also the values are normal not quenched, supports the monomer nature of the isolated complexes. The oxovanadium(V) complex $[\text{VO}(\text{L}_2)(\text{OH})_2]\cdot\text{H}_2\text{O}$ was found to be diamagnetic indicating d^0 and distorted octahedral in geometry.

3.3 Molar Conductance

Molar conductance values of the complexes $[\text{VO}(\text{L}_2)(\text{Cl})]\cdot\text{H}_2\text{O}$, $[\text{VO}(\text{L}_2)(\text{OH})_2]\cdot\text{H}_2\text{O}$, $[\text{VO}(\text{L}_3)(\text{Cl})]\cdot\text{H}_2\text{O}$ and $[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$ were measured in DMSO at 10^{-3} M concentration fall in the range of $2.8 - 9.6\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, justified the formulation of complexes as non electrolytic in nature. In some of the complexes in which Cl^- is

present as inner sphere coordinated ligand as neutral complexes, further verified by presence of $\text{M}-\text{Cl}$ band through IR data. The complexes $[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$ and $[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$ show values 89 and $125\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ respectively indicating their 1:1 electrolytic nature.

3.4 IR Spectra

The infrared absorption spectra is used as analytical tool to determine the ligands chelating ability and always compared with that of chelated complexes. The characteristics IR stretches of free ligands and as well as its complexes are presented in the Table 2. No characteristics absorption band was found for $>\text{C}=\text{O}$ of free ligands indicating the formation of semi- and thiosemicarbazone. The complexes show prominent bands appearing around 955 cm^{-1} and is assigned as $\text{V}=\text{O}$ stretching frequency. The $\text{C}=\text{N}$ stretching frequency for free ligands were observed around 1590 cm^{-1} and on complexation was shifted to $1532 - 1569\text{ cm}^{-1}$ of complexes justifies the coordination of imine nitrogen with vanadium [20]. In case of thiosemicarbazones an additional $\text{C}=\text{N}$ band also appeared at higher energy on complexation with metal ion in the range $1629 - 1635\text{ cm}^{-1}$ and is attributed due to loss of NH proton of free ligands [21].

Table 1. Electronic spectral data of oxovanadium complexes (cm^{-1})

Complex	Nujol Mull	Pyridine solution	ϵ_{max}	Tentative assignment
$[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$	i) Broad band in	i) 12,715-13,275	25 – 30	$d_{xy} \rightarrow d_{xz}, d_{yz}$
$[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$	the region 13,000	ii) 14,215-15,725	30 – 39	$d_{xy} \rightarrow d_{x^2-y^2}$
$[\text{VO}(\text{L}_2)(\text{Cl})]\cdot\text{H}_2\text{O}$	to 17,000	iii) 19,000-20,115	48 -50	$d_{xy} \rightarrow d_{z^2}$
$[\text{VO}(\text{L}_3)(\text{Cl})]\cdot\text{H}_2\text{O}$	ii) 18,000	iv) 26,000-27,500	3,950-4,750	Intra ligand and charge transfer
$[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$	iii) 25,500-26,500			

Table 2. Infrared spectral data of ligand (L_1 to H_2L_4) and its complexes with oxovanadium (cm^{-1})

Ligand/complex	$\nu_{\text{N}-\text{H}_2}, \nu_{\text{N}-\text{H}}$	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{C}-\text{S}}$	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{V}-\text{O}}$	$\nu_{\text{V}-\text{S}}$	$\nu_{\text{V}-\text{N}}$	$\nu_{\text{V}=\text{O}}$	$\nu_{\text{V}-\text{Cl}}$
L_1	3321-3243	1632	-	1585	-	-	-	-	-
HL_2	3325-3100	-	783	1590	-	-	-	-	-
HL_3	3375-3150	1630	-	1585	-	-	-	-	-
H_2L_4	3435-3100	-	825	1575	-	-	-	-	-
$[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$	3325-3115	1620	-	1555	439	-	365	950	343
$[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$	3375-3125	1625	-	1565	445	-	353	955	-
$[\text{VO}(\text{L}_2)(\text{Cl})]\cdot\text{H}_2\text{O}$	3298	-	719	1567	-	369	350	949	342
$[\text{VO}(\text{L}_2)(\text{OH})_2]\cdot\text{H}_2\text{O}$	3295	-	718	1559	-	378	352	961	-
$[\text{VO}(\text{L}_3)(\text{Cl})]\cdot\text{H}_2\text{O}$	3325-3115	1619	-	1560	459	-	358	955	345
$[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$	3415-3159	-	762	1553	-	375	348	948	-

The stretching frequency of CS band appearing in the region $765\text{--}835\text{ cm}^{-1}$ of free ligands of thiosemicarbazones and on coordination to vanadium the band is appreciable reduced due to deprotonation of thiolate form [22]. The free ligand of thiosemicarbazone is supposed to be thione-thiol tautomeric form in solution, see Fig. 2. Also V-S bond is assigned in the region 350 cm^{-1} confirming the coordination of sulphur atoms [23].

The M-N stretching frequency is further observed in the region $345\text{--}365\text{ cm}^{-1}$. In the complexes in which formulation shown that monodentate ligand Cl⁻ is coordinated to central vanadium ion, is justified in through appearance of a band below 345 cm^{-1} , attributed due to V-Cl band [24]. The tridentate behavior of the ligand can be justified from the IR data and further supported from literature data [25]. In the complex $[\text{VO}(\text{L}_2)(\text{H}_2\text{O})]$ a band of medium intensity at 3485 cm^{-1} and a shoulder at 3517 cm^{-1} is to be attributed to the asymmetric and symmetric O-H stretching vibration of the coordinated H_2O molecule.

3.5 ^1H NMR Spectra

^1H NMR spectral data of free ligands (L_1 , HL_2 , HL_3 and H_2L_4) and its complexes with oxovanadium was measured in DMSO-d_6 and selective data useful for establishing the proposed structure of the aforesaid ligands and its complexes are presented in Table 3. Though paramagnetic nature of complexes provides information not clear to explain much, yet it is along with IR data helpful in explaining certain chelation behaviour of ligands. In the spectra of free ligands the $-\text{NH}$ proton and $-\text{NH}_2$ proton give singlets as shown in the table. In the

complexes with ligands HL_2 and H_2L_4 the absence of $-\text{NH}$ proton signal further justified the proposed structure of the respective complexes in which M-S bond formed through deprotonation of S-H proton of the ligand in solution.

Table 3. ^1H NMR spectral data (DMSO-d_6) of free ligands (L_1 , HL_2 , HL_3 and H_2L_4) and its oxovanadium complexes (ppm)

Ligand/Complex	$-\text{NH}$	$-\text{NH}_2$	$\text{HC}=\text{N}$
L_1	10.90	7.98	7.30
HL_2	10.70	8.07	7.70
HL_3	11.13	7.93	7.80
H_2L_4	10.90	8.17	7.30
$[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$	10.72	8.23	7.65
$[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$	10.68	7.97	7.58
$[\text{VO}(\text{L}_2)(\text{Cl})]\cdot\text{H}_2\text{O}$	--	7.90	7.79
$[\text{VO}(\text{L}_2)(\text{OH})_2]\cdot\text{H}_2\text{O}$	--	8.15	7.50
$[\text{VO}(\text{L}_3)(\text{Cl})]\cdot\text{H}_2\text{O}$	10.90	8.10	7.85
$[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$	--	7.95	7.69

3.6 Mass Spectra

Mass spectra was conducted for free ligands and as well as its complexes (m/z values are presented in the experimental part). It is observed that the free ligand shows a series of peaks for different fragments of the ligand and as well as its intensities differ corresponding to the stabilities of different fragments whereas its complexes show only one peak further justifying their molecular composition and help in establishing the structure of the complexes.

3.7 Cyclic Voltammetric Studies

The electrochemical behaviors of the complexes are dependent on various factors such as distribution of unsaturation, chelated ring size,

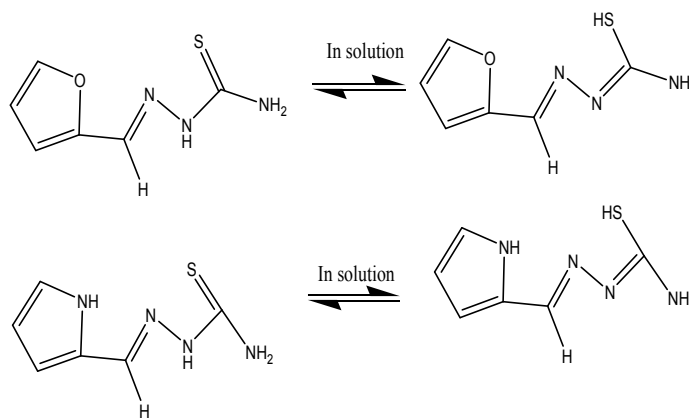
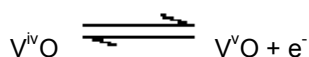


Fig. 2. Thione-thiol tautomeric form of thiosemicarbazone ligands in solution

substitution pattern on the ring, charge type, and coordination number [26,27]. It was studied Cyclic voltammetrically with supporting electrolyte as Tetraethyl ammonium perchlorate (0.1 mol L^{-1}) dissolved in DMSO and experiments were performed at room temperature. The concentration of the complexes was $10^{-3} \text{ mol L}^{-1}$. Voltammograms were recorded in the range of 0.00 to +1.0V with different scan rate from 50 mVs^{-1} to 150 mVs^{-1} , but not much change was observed. In all cases except the complex $[\text{VO}(\text{L}_2)(\text{OH})_2] \cdot \text{H}_2\text{O}$ showed a reversible one electron peak was observed ($i_{pa}/i_{pc} = 1$), indicating the oxidation as suggested below:



3.8 Microbial Studies

The antibacterial activities of the free ligands both semi and thiosemicarbazones and its complexes of oxovanadium were studied with some selective gram positive (*S. aureus*) and gram negative bacteria (*E. coli*) by normal disc diffusion method [28,29] (Table 4). Test bacteria cultures were performed in a nutrient agar media

on Petri dishes. The nutrient media was prepared with usual components and properly sterilized in an autoclave. Test solution of ligands and as well as complexes were prepared in the concentration $50 \mu\text{g}/\mu\text{L}$ and $100 \mu\text{g}/\mu\text{L}$ in DMSO and were tested against mentioned organisms. The standard used here is ampicillin solution of $50 \mu\text{g}/\mu\text{L}$. The zone of inhibition is calculated in mm. The zone Metal chelates are found to be more active in some cases may be d voltammetrically ue to effect of metal ions on the normal cell membrane and further can be explained on the basis of chelation theory. Both polar and nonpolar properties of metal chelates enable them to penetrate on surface of cells and tissues. Besides this it is further observed that thiosemicarbazone metal chelates are more bioactive than that of semicarbazone complexes, may be attributed due to presence of Sulphur in the compound.

The antifungal activities were studied against two pathogenic fungi, *A. niger* and *C. albicans* by the same method using the test solution in the concentration $50 \mu\text{g}/\mu\text{L}$ and $100 \mu\text{g}/\mu\text{L}$ in DMSO. This is reported in the Table 5.

Table 4. Antibacterial activity of ligands and complexes

Ligand/Complex	<i>E. coli</i>		<i>S. aureus</i>	
	50 $\mu\text{g}/\mu\text{L}$	100 $\mu\text{g}/\mu\text{L}$	50 $\mu\text{g}/\mu\text{L}$	100 $\mu\text{g}/\mu\text{L}$
L ₁	12	14	13	14
$[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$	13	15	15	17
$[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$	14	15	15	16
HL ₂	13	14	15	17
$[\text{VO}(\text{L}_2)(\text{Cl})] \cdot \text{H}_2\text{O}$	15	16	16	18
$[\text{VO}(\text{L}_2)(\text{OH})_2] \cdot \text{H}_2\text{O}$	13	14	15	16
HL ₃	14	16	16	18
$[\text{VO}(\text{L}_3)(\text{Cl})] \cdot \text{H}_2\text{O}$	14	17	15	16
H ₂ L ₄	15	16	16	17
$[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$	16	18	17	19
Ampicillin(Standard)	43	-	41	-

* Zone inhibition in mm

Table. 5 Antifungal activity of ligands and complexes

Ligand/Complex	<i>A. niger</i>		<i>C. albicans</i>	
	50 $\mu\text{g}/\mu\text{L}$	100 $\mu\text{g}/\mu\text{L}$	50 $\mu\text{g}/\mu\text{L}$	100 $\mu\text{g}/\mu\text{L}$
L ₁	8	9	10	9
$[\text{VO}(\text{L}_1)(\text{Cl})]\text{Cl}$	13	12	9	11
$[\text{VO}(\text{L}_1)(\text{H}_2\text{O})]\text{SO}_4$	12	14	13	14
HL ₂	14	13	13	15
$[\text{VO}(\text{L}_2)(\text{Cl})] \cdot \text{H}_2\text{O}$	15	16	14	15
$[\text{VO}(\text{L}_2)(\text{OH})_2] \cdot \text{H}_2\text{O}$	7	6	9	11
HL ₃	8	9	8	10
$[\text{VO}(\text{L}_3)(\text{Cl})] \cdot \text{H}_2\text{O}$	12	13	13	12
H ₂ L ₄	10	12	9	11
$[\text{VO}(\text{L}_4)(\text{H}_2\text{O})]$	14	15	12	14
Flucanazole (Standard)	29	-	27	-

* Zone inhibition in mm

The standard used here is Flucanazole. The zone inhibition is measured in mm.

4. CONCLUSION

The Ligand behaved as tridentate ligand. The donor sites of the ligands are well established with the help of different spectral data. The isolated complexes are monomer having square pyramidal in geometry, except the complex $[VO(L_2)(OH)_2] \cdot H_2O$, which is distorted octahedral in geometry. The selection of ligands and its complexes with VO^{2+} is well justified from their behavior as antibacterial and as well as antifungal activity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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