

Synthesis, characterization, magnetic, thermal and redox properties of oxovanadium(IV) complex of heterocyclic acid hydrazone

Jyothy Gopurathinkal Vijayan

Department of Chemistry, Christ University, Bengaluru-29, Karnataka, India

* Corresponding author at: Department of Chemistry, Christ University, Bengaluru-29, Karnataka, India.
 Tel.: +91.741.1019379. Fax: +91.741.1019379. E-mail address: jyothy.vijayan@res.christuniversity.in (J.G. Vijayan).

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ABSTRACT

The hydrazone ligand obtained from 2-thiophene carboxaldehyde and nicotinic hydrazide reacts with equimolar mixture of vanadyl acetyl acetonate in methanol to yield oxovanadium(IV) complex with 2-thiophenecarbanicotinic hydrazone. The prepared compound shows effective solubility in organic solvents such as acetonitrile, DMF and DMSO. Molar conductivity data of the complex revealed its non-electrolytic behavior in DMF and DMSO. EPR spectra of 2-thiophenecarbanicotinic hydrazonato oxovanadium(IV) was recorded in DMF at LNT and g and A values were calculated. The complex was proposed to be square pyramidal in geometry. Cyclic voltammogram of the complex in DMF was studied by changing the scan rates 50, 100, and 200 mV/sec. ΔE values of the complex showed the reversible criterion and ipc/ipa values which were close to 1 indicating that the redox couple as reversible. Thermogram of the complex was recorded to find the weight loss at different temperature ranges. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed mass number of the molecular ions.

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1. Introduction

There have been extensive studies on the physicochemical properties and structures of metal complexes containing hydrazone derivatives. In view of their chelating capability and pharmacological applications hydrazones have attracted considerable attention [1].

The design, synthesis and characterization of hydrazones and their metal complexes have come from their ease of synthesis, easily tunable steric and electronic properties and good stability in common organic solvents. Metal complexes containing hydrazones are found to serve as catalysts in several organic transformation reactions such as polymerization, epoxidation, reduction, oxidation, alkylation and condensation. Tahseen *et al.* [2] have studied the catalytic abilities of oxovanadium complexes with hydrazones. They have observed that the complexes are very effective in the conversion of benzoil to benzil. One of the characteristic features of oxovanadium complexes is that it is possible to tune the electronic and steric properties of complexes. In recent years, there is an exponential progress in the number of publications in catalysis involving oxovanadium complexes. Studies have revealed that oxovanadium complexes are active catalysts for stereo selective organic transformations including hydroxylation of styrene, aldol condensation, alkene epoxy-

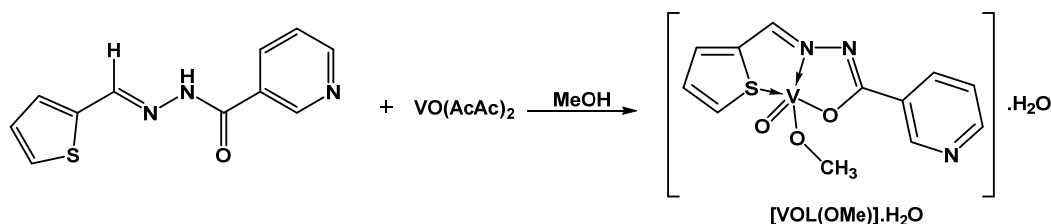
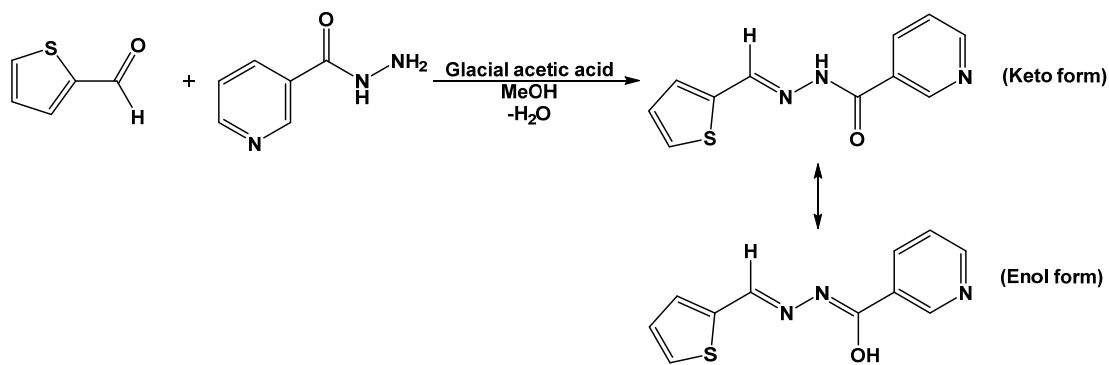
dation, Diels-Alder reactions and ring opening polymerization [3-5]. Catalytic activity increases with increasing $V(V)/V(IV)$ reduction potential of oxovanadium complexes. The oxovanadium complexes as catalysts have generally shown an effective activity (with no detectable leaching of metal) for oxidation and condensation reactions. Heterogenization of homogeneous catalyst has recently attracted the attention of chemists due to better selectivity and recyclability of the catalyst.

Aim of this work is to synthesize novel oxovanadium complex containing acid hydrazone as ligand and finding its magnetic, thermal and redox properties through characterization.

2. Experimental

2.1. Physical measurements

Microanalysis of carbon, hydrogen, nitrogen and sulphur in acid hydrazone and in its metal complex was carried out on an elemental model Vario EL III CHNS analyzer. Molar conductivities of the complex in DMF and DMSO (1×10^{-3} M) were measured at room temperature using a direct reading digital conductivity meter.



The magnetic susceptibility measurement on the complex was carried out at room temperature, using VSM method. Infrared spectra of the ligand and the complex were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR spectrophotometer as KBr pellets. ^1H NMR, ^{13}C NMR, ^1H - ^1H COSY, and ^1H - ^{13}C HSQC of the ligand were recorded using Bruker AMX 400 FT-NMR spectrometer with $\text{DMSO-}d_6$ as solvent and TMS as the internal standard. The EPR spectrum of the complex at liquid nitrogen temperature (LNT) in DMF was recorded on X-band JES-FA 200 ESR spectrometer. Cyclic voltammetry of the complex was carried out using a suitable reference, working and counter electrodes in the presence of a supporting electrolyte. The three electrode system consisted of a glassy carbon (working), platinum wire (counter), and Ag/AgCl (reference) electrodes. Measurements were made in DMF (1×10^{-3} M) containing 0.1 M tetrabutyl ammonium fluoroborate as supporting electrolytes. Cyclic voltammograms were recorded on an electrochemical analyzer. A TG-DTG analysis of the complex was carried out in the heating range of 15-900 °C by using a Perkin Elmer Diamond TG/DTG Analyzer. Mass spectrum of the complex was obtained from Ultra flextrimealdi TOF spectrometer (Bruker daltonics)

2.2. Materials

2-Thiophene carboxaldehyde, nicotinic hydrazide, methanol, glacial acetic acid, vanadyl acetylacetonate were procured from Sigma Aldrich and were used without further purification.

2.3. Preparation of acid hydrazone

Nicotinic hydrazide (0.14 g, 1 mmol) was dissolved in methanol (30 mL) and to this was added 2-thiophene carbaldehyde (0.11 mL, 1 mmol) followed by two drops of glacial acetic acid. The mixture was refluxed for 6 hours and kept aside for cooling when colorless 2-thiophenecarbanicotinic hydrazone crystals separated out. The mixture was filtered and the crystals were washed with methanol. The crystals were dried over P_4O_{10} under vacuum (Scheme 1).

Color: Colorless. Yield: 70%. M.p.: 238-240 °C. FT-IR (KBr, ν , cm^{-1}): 3236 $\nu(\text{NH})$, 1645 $\nu(\text{C}=\text{O})$, 1558 $\nu(\text{C}=\text{N})$, 846 $\nu(\text{C}-\text{S}-\text{C})$. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ , ppm): 11.978 (s, 1H, NH), 9.059 (s, 1H, C-H, Azomethine), 8.785-7.157 (m, 7H, Ar-H). ^{13}C NMR (150 MHz, CDCl_3 , δ , ppm): 148.5 C(1), 129.2 C(3), 128.6 C(4), 135.3 C(5), 138.8 C(6), 161.5 C(9), 131.2 C(11), 151.3 C(12), 152.2 C(14), 127.8 C(15), 143.5 C(16). Anal. calcd. for $\text{C}_{11}\text{H}_9\text{N}_3\text{OS}$: C, 57.13; H, 3.92; N, 18.17. Found: C, 57.34; H, 4.06; N, 18.56 %. UV/Vis (Acetonitrile, 1×10^{-4} M, λ_{max} , nm): 442 ($n-\pi^*$), 284 ($\pi-\pi^*$).

2.4. Preparation of oxovanadium(IV) complex of *N'*-[thio phen-2-ylmethylidene]pyridine-3-carbohydrazone [VOL(OMe)]H₂O

To a solution of 2-thiophenecarbanicotinic hydrazone (0.23 g, 1 mmol) in methanol (20 mL), vanadyl acetylacetonate (0.27 g, 1 mmol) dissolved in methanol (20 mL) was added. The reaction mixture was stirred at room temperature with a magnetic stirrer for 5 hours. The resulting solution was allowed to stand at room temperature for slow evaporation, when greenish brown colored precipitate separated out. It was filtered, washed with methanol and dried under vacuum (Scheme 2). Color: Greenish brown. Yield: 75%. M.p.: >300 °C. μ_{eff} (B.M.): 1.78. FT-IR (KBr, ν , cm^{-1}): 3074 $\nu(\text{O}-\text{H})$, 1597 $\nu(\text{C}=\text{N})$, 1522 $\nu(\text{C}=\text{N})$, 1366 $\nu(\text{C}-\text{O})$, 953 $\nu(\text{V}=\text{O})$, 823 $\nu(\text{C}-\text{S}-\text{C})$. Anal. calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4\text{SV}$: C, 41.63; H, 3.78; N, 12.14. Found: C, 41.40; H, 4.03; N, 12.10%. UV/Vis (DMF, 1×10^{-4} M, λ_{max} , cm^{-1}): 24390 ($n-\pi^*$), 36232 ($\pi-\pi^*$), 13175 ($d-d$). EPR: $g_{\parallel} = 1.965$, $g_{\perp} = 1.99$, $A_{\parallel}(\text{cm}^{-1}) = 199.92 \times 10^{-4}$, $A_{\perp}(\text{cm}^{-1}) = 60.11 \times 10^{-4}$. Cyclic voltammetric parameters: $E_{\text{pa}}(\text{V}) = 1.31$, $E_{\text{pc}}(\text{V}) = -0.55$, $E_{1/2}(\text{V}) = 0.39$, $i_{\text{pc}}/i_{\text{pa}} = 0.967$, $\Delta E_{\text{p}}(\text{V}) = -1.87$.

3. Results and discussion

The ligand was characterized by ^1H and ^{13}C NMR, IR, UV-Visible, and elemental analysis. Elemental analyses of the ligand suggest the formulae proposed. The bands observed at 1645 and 3236 cm^{-1} in the spectrum of 2-thiophenecarbanicotinic hydrazone are assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{N}-\text{H})$ modes,

respectively [6-10]. The presence of carbonyl group in the compound suggests the presence of amido form in the solid state. Thiophene ring absorption band for 2-thiophenecarbanicotinic hydrazone is observed at 846 cm^{-1} .

The electronic spectrum of substituted hydrazone was recorded in acetonitrile solution (1×10^{-4} M). UV-Vis spectra of the ligand displayed bands around 400 and 290 nm which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

The proton NMR spectrum of 2-thiophenecarbanicotinic hydrazine (Figure 1) recorded in $\text{DMSO}-d_6$ displayed a singlet at δ 11.98 ppm and this is assigned to NH proton at position 8. A signal at δ 9.1 ppm is attributed to the proton on azomethine carbon at position 6. The peaks due to protons on the thiophene and pyridine rings are in the range 7.16 to 8.8 ppm.

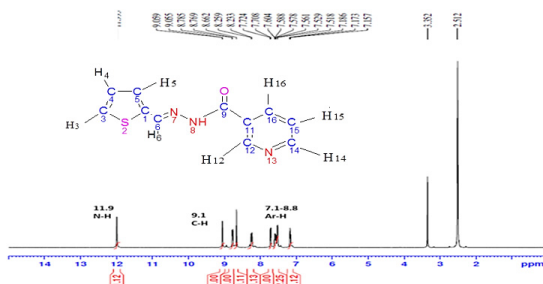


Figure 1. ^1H NMR spectrum of 2-thiophenecarbanicotinic hydrazine.

The ^{13}C NMR spectrum of 2-thiophenecarbanicotinic hydrazine in $\text{DMSO}-d_6$ was recorded (Figure 2). The ^{13}C NMR spectrum provided information about the carbon skeleton of the compound. Among all the carbons, the carbonyl carbon at position 9 is the most deshielded and it resonated at δ 161.5 ppm. The carbons adjacent to the ring nitrogen at positions 12 and 14 are also deshielded and these resonated at δ 151.3 and 152.2 ppm, respectively.

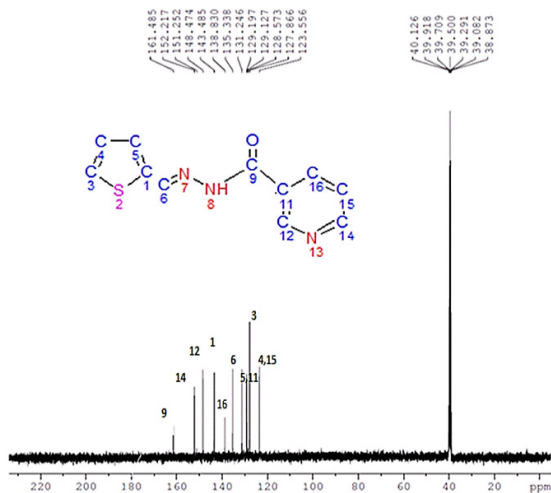


Figure 2. ^{13}C NMR spectrum of 2-thiophenecarbanicotinic hydrazine

Elemental analyses of the ligand suggest the formulae proposed. The complex is soluble in acetonitrile, DMF and DMSO but insoluble in other organic solvents. The solutions are non-conducting and the complex is non-electrolytic in nature. The magnetic moment of the complex was determined by Vibrating Sample Magnetometer (VSM) at room temperature. The value 1.78 is close to the spin only value of 1.73 B.M., which indicate that the complex is paramagnetic in nature having one unpaired electron. IR spectrum of 2-thiophenecarbanicotinic hydrazonato oxovanadium(IV) does

not show $\nu(\text{C}=\text{O})$ and $\nu(\text{N}-\text{H})$ bands at 1645 and 3236 cm^{-1} . This shows the coordination of ligand to the metal ion in the enolate form [11-14]. A new band has appeared at 1336 cm^{-1} and this is assigned to $\nu(\text{C}-\text{O})$. An intense band observed at 953 cm^{-1} is due to $\text{V}=\text{O}$ stretching 2-thiophenecarbanicotinic hydrazine showed a band at 1558 cm^{-1} due to $\nu(\text{C}=\text{N})$ of azomethine group and this has shifted to 1522 cm^{-1} in the complex implying the coordination of azomethine nitrogen to the central metal ion. A band at 1590 cm^{-1} is due to new $\nu(\text{C}=\text{N})$ (Figure 3).

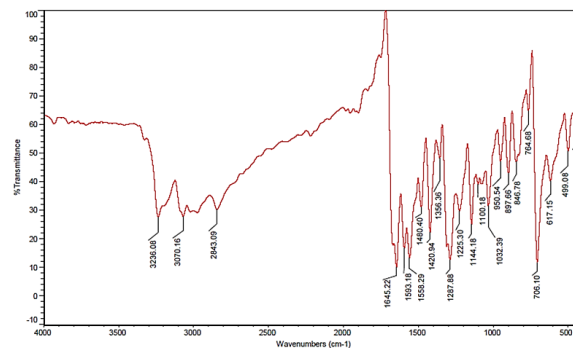


Figure 3. IR spectrum of 2-thiophenecarbanicotinic hydrazine.

The complex exhibits a broad band at 3070 cm^{-1} and this is due to the presence of lattice water [15-18]. In the free ligand 2-thiophenecarbanicotinic hydrazine, thiophene ring shows absorption band at 846 cm^{-1} . This band has shifted to lower wave number, 823 cm^{-1} in the complex, suggesting the participation of thiophene sulphur in complexation (Figure 4).

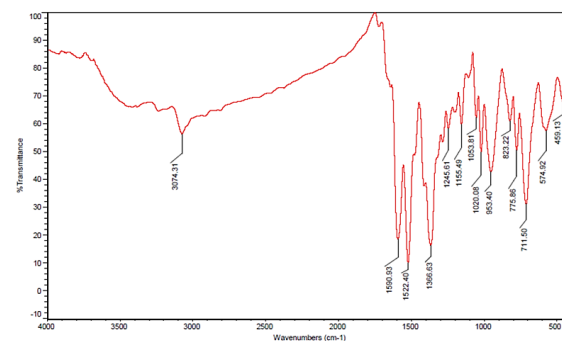


Figure 4. IR spectrum of $[\text{VOL}(\text{OMe})]\text{H}_2\text{O}$.

The electronic absorption spectrum of the complex is recorded in acetonitrile solution (1×10^{-4} M). The spectra exhibited bands around 280 and 400 nm and these are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively for the complexed hydrazone derivatives. The absorption bands are characteristic of square pyramidal environment around vanadium(IV).

The EPR spectra of $[\text{VOL}(\text{OMe})]\text{H}_2\text{O}$ was recorded in DMF at liquid nitrogen temperature (Figure 5). In the complex, the metal ion has oxidation state IV and hence has d^1 electron configuration. The EPR spectra of the complex have shown two sets of signals suggesting that the complex have square pyramidal geometry. As there are two sets of signals, one set (a to h) corresponding to parallel to the applied magnetic field direction (g_{\parallel}) and the other (1 to 8) perpendicular to the magnetic field direction (g_{\perp}), the latter set of signals, being more intense than the formal set of signals [19,20]. In the same way, there are two hyperfine splitting constants A_{\parallel} and A_{\perp} for square pyramidal complexes $g_{\parallel} < g_{\perp}$, $A_{\parallel} > A_{\perp}$. It is the characteristic of an axially compressed system with unpaired

electron in d_{xy} orbital [21,22]. The values of A_{iso} and g_{iso} are measured by $1/3(A_{||} + 2A_{\perp})$ and $(g_{||} + 2g_{\perp})$.

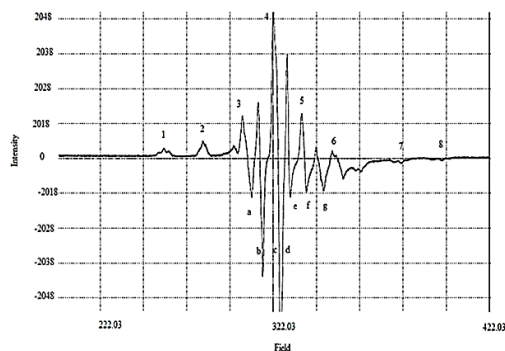


Figure 5. EPR spectrum of [VOL(OMe)]H₂O at LNT.

Electrochemical studies of oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone was performed using DMF as the solvent, tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at scan speeds of 50, 100 and 200 mV/sec to understand the redox behavior. The electrode system consisted of glassy carbon as working electrode, platinum wire as counter or auxiliary electrode and SCE as reference electrode. All the experiments were carried out at room temperature. The solutions were freshly prepared prior to use and were purged with nitrogen gas for 10 minutes to remove dissolved oxygen. Electrochemical nature of the complexes was studied with three scan rates i.e., 50, 100 and 200 mV/s. The redox nature of the complex was reversible. The redox properties of oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone was examined in DMF solution (in nitrogen atmosphere). The cyclic voltammograms of the complex showed a reversible reduction-oxidation peaks. The electrode process can be shown as $[V^{IV}OL(OMe)] \cdot H_2O \rightleftharpoons [V^{III}OL(OMe)] \cdot H_2O$. The complex is reversible in nature. [VOL(OMe)]₂H₂O shows a reductive response at -0.55 V vs SCE assigned to VO(IV) to VO(III) and an oxidative response at 1.32 V vs SCE which is assigned to the VO(III) to VO(IV) change and the process is thus reversible (Figure 6).

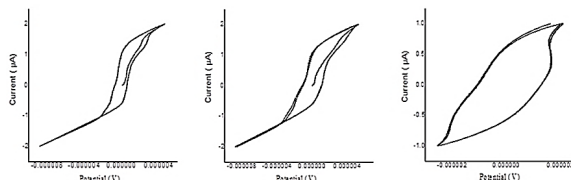


Figure 6. Cyclic voltammogram of [VOL(OMe)]H₂O (50, 100, 200 mV/s).

Thermogravimetric analysis of oxovanadium complex was carried out in the temperature range 15-900 °C. First decomposition step within the temperature range 139-267 °C for [VOL(OMe)]₂H₂O may be attributed to the loss of hydrated water molecule [23-25]. The second decomposition step with the range 267-400 °C for [VOL(OMe)]₂H₂O is reasonably accounted by the partial removal of organic moiety from the complex. This corresponds with the decomposition of the ligand moiety. A horizontal zone beyond 400 °C for the complex suggests the formation of ultimate pyrolysis product V₂O₅ (Figure 7).

MALDI-TOF mass spectra of complex in acetonitrile showed the presence of main peaks centered at particular m/z values. In MALDI (Matrix Assisted Laser Desorption Ionization) analysis of the molecular ions by time of flight mass spectra is used. It is a laser based soft ionization method. It is proved to be the most successful ionization method for

mass spectrometric analysis. With metal complex the matrix (α -cyano-4-hydroxy-cinnamic acid) may occupy a coordination site and additional peaks are expected (sample, matrix ratio is 1:1). MALDI spectrum of oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone as α -cyano-4-hydroxy-cinnamic acid mix showed a peak at m/z 347 (Figure 8). The molecular ion peak m/z 347 was assigned to $[VO_{C_{11}H_9N_3OS} (OCH_3)] \cdot H_2O$. The peak at m/z 231 corresponded to dissociated species $C_{11}H_9N_3OS$ which was due to the degradation of ligand [26,27]. The oxovanadium complex [VOL(OMe)]₂H₂O is colored and soluble in DMF, DMSO and acetonitrile. The proposed structure for the complex [VOL(OMe)]₂H₂O is square pyramidal.

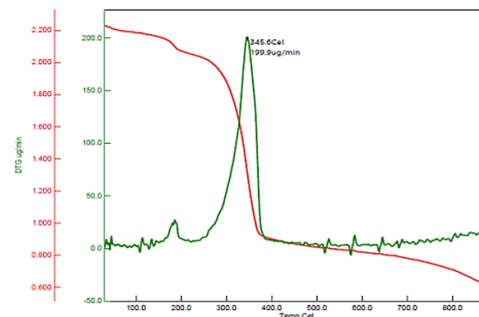


Figure 7. TG-DTG plot of [VOL(OMe)]₂H₂O.

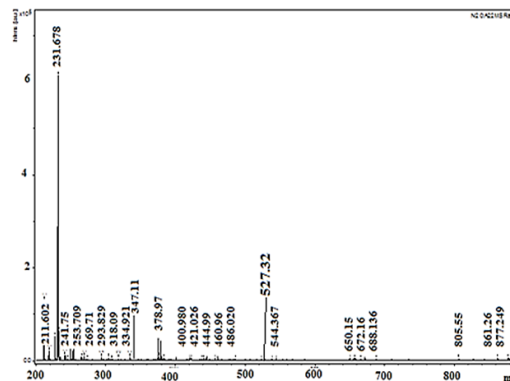


Figure 8. MALDI-TOF mass spectra of [VOL(OMe)]₂H₂O.

4. Conclusions

The acid hydrazone was characterized by CHNS, IR, UV-Vis, 1D and 2D NMR. The oxovanadium(IV) complex was characterized by elemental analysis, IR, UV-Vis, molar conductance measurements, magnetic susceptibility measurements, EPR spectra, cyclic voltammetry, thermal studies and MALDI-TOF mass spectra. Molar conductivity data of oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone revealed their non-electrolytic behavior in DMF and DMSO. Vanadium complex was found to be paramagnetic to the extent of one unpaired electron. IR spectral data showed the presence of lattice water and the coordination of hydrazone ligand to metal ion in enolic form. 1D and 2D NMR spectra displayed ¹H and ¹³C resonances for the hydrazone derivative. The complex was not used for NMR spectral studies, as they were paramagnetic. EPR spectra of 2-thiophenecarbanicotinic hydrazone oxovanadium(IV) was recorded in DMF at LNT and g and A values were calculated. The complex was proposed to be square pyramidal in geometry. The g values calculated showed that the unpaired electron was in d_{xy} orbital. Cyclic voltammogram of the complex in DMF were studied by changing the scan rates 50, 100, and 200 mV/sec.

ΔE values of the complex showed the reversible criterion and ipc/ipa values which were close to 1 indicating that the redox couple as reversible. Thermogram of the complex was recorded to find the weight loss at different temperature ranges. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed mass number of the molecular ions. The molecular ion peaks were less intense suggesting oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone possess lower stability in solution.

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References

- [1]. Sanjay, E. R.; Rao, A. K.; Yadav, H. S. *Curr. Res. Chem.* **2011**, *3*, 106-114.
- [2]. Tahseen, A.; Jabbar, S.; Omar, N. *J. Chem. Central* **2013**, *54*, 111-117.
- [3]. Rosu, T.; Pahontu, E.; Maxim, C.; Gulea, A. *Polyhedron* **2010**, *29*, 757-766.
- [4]. Chohan, Z. H.; Sumrra, S. H.; Youssoufi, M. H. Hadda, T. B. *Eur. J. Med. Chem.* **2010**, *45*, 3981-3998.
- [5]. Jian, L.; Liu, T.; Cai, S.; Wang, X. *Inorg. Biochem.* **2006**, *100*, 1888-1896.
- [6]. Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583-1590.
- [7]. Maurya, M. R. *Coord. Chem. Rev.* **2003**, *237*, 163-181.
- [8]. Rahman, B.; Husseine, H.; Zoppelaro, G. *Dalton Trans.* **2013**, *42*, 2803-2812.
- [9]. Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81-122.
- [10]. Mangalam, N. A.; Kurup, M. R. P. *Spectrochim. Acta* **2009**, *71*, 2040-2044.
- [11]. Abdel-Latif, S. A.; Hassib, H. B.; Issa, Y. M. *Spectrochim. Acta* **2007**, *67*, 950-957.
- [12]. Mishra, A. P.; Tiwari, A.; Jain, R. *Int. J. Res. Pharm. Sci.* **2011**, *3*, 167-172.
- [13]. Collison, D.; Gahan, B.; Garner, C. D. *J. Chem. Soc. Dalton Trans.* **1980**, 667-674.
- [14]. Dickson, F. E.; Kunes, C. J.; McGinnis, E. L. *Anal. Chem.* **1972**, *44*, 978-998.
- [15]. Clich, P. R.; Daniher, A. T.; Challen, P. R. *Inorg. Chem.* **1996**, *35*, 347-356.
- [16]. Davidson, A.; Edelstein, N.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 2799-2813.
- [17]. Dianu, M. L.; Kriza, A.; Musuc, A. M.; Kuriakose, M.; Kurup, M. R. P.; Suresh, E. *Struct. Chem.* **2007**, *18*, 579-584.
- [18]. Ray, A.; Banerjee, S.; Sen, S.; Butcher, R. J.; Mitra, S. *Struct. Chem.* **2008**, *19*, 209-217.
- [19]. Mangalam, N. A.; Sheeja, S. R.; Kurup, M. R. P. *Polyhedron* **2010**, *9*, 3318-3323.
- [20]. Sen, S.; Mitra, M.; Hughes, D. L. *Polyhedron* **2007**, *26*, 1740-1744.
- [21]. Datta, A.; Das, K.; Jhou, Y. M.; Huang, J. H.; Lee, H. M. *Acta Cryst. E* **2010**, *66*, m1271-m1271.
- [22]. Koh, L. L.; Kon, O. L.; Loh, K. W.; Long, Y. C. *Biochem.* **1988**, *72*, 155-162.
- [23]. Sreeja, P. B.; Kurup, M. R. P.; Kisore, A. *Polyhedron* **2004**, *23*, 575-581.
- [24]. Li, S.; Gao, S.; Liu, S. *Cryst. Growth Des.* **2010**, *10*, 495-503.
- [25]. Sridhar, S.; Saravanan, M.; Ramesh, A. *Eur. J. Med. Chem.* **2013**, *36*, 615-625.
- [26]. Pandey, M. K. R.; Devi, S.; Sreeja, P. B. *Asian J. Chem.* **2015**, *27*, 4135-4137.
- [27]. Rao, S. N.; Mishra, D. D.; Maurya, R. C.; Rao, N. N. *Polyhedron* **1997**, *16*, 1825-1829.