

## Synthesis and Characterization of Oxovanadium- N<sub>2</sub>S<sub>2</sub> Complexes

M. F. RAHMAN

Research Scholar

Department of Chemistry

University of Burdwan, Burdwan

India

ANIRUDDHA CHAKRABORTY

Assistant Professor

Union Christian Training College

Murshidabad, WB

India

### Abstract:

*Oxo and dioxovanadium (IV & V) complexes with Schiff base ligands are interesting because of their nature and biological activities. One of the oxovanadium (IV) known as VO<sup>2+</sup>tctsc (Oxovanadiumthiophene-2-carboxaldehydethiosemicarbazone) with a Schiff base named as thiophene-2-carboxaldehydethiosemicarbazone formed by the reaction of thiophene-2-carboxaldehyde and thiosemicarbazide is reported herein. The complex is synthesised by the reaction of vanadyl sulphate with the Schiff base in 1:2 molar ratios in acetic acid solution. The complex is insoluble in most of the organic solvents like acetic acid, methanol, ethanol, and THF, but soluble in DMSO and DMF. The complex compound has been characterized by elemental, conductometric, pH metric, IR, UV-Vis, FAB-Mass analyses. Single crystal XRD analysis and metal ions extraction is on progress.*

**Key words:** Synthesis, Schiff base, Oxovanadium(IV) complexation, Spectral analyses.

## **Introduction**

Schiff bases are very important in the field of coordination chemistry for complexation with transition metal ions. Depending upon the nature of their donor atoms in the ligands, a large number of complexes with different transition metal ions are reported. The most of the complexes which are prepared have involved combination of nitrogen, oxygen and sulphur donor atoms containing ligands. Some reported Schiff - base ligands complexes are [(bis[N(4-chlorophenyl)salicylideneiminato]oxovanadium(IV), *N,N'*-(3,3'-dipropylamine)bis(3methoxysalicylideneiminato)oxovanadium(I V)dihydrate, formed by the complexation of a N<sub>3</sub>O<sub>2</sub>-donor Schiff-base ligand [1]. In reference to the above oxovanadium(IV) complexes we report here one of the most interesting oxovanadium(IV) complex with a Schiff base N<sub>2</sub>S<sub>2</sub>-ligand known as thiophene-2-carboxaldehydethiosemicarbazone formed by the reaction of thiophene-2-carboxaldehyde and thiosemicarbazide. Thiosemicarbazones have been comprehensively investigated because it is largely due to their structural features and effective biological activities [2-3]. The biological activity of thiosemicarbazones would be enhanced by the groups of the parent aldehyde or ketone. Oxo and dioxovanadium(IV & V) complexes with thiosemicarbazones are interesting because of their significant pharmacological activities and catalytic roles in many biological systems and industrial process. The versatile N<sub>2</sub>S<sub>2</sub>-tetradentate ligands are known to accommodate many divalent transition metal ions while maintaining reactivity at the S-thiolate site of the respective N<sub>2</sub>S<sub>2</sub>-metal complexes. The vanadyl ion (VO<sup>2+</sup>) of interest for its pharmaceutical possibilities and its spin-label reporter properties for bioinorganic studies also shows an affinity for such mixed nitrogen/sulphur donor environments. A vanadium (IV) complex with general formula VO<sup>2+</sup>tctsc has been synthesized by the reaction of thiosemicarbazide and

thiophene-2-carboxaldehyde and their substituted compounds. The compound has been synthesized by elemental analysis, IR, UV-Vis, FAB-Mass, conductometric and pH metric analyses. Single XRD analysis is on progress. Attempts have been made to study the coordination around the oxovanadium(IV) centre and for extraction.

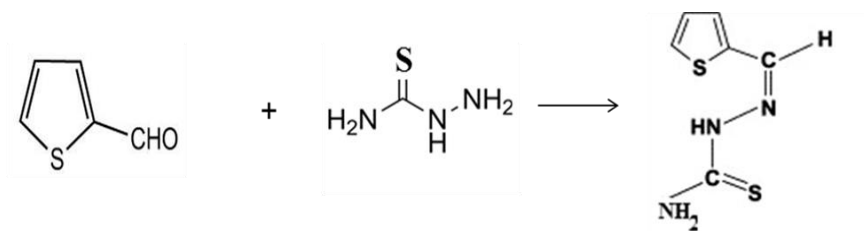
## **Materials and Methods**

### **Chemicals and Instruments**

Extra pure methanol, ethanol, acetic acid, DMSO, DMF from E. Merck, Germany, vanadyl sulphate pentahydrate(BDH, India) was of analytical grade reagent, thiosemicarbazide and thiophene-2-carboxaldehyde (Sigma and Aldrich) were used for the complexation. The UV-Vis spectra were recorded in DMF using SHIMADZU 2401 PC and the IR-spectra in KBr Pellets with Perkin-Elmer L 120-00A FT-IR spectrometer. The magnetic susceptibility measurements were carried out with a Gouy balance, using mercury tetrathiocyanatocobaltate(II) as a calibrant.

### **Synthesis of the ligand**

The ligand was prepared by the method for the production of thiosemicarbazones by the reaction of thiosemicarbazide and thiophene-2-carboxaldehyde according to the previously reported study [4-5]. In brief, the transparent mixture of thiosemicarbazide(1 mmol) in 5% acetic acid at 50<sup>o</sup> C, was added drop wise freshly distilled thiophene-2-carboxaldehyde (1mmol) for 5 minutes. The reaction mixture was stirred for another 30 minutes at 50<sup>o</sup> C. The yield of the reaction mixture was cooled down and washed with water (20 ml) and pure ethanol (20 ml) and finally dried at 70-80<sup>o</sup> C for at least 5 hours. The greenish yellow yield of 89.2% was heated in an oven at 80<sup>o</sup> C and finally crystallized from hot ethanol. The reaction scheme of the ligand is represented in figure 1:



### Synthesis of the Metal-ligand complex

Oxovanadium(IV) complex was prepared by addition of solid thiophene-2-carboxaldehydethiosemicarbazone (10.00 mmol 4.52 g) and the salt VOSO<sub>4</sub> · 5H<sub>2</sub>O (5.10 mmol 2.25g) in 5% acetic acid solution and the reaction mixture was stirred for 30 minutes at 50° C. The reaction was carried out at pH=7. Finally, a greenish yellow precipitate was filtered off, washed with hot water, and dried yield of the product was 79% (5.348 g). The complex was soluble in DME and DMSO, but insoluble in common organic solvents like benzene, chloroform, methanol, ethanol, THF and also less soluble in hot water[6-7]. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>6</sub>OS<sub>4</sub>V (IV): mp, 245.2°C, C, 32.72, H, 5.33, S, 29.29, N, 19.22, O, 3.66, V, 11.65%. Found: C, 32.71, H, 5.30, S, 29.26, N, 19.25, O, 3.65, V, 11.56%.

### Results and Discussions

#### FAB-Mass

Mass spectra of the ligand shows intense molecular ion peaks  $m/z$ : [M<sup>+</sup>/M+H]<sup>+</sup> 436.89. The mass spectra of oxovanadium(IV) complex shows intense peaks including [VOL<sub>2</sub>] and [VOL<sub>2</sub>+H]<sup>+</sup> that confirmed a structure of stoichiometry of 2:1 for ligand to vanadium(IV). The spectra of vanadium (IV) complex also show some peaks corresponding to [VOL]<sup>+</sup> and L fragments [8-12].

#### IR Spectra

The solid state properties of the ligand and vanadium (IV) complex were examined by IR spectroscopy. The characteristics

$\nu(\text{V}=\text{O})$  stretching at  $920\text{-}975\text{ cm}^{-1}$  was observed as reported for other oxovanadium(IV) derivatives [12-15] and it is not present in the spectrum of free ligand. IR spectra of the ligand showed that absence of bands at  $\sim 1735\text{ cm}^{-1}$  and  $3315\text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{NH}_2)$  stretching vibration and a strong  $\nu$ -band appeared at  $1612\text{-}1633\text{ cm}^{-1}$  assign to azomethine  $\nu(\text{HC}=\text{N})$  linkage showing that amino and aldehyde groups of starting materials are absent and have been converted into the ligand. The comparison of IR-spectra of the ligand and its vanadium complex indicated that the ligand here acting as a bidentate ligand. The band appearing at  $\sim 1630\text{ cm}^{-1}$  due to azomethine was shifted to lower frequency by  $\sim 15\text{ cm}^{-1}$  in complex, indicating participation of azomethine nitrogen in the interaction with the metal ion. The band appearing in  $3315\text{ cm}^{-1}$  assign to the new NH in the ligand was no longer found in the spectra of the metal complex indicating deprotonation and coordination of the nitrogen with the ion. Metal complex of the thiosemicarbazone results in the removal of band in the region of  $830\text{-}805\text{ cm}^{-1}$  from the spectra of the uncomplexed thiosemicarbazone. It is concluded that there is contribution from  $\nu(\text{C}=\text{S})$  stretching vibration. Another band raised in the region  $\sim 1656\text{ cm}^{-1}$  assigned for the  $\nu(\text{V}-\text{S})$ .

### UV-Vis Spectroscopy

The electronic absorption spectra of the ligand in the UV-Vis. ranges were carried out in DMF solution, exhibiting two bands in the  $433\text{-}344\text{ nm}$  and  $281\text{-}258\text{ nm}$  regions [15-20]. And intense band at  $\sim 433\text{-}344$  is attributed to the  $n\rightarrow\pi^*$  transitions of  $\text{C}=\text{S}$  group,  $\text{C}=\text{N}$  group and thiophene ring which are overlapped. The  $\pi\rightarrow\pi^*$  transitions of the thiophene ring and thiosemicarbazone imine function are rather weak, and observed at  $\sim 281\text{-}258\text{ nm}$ . These two bands are shifted to lower energies after complexation  $\sim 410\text{ nm}$  and  $\sim 325\text{ nm}$ . These bands are assigned due to charge transfer transition from the S to an empty d-orbital of the vanadium atom. The oxovanadium

complex exhibits two weak bands ~ 660 nm and ~ 530 nm. These weak bands may be assigned due to the transitions  $b_2(d_{xy}) \rightarrow e(d_{xz}, d_{yz})$  and  $b_2(d_{xy}) \rightarrow (d_{x^2-y^2})$ .

### Magnetic Properties

The effective magnetic moment ( $\mu_{\text{eff}}$ ) was measured using a Gouy balance [20-24]. Oxovanadium(IV) complexes show magnetic moment values in the range of 1.64-1.70 BM, which are in accordance with values reported oxovanadium(IV) complexes [22-26] with one unpaired electron indicating that the complexes are monomeric. This is in agreement with the  $\nu(\text{V}=\text{O})$  obtained. The measured magnetic moment of VO (IV)L complex of the ligand is 1.72 BM which is corresponding to a single electron of the  $3d^1$  system of square pyramidal geometry of the complex.

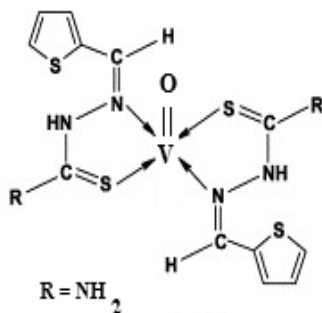
### Molar Conductance

Molar conductivity ( $\Lambda_M$ ) values of all the oxovanadium(IV) complexes were measured by the reported method [27-30]. The molar conductivity of this oxovanadium(IV) complex was measured in DMF and values lies between 2-5  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  indicating its non-electronic nature.

**Table 1: Physical and Analytical data of the Complex**

Molecular formula of the Complex	Colour Yield (%)	Analysis: Calcd/Found						Mol.Wt. Calcd/Found	$\Omega_M$ ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Electrolytic Nature
		C	H	S	N	O	V(IV)			
C <sub>12</sub> H <sub>14</sub> N <sub>6</sub> OS <sub>4</sub> V(IV)	Greenish							436.94 (435.89)	4.3	Non-electrolyte
	Yellow (79)	32.72	5.33	29.29	19.22	3.66	11.65			
		32.71	5.3	29.26	19.25	3.65	11.56			

## Proposed Structure of the Metal-Ligand Complex



## Conclusions

The complex of vanadyl ion with the synthesised thiosemicarbazone ligand has been obtained in solid state and characterized. The composition and the proposed structure of the oxovanadium(IV) complex has been established by elemental analysis and spectroscopic analyses such as: FAB-MS revealed the molecular ion peak and its fragmental ion peaks, IR spectra show that the azomethine moiety is the basic site for vanadium(IV) and ligand chelation, UV-Vis and magnetic measurement provided the square-pyramidal coordination of the metal ion, molar conductivity showed its non-electrolytic nature.

## REFERENCES

- Agarwal, Ram K., Lakshman SINGH, Deepak K. Sharma, and Ritu Singh. 2009. *Turk J Chem.* 29: 309-316. [12]
- Agarwal, Kailash Kumar and P.N. Saxena. 2011. *International Journal of Research in Pharmacy and Chemistry* 1(4). [15]
- Aliyu, Habu Nuhu and Abdullahi Mustapha. 2009. *African Scientist* 10(3) [11]

- Alyea, Elmer C., Terence D. Dee, and George Ferguson. 1985. *J. of Crystallographic and Spect. Research.* 15(1). [1]
- Arora, Rakhi, Neelam Singh, Shakshi Chaudhry and S. L. Vashist. 2004. *Asian Journal of Chemistry* 16(2): 654-658[25]
- Azevedo Marques, Ana Paula de, Edward Ralph Dockal, Fabiana C. Skrobot, Ieda Lucia Viana Rosa. 2007. *Inorganic Chemistry Communications* 10: 255-261[21]
- Bora, P. and H. S. Yadav. 2013. *Iranian Journal of Science and Technology, IJST* 37A3: 309-312[27]
- Cindric, Marina, Mirta Rubcic, Ivica Dilovic, Gerald Giester and Boris Kamenar. 2007. *Coartica Chemica Acta:* 80(3-4): 583-590[24]
- Doadrio, Antonio L., Jose Sotelo and Ana Fernandez-Ruano. 2002. *Quim. Nova.* 25(4): 525-528. [9]
- Garcia-Tojal, Javier, Africa Garcia Orad, Juan Luis Serra, Jose Luis Pizarro, Luis Lezama, Maria Isabel Arriortua, Teofilo Rojo. 1999. *Journal of Inorganic Biochemist* 75: 45-54. [2]
- Jalilian, Amir R., Mirsaeed Nikzad, Hassan zandi, Ali Nemati Kharat, Pejman Rowshanfarzad, Mehdi Akhlaghi, Fatemeh Bolourinovin. 2008. *Nuclear Medicine Review* 11(2): 41-47. [4]
- Jang, Yoon Jung, U.K. Lee and Bon Kweon Koo. 2005. *Bull Korean Chem. Soc.* 26(1) [16]
- Karakucuk-Iyidogan, Aysegul, Demet Tasdemir, Emine Elcin Oruc-Emire, and Jan Balzarini. 2011. *European J. of Medicinal chemistry* 46: 5616-5624[30]
- Kumer, Dubey Raj and Dwivedi Nalini. 2014. *Res. J. Chem. Environ.* 18 (3). [13]
- Lei-Zhen, Geng, Xing Jing, Wei Wei, Zhou Yin Zhuang. 2012. *Chinese J. Struct. Chem.* 31(4): 562-568[26]
- Mahalakshmi, N. and R Rajavel. 2011. *Asian Journal of Biochemical and Pharmaceutical Research* 2 (1) [7]



- Prasad, K. S., L. S. Kumar, S. C. Shekar, M. Prasad, H. D. Revanasiddappa. 2011. *Chemical Sciences Journal CSJ*-12[3]
- Rai, Amit, Ashish Sharma and Rupa Sirohi. 2011. *VSRD-TNTJ* (2)12: 604-608. [18]
- Rao P. Venkateswar and A. Venkata Narasaiah. 2003. *Indian Journal Chemistry* 42A: 1896-1899. [19]
- Rao, Anabothla Venkata Kantha, Suresh Bhagwanji Rewatkar. 2013. *Int. J. of Advancements in Research & Technology* 2(7)[28]
- Selbin J. 1966. *Coordination, Chemistry, Review* 1: 293. [5]
- Sellappan, R., S. Prasad, P. Jayaseelam and R. Rajavel, *Rasayan*. 2010. *J. Chemistry* 3(3): 556-562[6]
- Sharma, Reena. 2013. *Asian J of Adv., Basic Sci.* 1(1): 45-50[17]
- Singh, Sanjay, D. P. Rao, A. K. Yadava and H. S. Yadav. 2011. *Current Research in Chemistry* 3(2): 106-113[22]
- Singh, Sanjay, H. S. Yadav, A. K. Yadava, D. P. Rao. 2011. *Int. J. ChemTech* 3(4): 1863-1869[23]
- Symal, A. 1975. *Coordination, Chemistry, Review* 21: 309. [10]
- Temel, Hamdi, Umit Cakir and H. Ibrahim Ugras. 2004. *Marcel Dekker, Inc.* 34(4): 819-831. [8]
- Uivarosi, Valentina, Stefania Felicia Barbuceanu, Victoria Aldea, Corina-Cristina Arama, Mihaela Badea, Rodica Olar and Dana Marinescu. 2010. *Molecule* 15: 1578-1589[20]
- Vinayak, M.N., G.T. Kuchinad, S.K. Patil and N. B. Mallur. 2013. *Der Pharma Chemica* 5(4):43-50. [14]
- Yadav, Ashok Kumar, Hardeo Singh Yadav, Uma Shanker Yadav, and Devendra Pratap Rao. 2013. *International Scholarly Research Notices* Article ID871640, 5 pages. [29]