



## Synthesise and Charactrization of Cristaline Structure of Vanadium Complexe with 2-Pyridine Carboxaldehyde Schiff base

*Mir A. Naziri*\*<sup>1</sup>, *E. Sahin*<sup>2</sup>, *B. Shaabani*<sup>3</sup>,

1,2: *Deptatment of Inorganic Chemistry, Faculty of Chemistry, University of Ataturk, Erzurum, Turkey,*

1,3: *Deptment of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran,*

*E-mail: a.naziri@tabrizu.ac.ir*

### Abstract:

X-ray crystallographic studies led to the discovery of even more exotic types of bonding in inorganic chemistry, such as metal-metal double bonds, metal-metal quadruple bonds, and three-center, two-electron bonds. The chemistry of vanadium(V) is dominated by the stable oxovanadium cation ( $\text{VO}^{+3}$ ) which remains intact during many reactions. The redox properties of  $\text{VO}(\text{Salen})$  in acetonitrile in the presence of perchloric acid and provided evidence of what they took to be the disproportionation of  $\text{VO}(\text{Salen})$  to  $\text{VO}(\text{Salen})^+$ . Oxovanadium(IV) derivatives have been used as catalysts in the epoxidation of olefins and in the oxidation of sulfides with peroxides. In this reserch the ligand 4-Hydroxybenzhydrazide and 2- pyridine carboxaldehyde (L) has been prepared by condensation of 4-Hydroxybenzhydrazide with 2- pyridine carboxaldehyde respectively in the absolut ethanol as solvent. VO-complexe, VOL of thise ligand were synthesized by reactions of  $\text{NH}_4\text{VO}_3$  with ligand. The ligand and its complexe were characterized by X-ray, FT-IR, UV-Vis,  $^1\text{H-NMR}$ , analyse. And at least chemical behavior of ligand and its complexe were have been investigated.

**Keywords:** Crystallography, Schiff base, vanadium, Hydrazide, Pyridine

### Introduction:

X-ray crystallography is the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments [1]. And it is a tool used for identifying the atomic and molecular structure of a cristal, in wich the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions [1]. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean position of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. Because of catalytic and liquid crystal properties and too similar with anzims schiff base ligands and their complexes with transition elementals by the scientits were have been noticed[2]. At recent years the exsistence of vanadium compounds into the body of sea animals were argumented by the scientists.

Az for importance of schiff base ligands and their complexes, my purpose was in this reserch synthesis and study of hydrazide schif base and their complexes with vanadium[3].

In 1928 the structure of hexamethyl benzene established that hexagonal symmetry of benzene and showed a clear difference in bond length between the aliphatic C-C bonds and aromatic C-C bonds, this finding led to idea of resonance between chemical bonds, which had profound consequences for the development of chemistry.



### Experimental:

In this research the ligand (4-Hydroxybenzhydrazide and 2- pyridine carboxaldehyde) (L) has been prepared by condensation of 4-Hydroxybenzhydrazide with 2- pyridine carboxaldehyde respectively in the absolute ethanol as solvent, and it has three dentate. This ligand was recrystallized into the mixture of absolute ethanol and methanol.

VO<sub>2</sub>-complex, VO<sub>2</sub>L of this ligand were synthesized by reaction of NH<sub>4</sub>VO<sub>3</sub> with ligand (L). At first NH<sub>4</sub>VO<sub>3</sub> was dissolved into 10 ml absolute ethanol and heated for 30 minutes and stirred (because this salt is not soluble in absolute ethanol at normal conditions), then the mixture of Schiff base ligand (L) into the absolute ethanol as solvent was added equivalently into the container of reaction, and the set was refluxed for 6-7 hours. When the ligand was added into the container reaction, the color of the set changed into brown and that is confirmed that the complex was synthesized. But we were not able to obtain crystals from this method.

On the other hand for synthesis of this complex we applied the branch tube. In this method after 20 days we saw that the crystals of the complex were appeared, and after 5-10 days gathered them and characterized with: X-ray, FT-IR, UV-Vis, elemental analysis, <sup>1</sup>H-NMR and investigated of electrochemical behavior. These complexes are of a crimson color and were recrystallized into the absolute ethanol and n-hexane solution.

### Results and discussion:

Some physical characterizations of this ligand and its complex are summarized in table 1.

Table 1: Some Physical Properties of Ligand and its Complex

Compound	Molecular Weight	Yield%	Melting Point	Color
Ligand (L)	240	96	110	white
Complex VO <sub>2</sub> L	294	65	360	crimson

In figures 1, 2 and 3 the molecular structure of the complex (ammonium vanadate [NH<sub>4</sub>VO<sub>3</sub>] with ligand L (4-Hydroxybenzhydrazide and 2-pyridine carboxaldehyde)), unit cell and geometry of hydrogen bonds of the complex were shown.

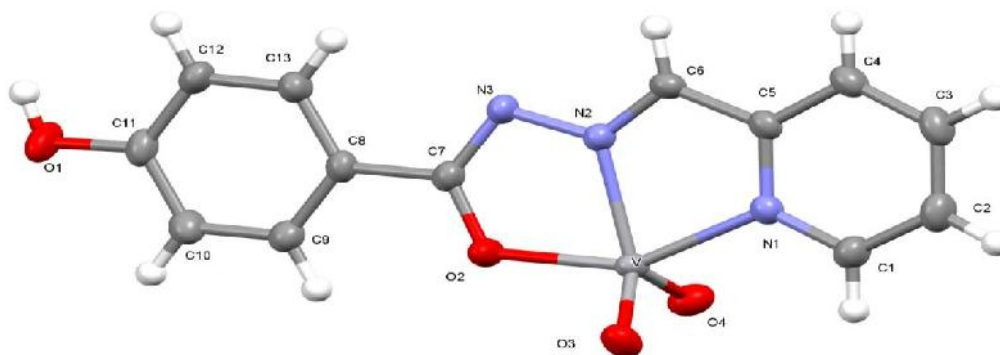


Figure 1: Molecular structure of complex Vanadium with ligand

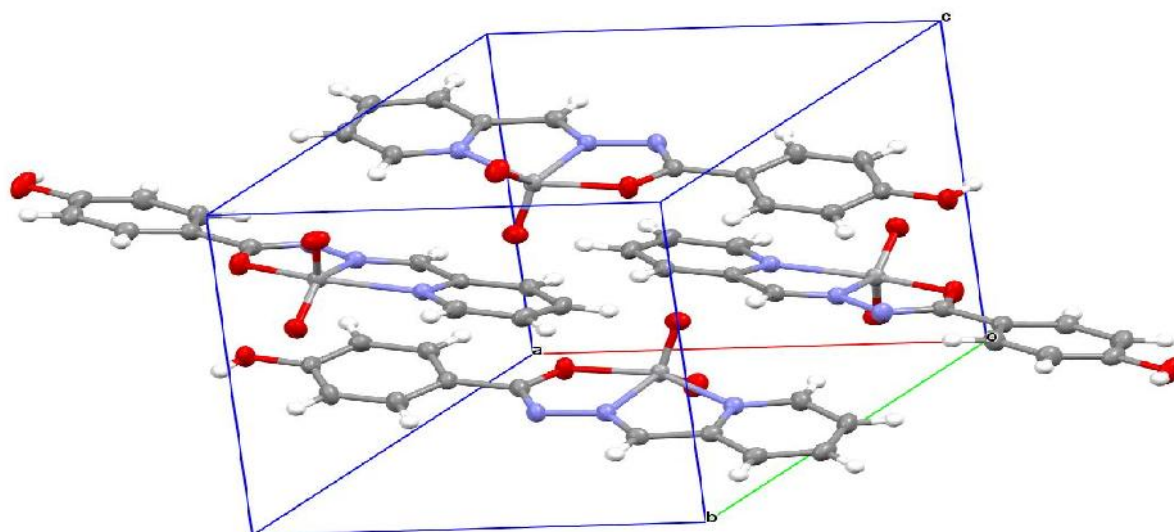


Figure2: Unit cell of complex Vanadium with ligand

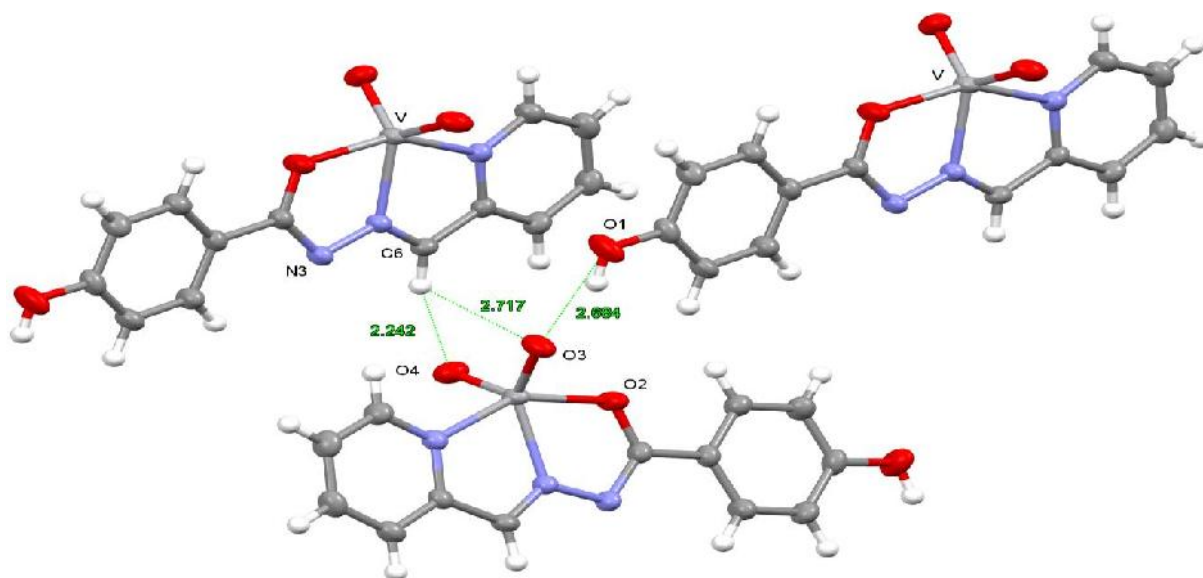


Figure3: The geometry of hydrogen bond of complex Vanadium with ligand

As shown in below tables, table 1, 2 and 3, the complete listing of bond distances (table 1) and Fractional atomic coordinates and isotropic temperature factors (Angstrom squared), with standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors (table 2), and Complete listing of bond angles (degrees) (table 3) are shown.



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Table 1  
Complete listing of bond distances (Angstroms)

V - O(4)	1.610(2)	V - O(2)	1.944(2)
V - O(3)	1.633(2)	O(2) - C(7)	1.307(3)
O(1) - H(1)	0.820(2)	O(1) - C(11)	1.360(3)
N(3) - N(2)	1.382(3)	N(3) - C(7)	1.310(3)
N(2) - C(6)	1.280(3)	N(1) - C(1)	1.336(3)
N(1) - C(5)	1.353(3)	C(2) - H(2)	0.930(3)
C(2) - C(1)	1.389(3)	C(2) - C(3)	1.374(4)
C(1) - H(1)	0.930(3)	C(7) - C(8)	1.473(3)
C(3) - H(3)	0.930(2)	C(3) - C(4)	1.385(3)
C(5) - C(4)	1.382(3)	C(5) - C(6)	1.457(3)
C(10) - H(10)	0.930(3)	C(10) - C(9)	1.381(3)
C(10) - C(11)	1.388(4)	C(8) - C(9)	1.391(3)
C(8) - C(13)	1.392(3)	C(9) - H(9)	0.930(3)
C(12) - H(12)	0.930(3)	C(12) - C(13)	1.380(3)
C(12) - C(11)	1.387(3)	C(4) - H(4)	0.930(3)
C(13) - H(13)	0.930(3)	C(6) - H(6)	0.930(2)

Table 2  
Fractional atomic coordinates and isotropic temperature factors  
(Angstrom squared)

	x	y	z	U(eq)
V	0.16623(3)	0.08570(2)	0.25475(3)	0.02977
O(4)	0.19808(15)	0.04976(12)	0.11519(15)	0.04269
O(2)	-0.02087(13)	0.11561(11)	0.21700(16)	0.04077
O(1)	-0.59408(13)	0.29983(14)	0.05084(17)	0.05225
H(1)	-0.61111	0.36297	0.06061	0.07837
O(3)	0.17208(14)	-0.01749(12)	0.35147(16)	0.04366
N(3)	0.02246(14)	0.29384(13)	0.25579(17)	0.03250
N(2)	0.14597(14)	0.24896(12)	0.28675(16)	0.02912
N(1)	0.35607(14)	0.14161(13)	0.33401(16)	0.03010
C(2)	0.58503(19)	0.12033(19)	0.41113(21)	0.04154
H(2)	0.65755	0.07541	0.42857	0.04984
C(1)	0.46252(19)	0.07949(17)	0.35816(21)	0.03723
H(1)	0.45436	0.00698	0.33899	0.04468
C(7)	-0.05909(18)	0.21501(15)	0.21963(19)	0.03147
C(3)	0.59809(19)	0.22768(18)	0.43754(20)	0.03939
H(3)	0.67969	0.25633	0.47207	0.04727
C(5)	0.36887(17)	0.24722(15)	0.36098(18)	0.02885
C(10)	-0.41763(19)	0.17940(17)	0.08478(20)	0.03830
H(10)	-0.47497	0.12502	0.05125	0.04596
C(8)	-0.19967(17)	0.23814(16)	0.17727(19)	0.03138
C(9)	-0.28635(19)	0.15740(17)	0.12720(20)	0.03543
H(9)	-0.25563	0.08797	0.12224	0.0425
C(12)	-0.37818(19)	0.36432(17)	0.14162(22)	0.04051



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H(12)	-0.40897	0.43378	0.14599	0.04861
C(4)	0.48841(19)	0.29279(17)	0.41218(19)	0.03517
H(4)	0.49507	0.36569	0.42927	0.04220
C(13)	-0.24724(19)	0.34166(17)	0.18407(22)	0.03886
H(13)	-0.19008	0.39615	0.21761	0.04663
C(6)	0.24587(18)	0.30623(15)	0.33244(19)	0.03099
H(6)	0.24042	0.37936	0.34627	0.03718
C(11)	-0.46371(18)	0.28297(18)	0.09237(19)	0.03596

Table 3  
Complete listing of bond angles (degrees)

O(4)-V-O(2)	103.1(1)	O(4)-V-O(3)	110.2(1)
O(2)-V-O(3)	101.8(1)	V-O(2)-C(7)	118.3(2)
H(1)-O(1)-C(11)	109.5(2)	N(2)-N(3)-C(7)	106.5(2)
N(3)-N(2)-C(6)	120.9(2)	C(1)-N(1)-C(5)	118.8(2)
H(2)-C(2)-C(1)	120.3(3)	H(2)-C(2)-C(3)	120.3(3)
C(1)-C(2)-C(3)	119.4(2)	N(1)-C(1)-C(2)	121.7(2)
N(1)-C(1)-H(1)	119.1(2)	C(2)-C(1)-H(1)	119.1(3)
O(2)-C(7)-N(3)	122.7(2)	O(2)-C(7)-C(8)	117.9(2)
N(3)-C(7)-C(8)	119.4(2)	C(2)-C(3)-H(3)	120.4(3)
C(2)-C(3)-C(4)	119.3(2)	H(3)-C(3)-C(4)	120.4(3)
N(1)-C(5)-C(4)	122.1(2)	N(1)-C(5)-C(6)	113.7(2)
C(4)-C(5)-C(6)	124.1(2)	H(10)-C(10)-C(9)	120.1(3)
H(10)-C(10)-C(11)	120.1(2)	C(9)-C(10)-C(11)	119.8(2)
C(7)-C(8)-C(9)	120.5(2)	C(7)-C(8)-C(13)	120.5(2)
C(9)-C(8)-C(13)	119.0(2)	C(10)-C(9)-C(8)	120.6(2)
C(10)-C(9)-H(9)	119.7(3)	C(8)-C(9)-H(9)	119.7(2)
H(12)-C(12)-C(13)	120.2(3)	H(12)-C(12)-C(11)	120.2(2)
C(13)-C(12)-C(11)	119.7(2)	C(3)-C(4)-C(5)	118.6(2)
C(3)-C(4)-H(4)	120.7(2)	C(5)-C(4)-H(4)	120.7(2)
C(8)-C(13)-C(12)	120.8(2)	C(8)-C(13)-H(13)	119.6(2)
C(12)-C(13)-H(13)	119.6(3)	N(2)-C(6)-C(5)	114.3(2)
N(2)-C(6)-H(6)	122.8(2)	C(5)-C(6)-H(6)	122.8(2)
O(1)-C(11)-C(10)	117.3(2)	O(1)-C(11)-C(12)	122.5(2)
C(10)-C(11)-C(12)	120.2(2)		

Absorbance frequencies of C=N group in complexes ( $1600\text{Cm}^{-1}$ ) in the comparison with free ligands ( $1650\text{Cm}^{-1}$ ) have shifted to lower wave numbers indications its coordination to metal center via N atom of imine (C=N) group. Wide peak around  $3440\text{Cm}^{-1}$  can be attributed to stretching of O-H bond belonging to hydroxysy of lignd at area can be could related to stretch vibration of OH group in complexe molecule.



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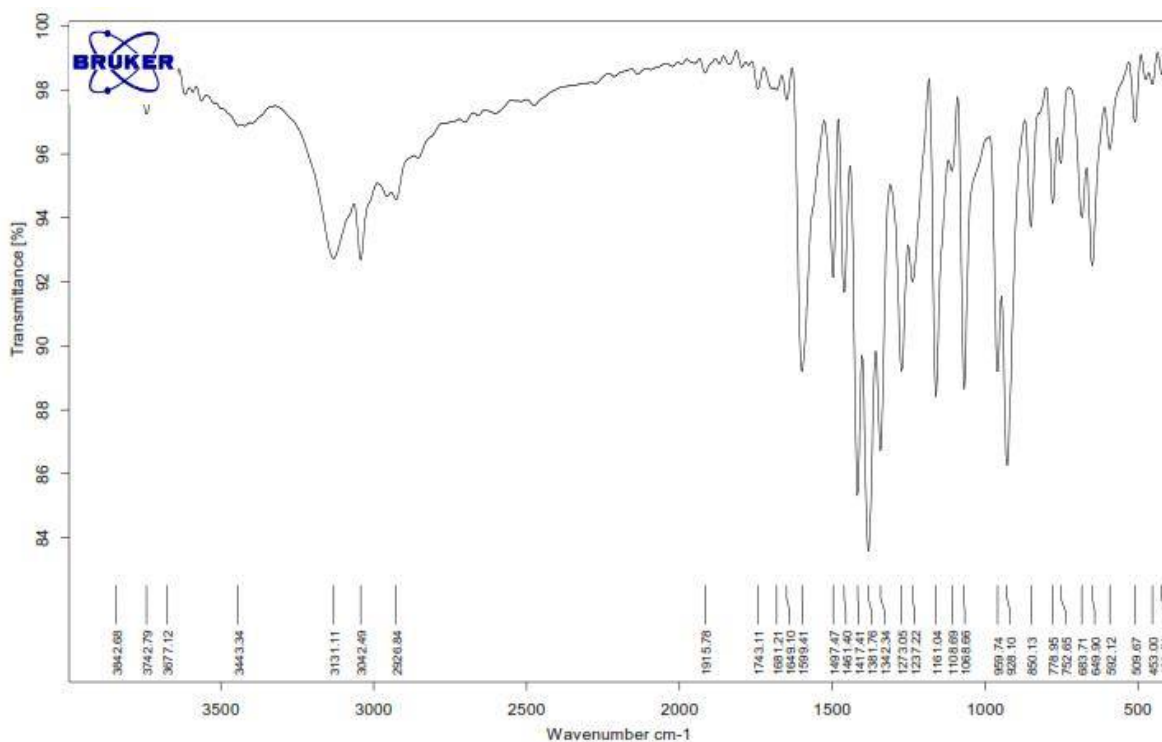
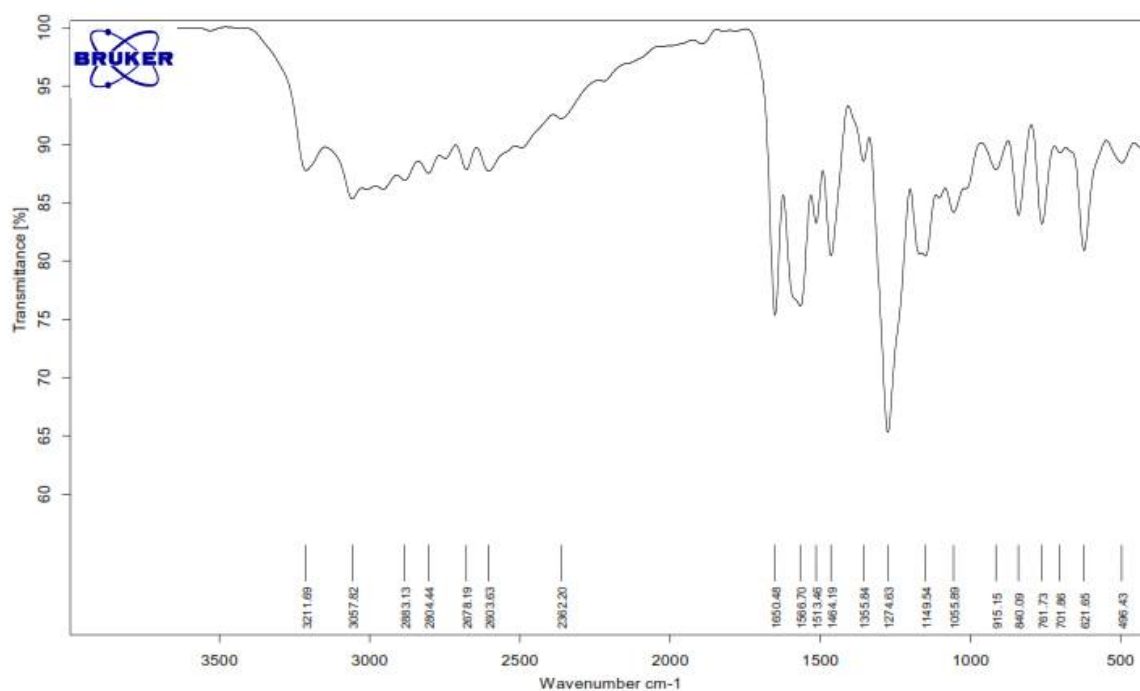


Figure4: FT-IR spectrum of Vanadium with ligand



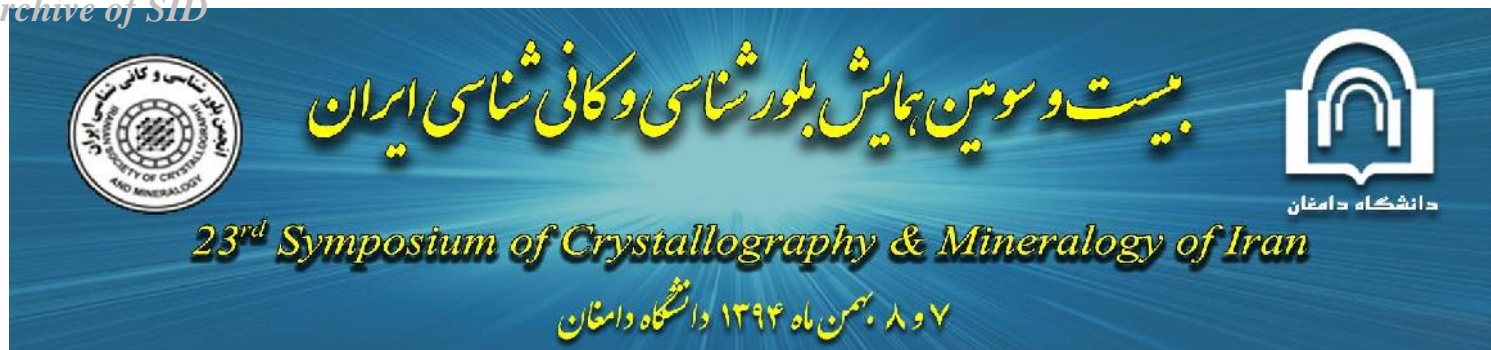


Figure5: FT-IR spectrum of ligand

#### Conclusion:

With considering X-ray structures and its data about complexes, and spectroscopic data, FT-IR, UV-Vis,  $^1\text{H}$ NMR and melting point of ligand and its complexes, we could conclude that ligand acted as a tridentate ligand coordination to Vanadium via N imine and O benzohydrazide and N pyridine atoms. With attention to X-ray structure ligand and complexes was reacted equivalently.

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