



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

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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 (VO^{+3}) which remains intact during many reactions. The redox properties of $\text{VO}(\text{Salen})$ in acetonitrile in the presence of perchloric acid 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 research the ligand 4-Hydroxybenzhydrazide and 2-pyridine carboxaldehyde (L) has been prepared by condensation of 4-Hydroxybenzhydrazide with 2-pyridine carboxaldehyde respectively in absolute ethanol as solvent. VO-complexes, VOL of this ligand were synthesized by reactions of NH_4VO_3 with ligand. The ligand and its complexes were characterized by X-ray, FT-IR, UV-Vis, $^1\text{H-NMR}$, analysis. And at least chemical behavior of ligand and its complex 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 crystal, in which 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 enzymes Schiff base ligands and their complexes with transition elements by the scientists have been noticed [2]. At recent years the existence of vanadium compounds in the body of sea animals were argued by the scientists.

As for the importance of Schiff base ligands and their complexes, my purpose was in this research synthesis and study of hydrazide Schiff 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 the 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.

VO₂-complex, VO₂L of this ligand were synthesized by reaction of NH₄VO₃ with ligand (L). At first NH₄VO₃ dissolved into 10 ml absolute ethanol and heated for 30 minutes and stirred (because this salt is not a solution in absolute ethanol at normal conditions), then the mixture of Schiff base ligand (L) into the absolute ethanol as solvent 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 reflux 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, ¹H-NMR and investigated the electrochemical behavior. These complexes have a crimson color and were recrystallized into the absolute ethanol and n-hexane solution.

Results and discussion:

Some physical characterization 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 ₂ L	294	65	360	crimson

In figures 1, 2 and 3 the molecular structure of the complex (ammonium vanadate [NH₄VO₃] with ligand L (4-Hydroxybenzhydrazide and 2-pyridine carboxaldehyde)), unit cell and geometry of hydrogen bonds of the complex were shown.

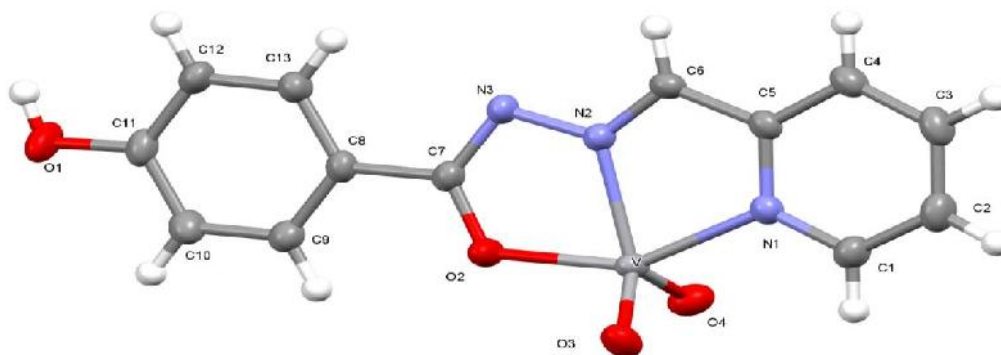


Figure 1: Molecular structure of complex Vanadium with ligand

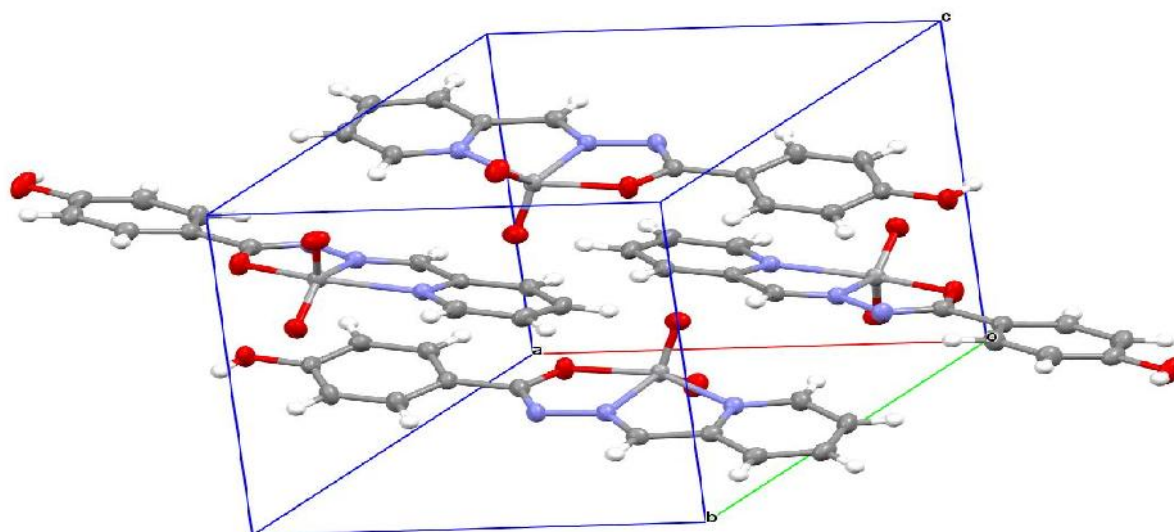


Figure2: Unit cell of complex Vanadium with ligand

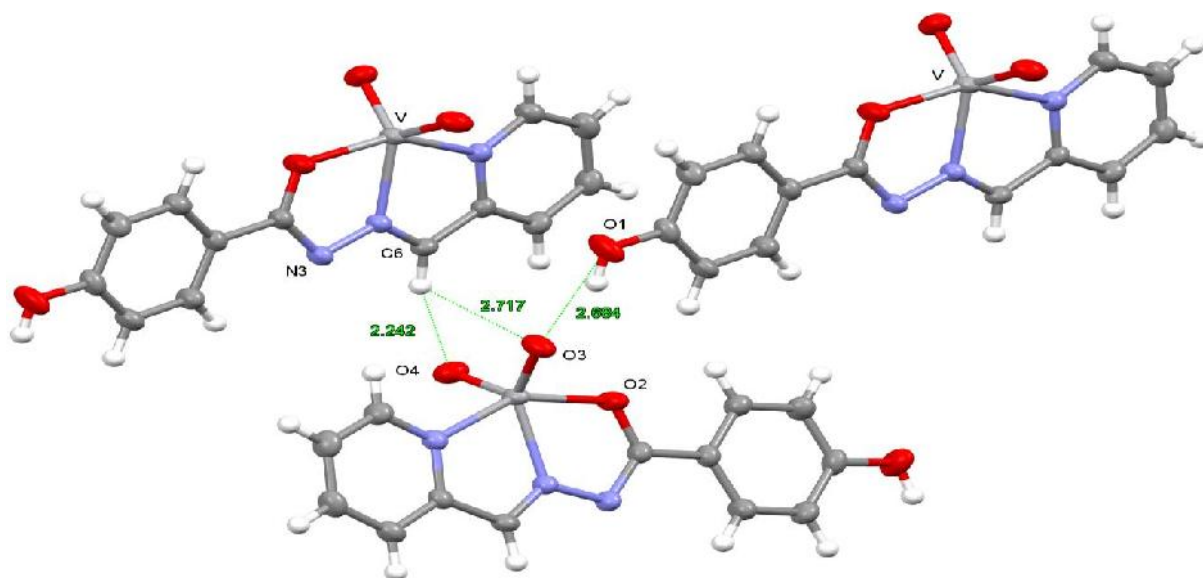


Figure3: The geometry of hydrogen bond of complex Vanadium with ligand

As shown in below tables, table1, 2 and 3, the complete listing of bond distances (table1) 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 (table2), and Complete listing of bond angles (degrees) (table3) 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 (1600cm^{-1}) in the comparison with free ligands (1650cm^{-1}) have shifted to lower wave numbers indicating its coordination to metal center via N atom of imine (C=N) group. Wide peak around 3440cm^{-1} can be attributed to stretching of O-H bond belonging to hydroxyl of ligand at area can be could related to stretch vibration of OH group in complex molecule.



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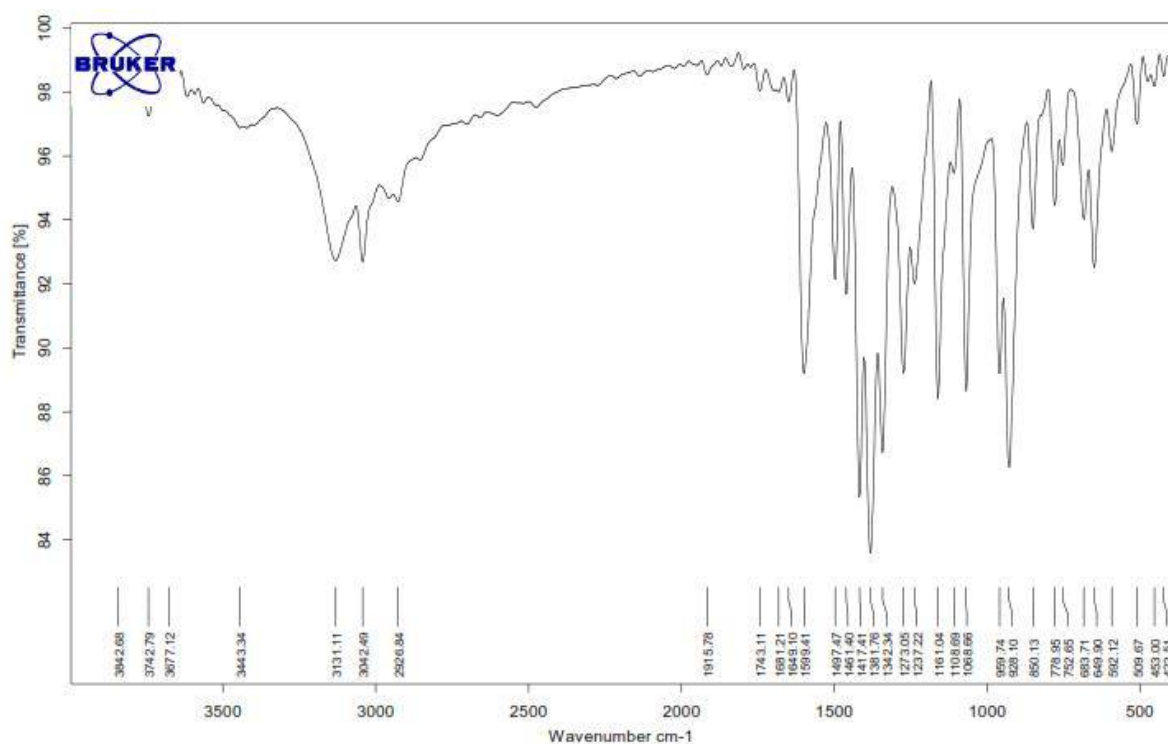
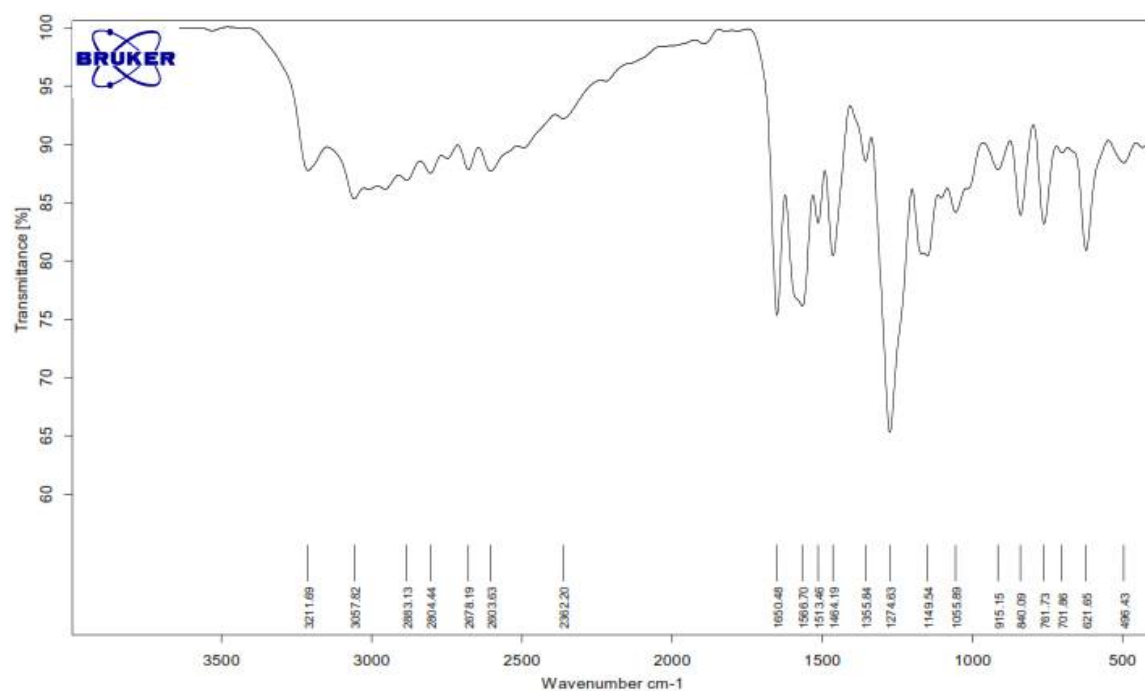


Figure4: FT-IR spectrum of Vanadium with ligand



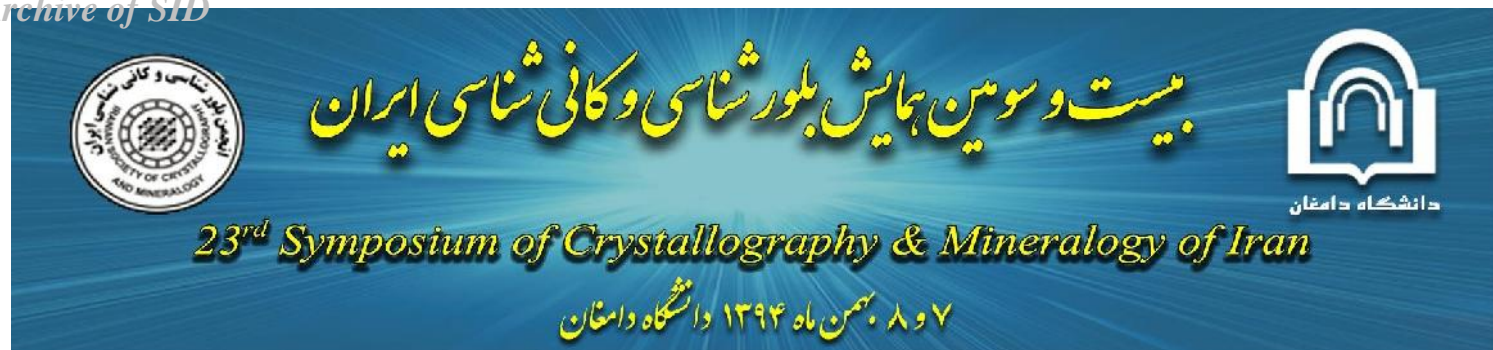


Figure5: FT-IR spectrum of ligand

Conclusion:

With considering X-ray structures and its data about complexes, and spectroscopic data, FT-IR, UV-Vis, ^1H 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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