

**SYNTHESIS AND CHARACTERIZATION OF OXOVANADIUM (IV)  
COMPLEXES WITH NEW SCHIFF BASES****Jitendra Kumar Pandey<sup>1\*</sup>, Shivani<sup>1</sup>, Harikesh Kumar<sup>1</sup>, Amit Masih<sup>1</sup>,  
S D Sharma<sup>1</sup> and Vivek Kumar Gaur<sup>2</sup>**<sup>1</sup>Department of Chemistry, St. Andrew's College, Gorakhpur, India-273001<sup>2</sup>DRDC, Ghaziabad, India**ABSTRACT**

Few oxovanadium (IV) complexes with new Schiff bases derived from different pyridine carboxylic acid hydrazides, has been synthesized and characterized. Tentative structural conclusions were drawn for the complexes based upon elemental analyses, conductances, magnetic moments and spectral (IR, Electronic and EPR) data. The X-band EPR spectra of all the complexes were recorded at room temperature and liquid nitrogen temperature. The room temperature EPR spectra do not show anisotropy because of rapid tumbling of molecules in solution. The spectral studies support square pyramidal geometry for the oxovanadium (IV) complexes.

**KEYWORDS:** Oxovanadium(IV), Schiff bases, IR, electronic, EPR**INTRODUCTION**

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions<sup>1, 2</sup>. Recently, considerable interest has been shown in the preparation of ligands derived from benzil / diacetyl monoxime. Oximes are widely recognized as versatile ligands and a number of complexes with various transition metals have been studied in

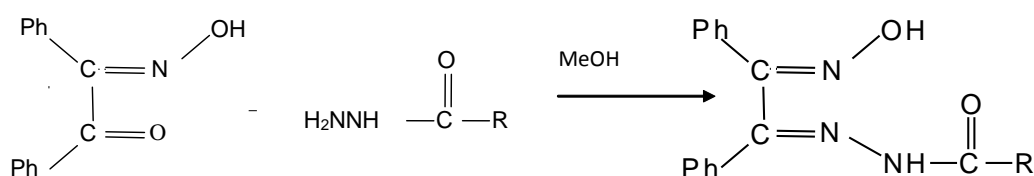
detail and have been reviewed<sup>3-4</sup>, much remains to be learned about the type of structures that are formed. It should be noted that the oxime function is a poor donor unless it is a part of chelate ring. The interest in such complexes continues because of their interesting activity<sup>3</sup> as polymer catalyst, fungicides and bactericides. Ibrahim et.al. reported coordination behaviour of aliphatic and aromatic hydrazone oximes towards first row transition metal ions. The ligational behaviour of biacetyl monoxime-4-phenyl

thiosemicarbazone towards cobalt(III), nickel(II) and copper(II) has been described<sup>5</sup>. Reddy and Lingappa reported<sup>6</sup> copper complexes of different sulphur containing oximes. It should be interesting to study ligands containing both oxime and enol / thiol moieties, as ligands containing mixed functions are expected to show interesting structural and functional properties. In this paper Synthesis of the complexes of oxovanadium (IV) sulphate

with new Schiff bases derived from different pyridine carboxylic acid hydrazides and benzil- $\alpha$ -monoxime and their characterization is reported.

## RESULTS AND DISCUSSION

The condensation of benzil- $\alpha$ -monoxime hydrazones with pyridine carboxylic acid hydrazides in methanol give rise to hydrazone ligands as shown below:



R	Abbreviation
C <sub>6</sub> H <sub>4</sub> N	BMNH <sub>2</sub>
C <sub>6</sub> H <sub>4</sub> N	BMINH <sub>2</sub>
C <sub>6</sub> H <sub>4</sub> N	BMPH <sub>2</sub>

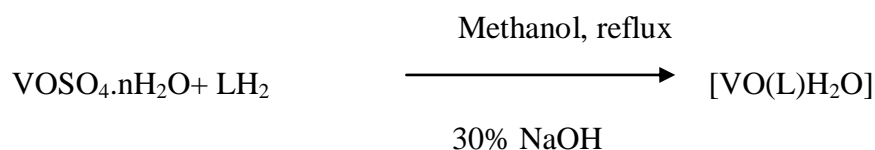
Where,

BMNH<sub>2</sub> = Hydrazone derived from benzil- $\alpha$ -monoxime and nicotinic acid hydrazide

BMINH<sub>2</sub> = Hydrazone derived from benzil- $\alpha$ -monoxime and isonicotinic acid hydrazide

BMPH<sub>2</sub> = Hydrazone derived from benzil- $\alpha$ -monoxime and picolinic acid hydrazide

A systematic study of the reactions of the oxovanadium(IV) sulphate with benzil- $\alpha$ -monoxime hydrazones in presence of sodium hydroxide in methanol was carried out. The [VO (L)H<sub>2</sub>O] type complexes were obtained according to the following equation:



( LH<sub>2</sub> = BMNH<sub>2</sub>, BMINH<sub>2</sub> or BMPH<sub>2</sub> )

The analytical data were compatible with a 1:1 metal to ligand stoichiometry. The complexes were greenish brown coloured solids; soluble in dimethylformamide and dimethylsulphoxide. The electrical conductances of the complexes in

dimethylformamide were consistent with their non-electrolytic nature. The presence of water molecule in the complexes was confirmed by thermogravimetric analysis. The results show the loss of one water molecule at ca. 195–220°C.

Table 1: Reactions of oxovanadium (IV) sulphate with benzyl- $\alpha$ -monoxime hydrazones

Complex	$\mu_{\text{eff}}$ (300K)	Electronic spectral bands( $\text{cm}^{-1}$ )			Charge-transfer bands
		${}^2B_2 \rightarrow {}^2E$	${}^2B_2 \rightarrow {}^2B_1$	${}^2B_2 \rightarrow {}^2B_1$	
[VO(BMN)H <sub>2</sub> O]	1.72	12600	17100	22300	26200
[VO(BMIN)H <sub>2</sub> O]	1.72	12700	17200	21600	26000
[VO(BMP)H <sub>2</sub> O]	1.75	12900	16900	22100	26100

### Magnetic Moments and Electronic Spectra

Room temperature magnetic moments of the oxovanadium(IV) complexes lie in the range 1.70–1.75  $\mu_B$ . These results are consistent with the formulation of the complexes as vanadium(IV),  $d^1$  species [ $\mu_{\text{eff}}$ (spin only)

=1.73 $\mu_B$ ]. The electronic spectral data measured in dimethylformamide are given in Table 1. Molecular orbital calculations by Ballhausen and Gray<sup>7,8</sup> predicts that the single  $d$ -electron in  $\text{VO}^{2+}$  is in the  $b_2$  ( $d_{xy}$  orbital); the predicted absorptions are  $b_2 \rightarrow e$  ( $d_{xz}$ ,  $d_{yz}$ ),

Table 2: Magnetic moments and electronic spectral bands of oxovanadium(IV) complexes with benzil- $\alpha$ -monoxime hydrazones

Reactants	Molar ratio	Refluxing Time (h)	Product	Colour	Yield (%)	Decomp. Temp (°C)
VOSO <sub>4</sub> .5H <sub>2</sub> O+BMNH <sub>2</sub>	1 : 1	25	[VO(BMN)H <sub>2</sub> O]	Greenish brown	60	240
VOSO <sub>4</sub> .5H <sub>2</sub> O+BMINH <sub>2</sub>	1 : 1	20	[VO(BMIN)H <sub>2</sub> O]	Greenish brown	50	160
VOSO <sub>4</sub> .5H <sub>2</sub> O+BMPH <sub>2</sub>	1 : 1	25	[VO(BMP)H <sub>2</sub> O]	Greenish brown	65	230

$b_2 \rightarrow b_1(dx^2-y^2)$  and  $b_2 \rightarrow a_1(dz^2)$ . The spectra of all the complexes show bands at ca. 12500–13000, 16500–17200 and 21500–22400  $\text{cm}^{-1}$ , which are assigned to these transitions, respectively. In addition, the complexes also show one band in the 25,800–26,200  $\text{cm}^{-1}$

range which may be due to a charge-transfer, probably  $d-\pi^*$ .

### Infrared Spectra

The most characteristic features of the IR spectra of benzil- $\alpha$ -monoxime hydrazone

(LH<sub>2</sub>) have been determined by a careful comparison of the spectra of ligands with both pyridine carboxylic acid hydrazides and benzil- $\alpha$ -monoxime. In the oxovanadium(IV) complexes, the ligands behave in a tridentate way, coordinating via the azomethine nitrogen (CN<sup>1</sup>), the oxime oxygen (NOH) and the carbonyl oxygen in the enol form (=C-OH), with displacement of two hydrogens from the latter two groups. The mode of coordination has been determined by careful comparison of the infrared spectra of the complexes with the ligands.

The spectra of ligands show three bands at ca. 1675, 1635 and 1575 cm<sup>-1</sup> assigned to  $\nu$  (CO),  $\nu$  (CN<sup>1</sup>) and  $\nu$  (CN<sup>2</sup>), respectively. The strong band observed at ca. 940 cm<sup>-1</sup> in the spectra of the ligands, which is, absent in the spectra of acid hydrazides, is attributed to the  $\nu$  (N=O) vibration. In addition, the two bands at ca. 3320 and 3170 cm<sup>-1</sup> in the spectra of the ligands are assigned to the oxime NOH and NH groups, respectively.

The bands at ca. 3320 and 1675 cm<sup>-1</sup> attributable to  $\nu$  (OH) and  $\nu$  (C=O) vibrations, respectively, disappear, with the simultaneous appearance of new bands at ca. 1240 and 1645 cm<sup>-1</sup>, assigned to  $\nu$  (C-O)<sup>9,10</sup> and  $\nu$  (C=N), respectively. The negative shift of  $\nu$  (C=N<sup>1</sup>) to a lower wave number and a positive shift of  $\nu$  (NO) to a higher wave number also support complexation. The appearance of new bands in the low frequency region at 440–420 cm<sup>-1</sup> and

395–375 cm<sup>-1</sup> may be assigned to  $\nu$  (V-O) and  $\nu$  (V-N) respectively.

The ligands contain one pyridine ring. The pyridine ring vibrations most affected by pyridine nitrogen coordination to a metal atom or 8a (pyridine ring deformation) 6a (in-plane ring deformation) and 16b (out-of-plane deformation). These vibrations appear at 1550, 1620 and 410 cm<sup>-1</sup>, respectively; in the free ligand. In the oxovanadium(IV) complexes, these bands appear almost at the same position indicating non-coordination of pyridine nitrogen to metal. In complexes, new bands appear at ca. 975 cm<sup>-1</sup>, assignable to  $\nu$  (V=O) vibration<sup>10</sup>. In addition, all complexes show a strong band at ca. 3400 cm<sup>-1</sup> which may be assigned to  $\nu$  (OH) of the coordinated water molecule.

### Electron Spin Resonance Spectra

The X-band ESR spectra of oxovanadium(IV) complexes are recorded at room temperature and at liquid nitrogen temperature. The room temperature spectra exhibit eight lines due to hyperfine splitting of <sup>51</sup>V, whose nuclear spin number I= 7/2. This confirms the presence of a single vanadium (IV) cation, hence the complexes are monomer.

The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and only g-average values are obtained. The g<sub>av</sub> values determined from the spectra are ca. 1.98, similar to the spin-only

value (free electron value) of 2.0023 suggesting little spin-orbital coupling<sup>11</sup>.

The anisotropy is clearly visible in the spectra at liquid nitrogen temperature and bands

due to  $g_{||}$  and  $g_{\perp}$  are observed separately. The  $g_{||}, g_{\perp}, A_{||}$  and  $A_{\perp}$  values are given in Table 3, which are in good agreement for a square-pyramidal geometry.

Table 3: ESR parameters of oxovanadium(IV) complexes with benzil- $\alpha$ -monoxime hydrazones

Complex	$g_{av}$	$g_{  }$	$g_{\perp}$	$A_{av}$	$A_{  }$	$A_{\perp} \times 10^4 \text{ cm}^{-1}$
[VO(BMN)H <sub>2</sub> O]	1.980	1.970	1.986	106.88	187.46	66.60
[VO(BMIN)H <sub>2</sub> O]	1.981	1.967	1.989	108.73	192.00	67.10
[VO(BMP)H <sub>2</sub> O]	1.977	1.972	1.980	108.00	190.00	67.00

## Experimental

All the chemicals used were of AnalaR grade. All solvents used were distilled before use. The ligands were prepared by the condensation of benzil- $\alpha$ -monoxime with appropriate hydrazide as reported in the literature.

## Preparation of complexes

Oxovanadium(IV) sulphate (0.01mol) in methanol (20 cm<sup>3</sup>) was added to a refluxing methanolic solution (20 cm<sup>3</sup>) of

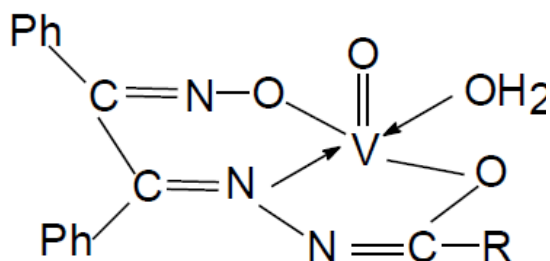
ligands(0.01mol) containing aqueous ethanolic solution of sodium hydroxide (30%, 5 cm<sup>3</sup>). The reaction mixture was refluxed for 15- 25 h, when colour of the solution changed from greenish-blue to greenish brown. The volume of the solution was reduced. Dark greenish brown coloured crystalline precipitate was obtained on keeping the solution in refrigerator for 6 h, which was filtered off, washed with cold methanol and ether and dried in vacuo. Yield: 50-60%.

Table 4: Analytical data of oxovanadium (IV) complexes with with benzil- $\alpha$ -monoxime hydrazones

Complex	Molecular formula	Found (%)				Calcd. (%)			
		C	H	N	V	C	H	N	V
[VO(BMN)H <sub>2</sub> O]	[C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> V]	56.1	3.6	13.0	11.8	56.2	3.8	13.1	11.9
[VO(BMIN)H <sub>2</sub> O]	[C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> V]	56.4	3.5	13.2	11.6	56.2	3.8	13.1	11.9
[VO(BMP)H <sub>2</sub> O]	[C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> V]	56.0	3.6	12.9	11.5	56.2	3.8	13.1	11.9

## CONCLUSION

On the basis of the studies, the following structure may be tentatively proposed for these oxovanadium (IV) complexes:



## ACKNOWLEDGEMENTS

Authors are thankful to the Principal, St. Andrew's College, Gorakhpur for his support and providing laboratory & library facilities.

## REFERENCES

1. M. R. Yaftian, S. Rayati, R. Safarballi, N. Torabi., *Trans. Met. Chem.*, 32, 374(2007).
2. P. P. Dholakiya, M. N. Patel, *Synth. React. Inorg. Met-Org. Chem.*, 32, 753(2002).
3. A. Chakravorty, *Coord. Chem. Rev.*, 13, 1(1974).
4. V.K. Sharma, O.P. Pandey and S.K. Sengupta, *Synth. React. Inorg. Met.-Org. Chem.*, 21, 1587 (1991).
5. R. Ghosh, K. Ray, R. Saha and P. Koky, *Indian J. Chem.*, 23A, 245(1984).
6. K.H. Reddy and Y. Lingappa, *Transition Met. Chem.*, 19, 487(1994).
7. C.J. Ballhausen and H.B. Gray, *Inorganic Chem.*,1, 111(1962).
8. N.S. Biradar, B.R. Patil and V.H.Kulkarni, *J.Inorg. Nucl. Chem.*,37, 1901(1975).
9. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination compounds", Wiley Interscience, New York,1970.
10. J.K.pandey, H. Kumar and Km Shivani, *Int. J. Res. Eng. Biol.*,2(5),81(2014).