

# SYNTHESIS AND MAGNETO-SPECTRAL STUDIES OF THE TERNARY COMPLEXES OF VO (IV) AND ZrO(IV)

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**Abstract:** Oxovanadium (IV) is one of the most stable and well established oxo metal species. Vanadium complexes have considerable attention recently due to their biochemical importance. Vanadium may replace molybdenum in nitrogenase with maintenance of enzymatic activity, complexes of oxovanadium (IV & V) have been reported as potential antimicrobial, insect sterilizing and ovicidal agents. Oxovanadium (IV) chelates of teradentate Schiff bases have been used as model compounds for some naturally occurring vanadium complexes. Oxovanadium (IV) complex of the schiff base derived from salicylhydrazide-6-methyl-4-hydroxy-3-acetyl coumarin has been reported. Oxovanadium (IV) complexes with isonitrosoacetophenone thiosemicarbazone and 4-chloroisnitrosoacetophenone thiosemicarbazone have been synthesized and characterized. Mixed ligand complexes of oxovanadium (IV) with indole-3-thiohydrazide as primary and 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carboxylic acid as co-ligand has been synthesized and characterized on the basis of analytical, conductance, magnetic and spectral studies.

**Keywords:** Oxovanadium, magnetic moments, carboxyazobenzene, Spatial Bands

## Introduction

Spectral and thermal investigation of some biligand complexes of VO(IV) and ZrO(IV) has been carried out by Agarwal and Lal. Few Schiff base complexes of VO(IV) possessing subnormal magnetic moment, are reported in the literature. Sinha and co-workers have reported oxovanadium(IV) complexes with imidazole, benzimidazole and substitute benzimidazoles. Because of the presence of vacant inner d-orbital, zirconium has tendency to expand its covalency with corresponding increase in co-ordination number. Co-ordination number greater than that of four is achieved by donation of electrons from ligand in to the d-orbitals of zirconium ion. The co-ordination number of Zr<sup>4+</sup> in oxozirconium(IV) complexes varies from 5 to 8, but the co-ordination number 5 & 7 are quite common. Ramamurthy and Patel were the first to synthesize pyridine-N-oxide complexes of oxozirconium(IV) perchlorate and found that the C.N. of Zr in this complex is 7 and has the face-centred octahedral or trigonal prismatic geometry. Agarwal and Rastogi have also studied the ligational behaviour of 4-cyanopyridine-N-oxide towards oxozirconium(IV) ions and found that the order of stability of the complexes is:  $I < ClO_4 < NCS < Br < Cl < NO_3$ .

Determination and separation of Zr(IV) was carried out by Sinha and co-workers using 2'-mercapto maleianilic acid as gravimetric reagent. Complexes of Zr(IV) with Mannich bases  $\beta$ -(p-dimethyl-aminoanilino)-methyl salicylic acid hydrazide and  $\beta$ -( $\alpha$ -naphthylamino)-2, 3, 4-trihydroxy propiophenone with 1:2 (M:L) stoichiometry have been prepared and characterized. Some oxozirconium(IV) Schiff base complexes have been studied by Shukla and co-workers. Some macrocyclic complexes of ZrO(IV) have been prepared and investigated.

## Review of Related work

The configuration with the maximum possible number of unpaired electrons are called the high-spin configuration, and those with the minimum number of unpaired spins are called the low-spin or spin-paired configuration. The electronic spectra have been used in the past in assigning the tetrahedral, square planar and octahedral geometries as well as polymeric intra-molecular linkages. Actually, electronic spectral studies include the correlation of the physical properties of compounds with the nature and position of the ligand atoms which surround the central ion. These measurements have been found competent to explain satisfactorily the deviation in magnetic moment values of transition metal complexes from spin-only values. The ternary complexes of Cr(III) and Fe(III) with isonitrosoacetophenone-naphthalene-1-acetic acid hydrazides as primary and thiourea, N-phenylthiourea and thioacetamide as co-ligand exhibited bands in the range 17,400-17,800 cm<sup>-1</sup> and 23,100-23,500 cm<sup>-1</sup> in former case which may be assigned to the following transitions:

$^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$  and

$^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$

These transitions are characteristic of an octahedral stereochemistry of Cr(III) complexes. In later case Fe(III) complexes exhibited bands in the range 16,650-17,100, 21,800-22,200 and 24,700-25,100 cm<sup>-1</sup>. These bands are tentatively assigned as:

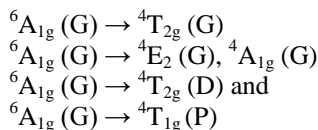
$^6A_{1g} \rightarrow ^4T_{1g}(G)$ ,

$^6A_{1g} \rightarrow ^4T_{2g}(G)$  and

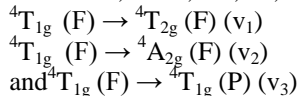
$^6A_{1g} \rightarrow ^4E_g(G)$

Parameters 10 Dq, B and  $\beta$  for the complexes have been calculated. The electronic spectra of the ternary complexes of Mn(II), Co(II & III), Ni(II) and Cu(II) with 4-chloroisnitrosoacetophenone nicotinic acid hydrazide as primary and thiosalicylic acid and 2-amino thiophenol as co-ligands was studied. In Mn(II) complexes, the electronic spectra exhibit the bands in the range- 18,400-18,800, 22,600-23,200, 24,800-25,300, 28,500-29,000 and 34,800-35,300 cm<sup>-1</sup> which may be assigned to the following transitions:

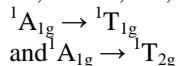
$^6A_{1g}(G) \rightarrow ^4T_{1g}(G)$



These spectral observations indicated octahedral stereochemistry of Mn(II) complexes. The electronic spectra of the Co(II) complexes show bands at 9,600-9,800, 17,800-18,400 and 21,600-22,300  $\text{cm}^{-1}$  corresponding to



transitions respectively, characteristic of octahedral geometry. In Co(III) complexes, the electronic spectra exhibit three bands in the range 19,000-19,400, 25,600-26,100 and 34,000-34,450  $\text{cm}^{-1}$ . The first two bands are assigned to the following transitions:



The third band may be due to charge transfer transition. The observed bands suggest the octahedral geometry for the complexes under study. The electronic spectra of Ni(II) complexes exhibit a d-d band in the range 17,600-13,850  $\text{cm}^{-1}$ ,  $v_3$  band in 22,700-23,000  $\text{cm}^{-1}$  and one weak band ( $v_1$ ) at 12,200-12,350  $\text{cm}^{-1}$  corresponding to square planar geometry. In some Ni(II) complexes the spectra exhibit three bands at 9,750-10,000, 14,900-15,300 and 24,800-25,400  $\text{cm}^{-1}$  corresponding to octahedral field around Ni(II) ion. The visible spectra of Cu(II) complexes exhibit a band in 15,200-15,500  $\text{cm}^{-1}$  range characteristic of the transition  ${}^3B_{1g} \rightarrow {}^2B_{2g}$ , and another band at 18,650-18,980  $\text{cm}^{-1}$  range assignable to the transition  ${}^2B_{1g} \rightarrow {}^2E_g$ . The transitions indicated the presence of square planar environment of the ligand molecules around the metal ion. In some Cu(II) complexes the electronic spectra show a broad asymmetric ligand field band in 14,000-15,000  $\text{cm}^{-1}$  range along with a CT band in the range 25,700-26,200  $\text{cm}^{-1}$ . The ligand field band can be assigned to the transition  ${}^2E_g \rightarrow {}^2T_{2g}$  in a distorted octahedral field under  $D_{4h}$  symmetry.

### MEGNATIC STUDIES

At room temperature the magnetic moments of the VO(IV) complexes (Table-6.2) lie in the 1.84-1.87 BM which is quite near to the spin-only value corresponding to one-unpaired electron. The normal values show that the spin-spin interaction does not exist in these compounds. In these complexes orbital contribution is almost quenched. These values are in the range of VO(IV) complexes having symmetry lower than octahedral. These values also suggest that there is no significant antiferromagnetic interaction between pairs of VO(IV) ions in the said complexes in solid state. These complexes, therefore, show penta co-ordinated configuration and in the absence of steric hindrance they are expected to possess square pyramidal structure with donor atoms of the ligands in square plane and the oxygen atom of VO(IV) placed at the axial position.

ZrO(IV) complexes are diamagnetic.

### ELECTRONIC SPECTRA

Selbin in the two review articles has summarized the electronic spectral data of a of VO(IV) complexes. In these complexes, three low intensity absorption bands are observed in the spectral region 8,300-28,600  $\text{cm}^{-1}$ . These are often called d-d or ligand field bands, but for convenience Selbin refer to these as band-I (between 11,000-16,000  $\text{cm}^{-1}$ ), band-II (between 14,500-19,000  $\text{cm}^{-1}$ ) and band-III (between 21,000-30,000  $\text{cm}^{-1}$ ). In these cases, the band-III is not always observed, being often buried beneath a high intensity charge transfer band. According to Vonquickenbome and Mc Glynn, the first band which is centered in the 11,000-16,000  $\text{cm}^{-1}$  has been assigned to an unresolved band resulting from  $dxy \rightarrow dyz$ ,  $dxz$  ( ${}^2B_2 \rightarrow {}^2E$ ) transition. The second shoulder observed in 14,500-19,000  $\text{cm}^{-1}$  range is attributed to  $dxy \rightarrow dx^2-dy^2$  ( ${}^2B_2 \rightarrow {}^2B_1$ ) and the third band may be assigned to the transition  $dxy \rightarrow dz^2$  ( ${}^2B_2 \rightarrow {}^2A_1$ ).

Table 1.1 Spatial Bands( $\text{cm}^{-1}$ ), Dq, Ds and Dt Values VO(IV) Ternary Complexes

S. No.	COMPLEX	BAND-I	BAND-II	BAND-III	Dq( $\text{cm}^{-1}$ )	Ds( $\text{cm}^{-1}$ )	Dt( $\text{cm}^{-1}$ )
1	2	3	4	5	6	7	8
1.	$[\text{VO}(\text{C}_{12}\text{H}_{10}\text{N}_2\text{SO}_2)(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)]\text{Cl}$	12,250	17,300	23,000	1730	-3524	1679
2.	$[\text{VO}(\text{C}_{17}\text{H}_{13}\text{N}_3\text{S})(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)]\text{Cl}$	13,000	16,500	23,300	1650	-3779	1663
3.	$[\text{VO}(\text{C}_{13}\text{H}_{11}\text{N}_3\text{S})(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)]\text{Cl}$	12,600	16,900	23,200	1690	-3647	1658

The spectra of the ternary complexes of VO(IV), under study, show bands at 12,250-13,000, 16,500-17,300 and 23,000-23,300  $\text{cm}^{-1}$  corresponding to d-d transitions. In addition to these bands, some high intensity bands also occur in the spectra which exist in ultra violet region. On the basis of the position spectral bands, a five co-ordinate square-pyramidal structure is suggested for the ternary complexes. The spectral band along with the calculated values of Dq, Ds (axial parameters) and Dt (equatorial parameter) are tabulated in Table-6.3. Ds and Dt have been calculated with the help of the following equations:

$$-3D_s + D_t = 12,250-13,000 \text{ cm}^{-1} \dots\dots\dots(1)$$

$$10 D_q = 16,500-17,300 \text{ cm}^{-1}$$

10Dq -4Ds-5D = 23,000-23,300 cm<sup>-1</sup>

## IR STUDIES

The mode of linkage of the attached ligands is ascertained by the careful comparison of the IR spectra of the ligands with those of ternary complexes.

$\nu(\text{C}=\text{N})$  bands in region 1,650-1,620 cm<sup>-1</sup> in heterocyclic thiohydrazones, under study show a negative shift of 15-25 cm<sup>-1</sup> in spectra of all the complexes suggesting that the metal ion is co-ordinated through azomethine nitrogen. Further, the shifting of a medium band due to  $\nu(\text{N}-\text{N})$  (960-950 cm<sup>-1</sup> in ligands) to higher frequency region (980-970 cm<sup>-1</sup>) in all the ternary complexes supports the N-bonding of the C=N group to the central metal ions. Thioamide bands-I & II in region 1,530-1,515 cm<sup>-1</sup> and 1,305-1,290 cm<sup>-1</sup> respectively in the spectra of heterocyclic thiohydrazones show positive shift of cm<sup>-1</sup> and 10-30 cm<sup>-1</sup> in the spectra of all the ternary complexes this change in the position of the thioamide bands (compared with ligands) is indicative of the participation of sulphur of the thioamide group in band formation with metal ions. The positive shift in these bands in all the ternary complexes are due to co-ordination through sulphur.  $\nu(\text{C}=\text{S})$  vibrations, characteristic of thiocarbonyl group observed in region 840-810 cm<sup>-1</sup> get shifted to a lower frequency region 800-785 cm<sup>-1</sup> in the spectra of all ternary complexes which is suggestive of the co-ordination of thiocarbonyl sulphur in thione form in the complexes. The bands due to N-H group in region 3,190-3,175 cm<sup>-1</sup> is located at the same position in the spectra of all the complexes showing that the nitrogen of the imino group is not involved in the bonding.

The pyridine ring vibrations are found as such in the complexes with 2-pyridine-2-carboxaldehyde-1'-thionaphthoyl-hydrazone and 2-pyridine-2-carboxaldehydethiobenzoylhydrazone as primary ligands showing that pyridinic nitrogen is not involved in co-ordination in these ternary complexes. While in ternary complexes at serial nos. 4-6 (Table-6.4) these vibrations are shifted from 1,600-1,400 cm<sup>-1</sup> region to higher frequency region 1,640-1,450 cm<sup>-1</sup> showing that pyridinic nitrogen is involved in co-ordination in these ternary complexes. In addition, a positive shift (10-15 cm<sup>-1</sup>) has been observed in the vibrations associated with C-H out of plane deformation  $\nu(\text{C}-\text{H})$  due to tightening of the aromatic ring on complexation.

A band observed at 1,610 cm<sup>-1</sup> and 1,615 cm<sup>-1</sup> respectively in the spectrum of CPANA and 2-hydroxy-5-methyl-2'-carboxyazobenzene, assigned to  $\nu \text{N}=\text{N}$  gets shifted to ~1,590-1,580 cm<sup>-1</sup> in all ternary complexes under study, showing the co-ordination through nitrogen atom of azo group.

In the spectra of all ternary complexes, appearance of bands at ~1,620 cm<sup>-1</sup> and ~1,425 cm<sup>-1</sup> instead of 1,590 cm<sup>-1</sup> and 1,400 cm<sup>-1</sup> (in the spectrum of ligand) corresponding to  $\nu_{\text{asym}} \text{COO}$  and  $\nu_{\text{sym}} \text{COO}$  vibration confirm chelation through the O-atom of the deprotonated carboxyl group of CPANA and HMCAB. The observed difference ( $\Delta \nu_{\text{COO}} \sim 190 \text{ cm}^{-1}$ ) further supports the fact. The frequency band characteristic of  $\nu \text{C}=\text{O}$  appearing in region 1,720-1,715 cm<sup>-1</sup> in the spectrum of CPANA and 2-hydroxy-5-methyl-2'-carboxyazobenzene remains unaltered.

## Conclusion

The synthesized ternary complexes of VO(IV) and ZrO(IV) are non-hygroscopic and air stable. These are less soluble in common organic solvents but fairly soluble in DMF and DMSO. Analytical data reported in Table-8.1 suggested the composition of the ternary complexes of VO(IV) and ZrO(IV) are  $[\text{VO}(\text{L})_2]\text{Cl}$  and  $[\text{Zr}(\text{O}(\text{L})_2)(\text{H}_2\text{O})]\text{Cl}$  respectively (where L=hydroxylbenzene-2-carboxaldehyde-2'-furanthiocarboxyhydrazone / pyridine-2-carboxaldehyde-1'-thionaphthoylhydrazone / pyridine-2-carboxaldehydethiobenzoylhydrazone and  $\text{L}_2'\text{H} = 2\text{-hydroxy-5-methyl-2'-carboxyazobenzene}$ ). A white curdy precipitate is obtained by the addition of alcoholic silver nitrate to the solution of all the complexes showing the presence of ionic chlorid in them.

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