

OXOVANADIUM (IV) COMPLEXES OF 3-(2-CARBOXY, 2HYDRXY DIPHENYL AMINO METHYL) SALICYLIC ACID HYDRAZIDE AND 3-(DIPHENYL AMINO METHYL) 5-MITRO SALICYLIC ACID HYDRAZIDE

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Abstract

All the synthesised Oxovanadium (IV) coordination compounds show magnetic moment values in the range 1.69 - 1.73 B.M. which are quite near to the spin-only value of one unpaired electron as expected in the case of Oxovanadium (IV) complexes. The normal magnetic moment values show that the spin-spin interaction does not exist in them.

Keywords: Vanadium Chelates.

Introduction

The oxometal cation, VO^{+2} is regarded to possess very high stability. This ion forms stable complexes with different ligands. The complexes of VO^{+2} with macrocyclic ligand derived from 2, 6-dipicolinoyl-dihydrazine and β -diketones have been studied. The stability constants of chelates of $4-$ (O-Methoxy phenyl) thiosemicarbazide with Ni^{+2} and VO^{+2} metal ions have been determined by Saxena and Agarwal. Oxovanadium chelates of tetradentate Schiff bases have been used as model compounds for some naturally occurring vanadium complexes. The synthesis and characterization of some tetradentate Schiff base complexes of Oxovanadium (IV) has been reported. Few Schiff base complexes of VO^{+2} possessing subnormal magnetic moment are reported in literature. A few of them are synthesised from the hydrazones of salicylaldehyde and their various stereochemistries viz. D_{3h} , D_{4h} , D_{3v} , or C_{2v} have been discussed in detail. Few dimeric compounds, with phenoxide or Vanadyl - oxygen bridged, having subnormal magnetic moments, are more common.

Thorough survey of the literature showed that the coordination compounds of Oxovanadium (IV) with acid hydrazide Mannich bases, namely - 3-(2-carboxy, 2'-hydroxy diphenyl amino methyl) salicylic acid hydrazide (CHDAHSAH) and 3-(Diphenyl amino methyl) 5-nitro salicylic acid hydrazide (DMSAH), have not so far been studied. It was, therefore, thought to synthesize these coordination compounds and study their structures. In the present chapter we are aimed to establish the structure of these compounds on the basis of analytical, conductance, magnetic moment, electronic and IR spectral measurements.

Preparation and Isolation of Compounds:

**$VO(CHDAMSAH)Cl$, $VO(DAMNSAH)Cl$,
 $VO(CHDAMSAH)Br$, $VO(DAMNSAH)Br$,
 $VO(CHDAMSAH)NO_3$ and $VO(DAMNSAH)NO_3$**

For preparation of coordination compounds vanadyl sulphate ($VOSO_4 \cdot 2H_2O$) of DH nitrate has been used. The chloride, bromide and nitrate salts have been obtained by the interaction of equimolar solutions of vanadyl sulphate and the appropriate barium salts. After the removal of precipitated barium sulphate from the hot solution, the filtrate has been put to vacuum distillation. Vanadyl chloride gave crystals, while the synthesis of the

co-ordination compounds of vanadyl bromide and vanadyl nitrate has been carried out by using the concentrated solutions, Ethanolic solution of the respective vanadyl salt was added to the hot ethanolic solution of the ligand (10 m mol). The mixed solution was thoroughly stirred and refluxed for about an hour over a water bath. The solution on concentration and cooling yielded crystalline products. The compounds were filtered, washed with distilled water, ethanol and dried in a oven at ~ 80°C. Yield ~58 % these compounds are insoluble in water and common organic solvents i.e. chloroform, acetone, ethanol, methanol but their considerable solubility was observed in DMF and DMSO.

Result and Discussion:

Vanadium metal was determined gravimetrically by the reported procedure. Elemental analysis (Table - I) of the synthesised co-ordination compounds showed 1:1 (Metal-Ligand) stoichiometry. The compounds are stable and non-hygroscopic. The color, melting point and the conductivity data are also recorded in Table - I. The molar conductance values in DMSO lie in the range 39.8 - 41.2 ohm⁻¹ cm² mol⁻¹ indicating the

1:1 electrolytic nature of the co-ordination compounds. Thus the anions are not co-ordinated in any case.

Magnetic and Electronic Spectral Studies:

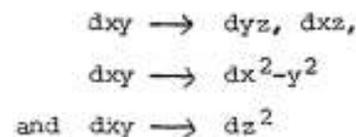
All the synthesised Oxovanadium (IV) co-ordination compounds show magnetic moment values in the range 1.69 - 1.73 B.M. which are quite near to the spin-only value of one unpaired electron as expected in the case of Oxovanadium (IV) complexes. The normal magnetic moment values show that the spin-spin interaction does not exist in them.

The Oxovanadium (IV) complexes probably exhibit penta co-ordinated molecules and in the absence of steric hindrance they are expected to have square pyramidal structure with co-ordinating atoms of the Mannich bases in the square plane and the oxygen atom in the axial position. The effective electronic configuration of Oxovanadium (IV) is d¹. For Oxovanadium (IV) compounds (d¹), only one spin allowed band is expected due to the transition ${}^2T_{2g} \rightarrow {}^2E_g$ in octahedral.

TABLE-I
Ox vanadium (IV) Co-Ordination Compounds of Chadmsah and Damn Sah

Compounds	Analysis %: Calcd. (Found)					Colour	M.P (°C.)	μ _{eff} M.P.	Conductivity ΔM (Ohm ⁻¹ cm ² Mo ⁻¹)
	Metal	C	H	N	Halogen				
[Vo(C ₂₁ H ₁₈ N ₃ O ₅)]Cl	10.30 (10.24)	50.96 (49.94)	3.64 (3.60)	8.49 (8.44)	7.17 (7.10)	Green	152	1.69	39.8
[Vo(C ₂₀ H ₁₇ N ₄ O ₄)]Cl	10.62 (10.70)	50.05 (48.95)	3.54 (3.52)	11.68 (10.61)	7.40 (7.34)	Brown	168	1.71	41.0
[Vo(C ₂₁ H ₁₈ N ₃ O ₅)]Br	9.45 (9.49)	46.76 (47.84)	3.34 (3.38)	7.79 (7.84)	14.82 (14.70)	Green	146	1.73	40.8
[Vo(C ₂₀ H ₁₇ N ₄ O ₄)]Br	9.72 (9.63)	45.81 (46.74)	3.24 (3.26)	10.69 (10.62)	15.25 (15.40)	Brown	175	1.70	41.2
[Vo(C ₂₁ H ₁₈ N ₃ O ₅)]No	9.77 (9.72)	48.37 (47.38)	3.45 (3.40)	10.74 (10.71)	--	Green	158	1.71	41.0
[Vo(C ₂₀ H ₁₇ N ₄ O ₄)]No	10.06 (9.90)	47.43 (46.49)	3.36 (3.32)	15.41 (15.34)	--	Green	184	1.73	40.6

environment but on lowering of the symmetry T_{2g} and E_g terms yield B_{2g}, E_g and ¹A_{1g}, B_{2g} terms as a result of further splitting. The d-orbitals of Vanadium get Split giving the following electronic transitions:



Oxovanadium (IV) complexes generally exhibit three bands lying in the range 11,000 to 15,000 cm⁻¹

¹ (band I), 15,000 to 20,000 cm⁻¹ (band II) and 21,000 to 30,000 cm⁻¹ (band III), corresponding to d-d transitions,



and ${}^2B_2 \rightarrow {}^2A_1$ respectively.

The present co-ordination compounds of Oxovanadium (IV) show bands at 12,500 - 12,800

and 16,800 - 17,130 cm⁻¹ and a weak shoulder at about 22,500 cm⁻¹. On the basis of electronic spectral studies five co-ordinate square pyramidal structure is suggested for these compounds. The electronic spectral bands are tabulated in Table - II.

IR Studies:

Significant structural changes have taken place in the ligands on chelation with metal ion. Diagnostic IR

Table - II

ELECTRONIC SPECTRAL DATA OF OXOVANADIUM (IV) CO-ORDINATION COMPOUNDS WITH 3 - (2 - CARBOXY, 2' - HYDROXY DIPHENYL AMINO METHYL SALICYLIC ACID HYDRAZIDE AND 3 - (DIPHENYL AMINO METHYL) 5 - NITRO SALICYLIC ACID HYDRAZIDE

Sl. No.	Compounds	Band I and its assignments	Band II and its assignments	Band III and its assignments
1.	[Vo (C ₂₁ H ₁₈ N ₃ O ₅)] Cl	12,650	² B ₂ → ² E	16,800 ² B ₂ → ² B ₁ 22,450
2.	[Vo (C ₂₀ H ₁₇ N ₄ O ₄)] Cl	12,500	-	16,950 24,500
3.	[Vo (C ₂₁ H ₁₈ N ₃ O ₅)] Br	12,800	-	17,100 22,480
4.	[Vo (C ₂₀ H ₁₇ N ₄ O ₄)] Br	12,700	-	17,100 22,500
5.	[Vo (C ₂₁ H ₁₈ N ₃ O ₅)] NO ₃	12,750	-	17,150 22,500
6.	[Vo (C ₂₀ H ₁₇ N ₄ O ₄)] NO ₃	12,680	-	17,100 22,450

frequency bands, characteristic of co-ordination are summarized in Table - III.

The ligands show a band at about 3,260 cm⁻¹ due to the superimposed stretching vibrations of -NH bands of the hydrazide amino and amino groups. It suffers a depression of 40 - 60 cm⁻¹ in the chelates, which clearly shows the co-ordination of hydrazinic -NH₂ to the metal ion. Further a strong band. (amide I st band) found at about 1,650 cm⁻¹ in the spectra of ligands (CHDAMSH and DAFNSAH), shows a negative shift of 25 - 35 cm⁻¹ the chelates species. This indicates the participation of the carbonyl oxygen in co-ordination.

On a careful comparison of the IR spectra of the ligands with that of Oxovanadium (IV) co-ordination compounds, it is observed that the

absorption band characteristic of phenolic -OH group, found at 3,470 - 3,480 cm⁻¹ in the spectra of ligands, is found slightly weak in the spectra of CHDAMSAH co-ordination compounds while this band is absent in the spectra of DAMNSAH co-ordination compounds.

The weak intensity of the band (due to -OH) in the spectra of CHDAMSAH co-ordination compounds seems to be due to the deprotonation of only one phenolic group during the process of co-ordination. The phenolic -OH group present in the amino moiety is assumed not to take part in co-ordination as this is not suitably located for taking part in chelation. The band observed at 1,320 cm⁻¹ in the spectra of the ligand (due to tertiary amino group) gets shifted to lower frequency region.

TABLE—III
MAIN IR FREQUENCY BANDS WITH THEIR ASSIGNEMENTS IN OXOVANDIUM (IV) COMPLEXES WITH CHDAMSAN AND DAMNSHA

Compounds	νC=O	ν NH ₂	νC-N (Tertiary amine)	ν V=O	ν C-H (Aromatic)	ν M-O	ν M-N	νM-X	νCN+ S NH
[VO(C ₂₁ H ₁₈ N ₃ O ₅)Cl]	1615sh	3220	1290	980	30 25 w	660	580	240	1545
[VO(C ₂₁ H ₁₈ N ₃ O ₅)Cl]	1620sh	3205	1280	975	30 20 w	655	590	240	1550
[VO(C ₂₁ H ₁₈ N ₃ O ₅)Br]	16120sh	3200	1280	980	30 15 m	650	585	180	1550
[VO(C ₂₁ H ₁₈ N ₃ O ₅)Br]	1610sh	3210	1285	985	30 20 w	655	570	175	1545
[VO(C ₂₁ H ₁₈ N ₃ O ₅)NO ₃]	1620sh	3200	1280	980	30 25 w	655	580	--	1550
[VO(C ₂₁ H ₁₈ N ₃ O ₅)NO ₃]	1615sh	3215	1290	975	30 20 w	660	575	--	1540

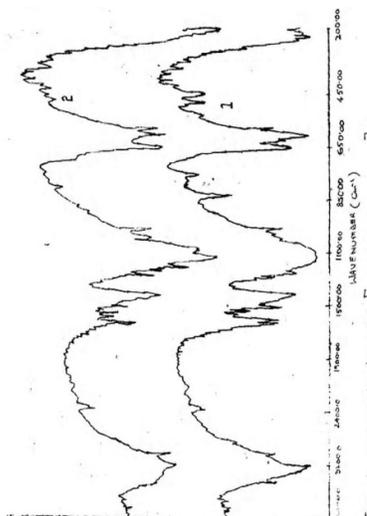


Fig 1 IR Spectra of $[VO(C_{20}H_{17}N_4O_2)_2]NO_3$
 Fig 2 IR Spectra of $[VO(C_{21}H_{18}N_3O_5)Cl]$

i.e. $1,290 - 1,280\text{ cm}^{-1}$ in the spectra of coordination compound which suggests the nitrogen atom also takes part in the process. Thus both the ligands show tetrahedral nature in their co-ordination compounds under study.

The frequency bands observed at $1,640$ and $1,415\text{ cm}^{-1}$ in the spectra of CHDAMSAH (due to $\nu(\text{C=O})$) and in the spectra of DAMNSAH at $1,305\text{ cm}^{-1}$ (due to nitro group), are found almost at the same positions in the spectra of their co-ordination compounds with Oxovanadium (IV) which suggests that they do not take part in chelation.

The appearance of a band at about $1,355\text{ cm}^{-1}$ in the spectra of last two co-ordination compounds shows the presence of ionic nitrate in these compounds. The frequency band due to $\nu(\text{M-Cl})$ and $\nu(\text{M-Br})$ are observed at Ca. 240 and $175 - 180\text{ cm}^{-1}$ respectively. Vanadium-oxygen stretching frequency band, characteristic of VO multiple bond, is seen at $\sim 980\text{ cm}^{-1}$ in the spectra of these co-ordination compounds. The appearance of two new bands in the regions $660 - 650\text{ cm}^{-1}$ and $590 - 570\text{ cm}^{-1}$ in the spectra of these compounds suggested M-O and M-N bond formation respectively.

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