

Synthesis and Characterization of Oxovanadium(IV) Complexes Derived from Schiff Bases

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Schiff bases like 5-chloro salicylaldehyde morpholine N-thio hydrazone (SMTH), butyrophenone semicarbazone (BSC), 3-hydroxy benzaldehyde isonicotinic acid hydrazone (HBINAH) and bis(2-hydroxy-1-naphthaldehyde)malonyl dihydrazone BNHMDH are formed by the condensation of different carbonyl and amino compounds. The complexes of these Schiff bases of VO(IV) have been synthesized and characterized by elemental analyses, molar conductance, infrared and electronic spectral studies.

Key Words: Oxovanadium(IV) complexes, Schiff bases.

INTRODUCTION

There is growing interest^{1,2} on the chemistry of hydrazones derived from acid hydrazides and aldehydes/ketones due to their structural and biological significance.

The chemistry of oxovanadium(IV) has received considerable attention³ as the VO²⁺ unit can readily coordinate four, five and six donor atoms to form VOL₄, VOL₅ and VOL₆ type of complexes⁴, respectively. Additional interest has been generated due to the discoveries of the interesting biological importance of vanadium due to existence of vanadoenzyme⁵ several invertebrates like *Phallusion mammilata* accumulate vanadium upto 1900 ppm. This amount is 10 fold more in concentration with respect to sea water in which it lives⁶. Vanadium is believed to play a key role in oxygen transport cycle⁷ and is also to be known an essential nutrient in higher life form⁸ where it is involved in phospholipid oxidation, sulphur metabolism and cholesterol biosynthesis⁹.

EXPERIMENTAL

All chemicals used were of analytical grade. The ligands were prepared by different carbonyl and amino compounds. Elemental analyses were carried out at RSIC, CDRI, Lucknow. Conductivity measurement were carried out at Philips conductivity bridge model PR 9500 with a dip type conductivity cell at Department of Chemistry, Bareilly College, Bareilly. The conductance of complexes were measured in methanol, DMF and DMSO at 10⁻³ M dilutions (25 °C). Magnetic susceptibility of the complexes were determined by Gouy method at the Department of Chemistry, Bareilly College,

Bareilly. The sample tube was calibrated with CuSO_4 . The IR spectra of complexes were recorded with Perkin-Elmer Spectrometer model 651 in KBr phase at RSIC, CDRI, Lucknow. The visible spectra were recorded with Beckmann DU-2 spectrophotometer in the range of $750\text{-}300\text{ cm}^{-1}$ at Department of Chemistry, Bareilly College, Bareilly.

Preparation of ligand: The Schiff bases were prepared by the condensation of respective carbonyl and amino compounds. The amino compound was dissolved in ethanol and refluxed for *ca.* 0.5 h. The requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for *ca.* 6 h and kept for 24 h. The crystals of ligand were obtained and purified by recrystallization. The purity of ligand was checked by elemental analysis and melting point.

Preparation of VO(IV) complexes: All vanadyl complex of schiff bases were prepared by general method. The salt $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in water and added to a warmed, stirred solution of the corresponding schiff base. The resulting solution was refluxed for 6-7 h and concentrated to half of the volume. The resulting precipitate was filtered by suction and then dried *in vacuo* over anhydrous calcium chloride.

RESULTS AND DISCUSSION

Elemental analyses revealed that the oxovanadium(IV) complexes have the compositions $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{SCIVO} \cdot 3\text{H}_2\text{O}$, $(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O})_3\text{VOCl}_3 \cdot 2\text{H}_2\text{O}$, $(\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3)_2\text{-VOCl} \cdot 2\text{H}_2\text{O}$ and $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_4\text{VOICl}_2 \cdot 2\text{H}_2\text{O}$. The electrolytic nature of oxovanadium(IV) complexes measured in DMF, DMSO and methanol at 10^{-3} dilution indicate that SMTH complex is nonelectrolytic in nature where as BSC, HBINAH and BNHMDH complexes are 1:2 electrolytic nature.

The oxovanadium(IV) complexes are paramagnetic in nature. The value of magnetic moment varies from 1.64 to 1.71 BM which is very close to the calculated value for d^1 system. The oxovanadium(IV) complexes appear to have distorted octahedral geometry due to V=O bond.

The electronic spectral bands of the present oxovanadium (IV) complexes were observed as broad bands between 405-450 nm which are generally not much shifted in DMSO.

Molar extinction coefficient ($\epsilon = 3240\text{-}1200$) $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ of the bands suggests that they are charge transfer (LMCT) in origin. An additional band observed at 570-600 nm may be assigned to ${}^2\text{B}_2(d_{xy}) \rightarrow {}^2\text{B}_1(d_{x^2-y^2})$ transition^{10,11}.

The ESR spectra of vanadyl complexes were recorded in DMSO solution at 300 K and 77 K. The room temperature polycrystalline ESR spectrum was identical with the spectrum of the frozen glass. The spectra of the complexes are typical eight line patterns which shows that it is a monomer. The polycrystalline spectrum reveals that there are total sixteen lines with the narrow eight lines perpendicular bunch enveloped within eight line parallel bunch. The resolution of the ESR spectra into parallel and perpendicular regions even in room temperature polycrystalline ESR

spectrum may be due to a large intermolecular distance offered by macromolecular polydentate nature of the schiff bases causing negligible intermolecular dipolar broadening¹².

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE OXOVANADIUM (IV) COMPLEXES

| Name and m.f. | Colour | m.p. (°C) | Elemental analysis % | | | | μ_{eff} (BM) | AA |
|---|--------------------|--------------|----------------------|----------------|------------------|------------------|----------------------------|-------|
| | | | C | H | N | M | | |
| 5-Chlorosalicylaldehyde morphine N-thiohydrazone oxovanadium(IV) $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2\text{SClVO}_3\text{H}_2\text{O}$ | Light green | 260 | 34.16 (33.19) | 3.55 (4.09) | 9.96 (9.50) | 12.09 (11.07) | 1.64 | 10.00 |
| Butyrophenone semicarbazone oxovanadium(IV) chloride $(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_3)\text{VOCl}_3 \cdot 2\text{H}_2\text{O}$ | Yellowish green | 320 | 50.22 (50.33) | 5.77 (5.86) | 15.97 (16.94) | 6.46 (5.07) | 1.71 | 85.75 |
| 3-Hydroxy benzaldehyde isonicotinic acid hydrazone Oxovanadium(IV) chloride $(\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3)_2 \cdot \text{VOCl}_2 \cdot 2\text{H}_2\text{O}$ | Orange | 245 | 50.56 (50.93) | 3.56 (4.03) | 16.37 (16.93) | 8.26 (9.37) | 1.69 | 89.68 |
| Bis(2-hydroxy-1-naphthaldehyde) dihydrazone oxovanadium(IV) chloride $(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2)_2 \text{VOCl}_2 \cdot 2\text{H}_2\text{O}$ | Olive coloured | 270 | 44.34 (43.05) | 3.07 (3.91) | 8.34 (7.66) | 15.46 (14.26) | 1.69 | 85.00 |

AA = Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$).

The IR spectra of 5-chloro salicylaldehyde morpholine N thio hydrazone show bands at 3190 and 1630 cm^{-1} which have been assigned to the bands of phenolic OH and $\nu(\text{C}=\text{S})$. These bands are disappeared on complexation with VO(IV) and a new band at $760\text{-}740 \text{ cm}^{-1}$ were observed which suggests the coordination of metal ion through thiol sulphur and phenolic oxygen *via* deprotonation. The $\nu(\text{C}=\text{N})$ shows lowering by 15 cm^{-1} which indicates coordination through azomethine nitrogen atom. This is further substantiated by the appearance of azine chromophore¹³ ($>\text{C}=\text{N}-\text{N}=\text{C}<$) around 1600 cm^{-1} . Thus in these complexes the ligand functions in a dibasic tridentate fashion and shows bonding through O, N and S atoms.

The appearance of a new band at 3300 cm^{-1} in the spectrum of complex indicate the presence of co-ordinated water molecules show rocking and wagging modes. This is further supported by thermogravimetric analysis in which the percent weight loss of two water molecules occurs above $160 \text{ }^\circ\text{C}$ ¹⁴.

This IR spectrum of butyrophenone semicarbazone exhibits a number of important bands. Some bands change their frequency on complexation. The ligand coordinates through carbonyl oxygen and nitrogen of the C=N group. The band of 1670 cm^{-1} for $\nu(\text{C}=\text{O})$ and at 1570 cm^{-1} for $\nu(\text{C}=\text{O})$ and at 1570 cm^{-1} for $\nu(\text{C}=\text{N})$ ¹⁵ shifts lower side by $30\text{-}60 \text{ cm}^{-1}$ on complexation. This lowering in infrared frequencies indicates that coordination takes place through oxygen of C=O group and nitrogen of C=N

group. Another band in the ligand spectra in the region of 3500-3100 cm^{-1} arises due to $\nu(\text{NH})$ modes of NH and NH_2 groups¹⁶⁻¹⁸. These bands showed no definite pattern of shifts on complex formation and are probably not involved in coordination.

The IR spectra of 3-hydroxy benzaldehyde isonicotinic acid hydrazone shows bands at 3400, 1610, 1645 and 3190 cm^{-1} which may be assigned to N-H, C=O, C=N and phenolic OH group, respectively. On complexation with oxovanadium(IV) the peak for C=N has shifted to 1640 cm^{-1} and that for C=O has shifted to 1660 cm^{-1} while other peaks are not affected on complexation. This shifting shows that N atom of the azomethine and O atom of the carbonyl group of the ligand participates in coordination. The 1,3-disubstitution pattern of phenyl nucleus is represented by a peak appearing¹⁹⁻²² at 775 cm^{-1} .

On complexation a new band appears at 3330 cm^{-1} which may be attributed to $\nu(\text{OH})$ vibrations of coordinated water. The OH rocking and wagging bands appeared at 800 and 720 cm^{-1} , respectively²³.

The IR spectra of *bis*(2-hydroxy-1-naphthaldehyde) malonyl dihydrazone shows band at 1697 and 1661 cm^{-1} which may be assigned to $\nu(\text{C}=\text{O})$ stretching vibrations. The spectrum of the complex shows the absence of bands in the region of 1700-1630 cm^{-1} in combination with presence of two strong band at almost equal intensity in the 1630-1597 cm^{-1} region attributable to stretching vibration of $\nu(\text{C}=\text{N})$ group²⁴. This indicates the condensation of NH_2 group of malonyl dihydrazone with CO group of 2-hydroxy-1-naphthaldehyde leading to the formation of C=N linkage. The complex does show any band in the region of 3550-3000 cm^{-1} which could be assigned to stretching vibration of either NH group of NH_2 group of hydrazide.

Another strong band in the spectra of complex appeared at 3250 cm^{-1} which may be due to $\nu(\text{OH})$ vibration of either coordinated water molecule or naphtholic OH group but the loss of weight in TGA corresponding to two water molecules above 160 °C indicates the presence of coordinated water molecule.

A weak band at 1030 cm^{-1} in the spectrum of the ligand may be assigned N=N in free dihydrazone²⁵. This band splits in to two bands at 1036 and 1054 cm^{-1} in the spectrum of complex and shows a shift of about 15 cm^{-1} to higher frequency indicating coordination of only one hydrazinic nitrogen atom of each hydrozone²⁶.

The IR spectra of all complexes exhibit a strong band near 1000 cm^{-1} which has been assigned to the $\nu(\text{V}=\text{O})$ ²⁷. In contrast several oxovanadium(IV) complexes have been reported in which this stretching mode appears at quite lower^{28,29} wave no. around 900 cm^{-1} . In this work the $\nu(\text{V}=\text{O})$ is found at 960-910 cm^{-1} .

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