



Synthesis and Characterisation of Vanadium Metal Complexes Obtained From Hydrazone Derivatives

KEYWORDS

2-hydroxy benzoylhydrazide; Aldehydes; Vanadyl sulphate; characterization.

MEGHANA E. MHADAYE

R. M. PATIL

Department of chemistry, The Institute of science, 15, Madam Cama Road,

Department of chemistry, The Institute of science, 15, Madam Cama Road,

ABSTRACT The hydrazones were obtained by condensation of 2-hydroxy benzoyl hydrazide with various aldehydes viz. benzaldehyde, *p*-methoxybenzaldehyde, *p*-methylbenzaldehyde, *p*-bromobenzaldehyde and α -naphthaldehyde. The vanadium metal complexes have been prepared by treating vanadyl sulphate with different hydrazone derivatives. The hydrazone derivatives and metal complexes have been characterized by elemental analysis and various physicochemical techniques such as IR, ¹H-NMR, mass spectroscopy, electronic absorption, molar conductance, magnetic susceptibility and TG-DTA analysis.

INTRODUCTION

Interest in coordination chemistry of benzoylhydrazide has been subject of enthusiastic research since they show a wide range of catalytic properties, especially derived from substituted aromatic aldehydes. The coordination chemistry of oxovanadium (IV) (i.e. VO²⁺ or Vanadyl ion) is more interesting and rather more important because of two main reasons. Firstly the vanadyl complexes are finding more and more importance in biological systems. Secondly the coordination number and geometry of this metal is highly ligand dependant. Moreover vanadyl ion is less toxic and attracting attention of young chemists for the synthesis of efficient bioactive compounds with low toxicity¹.

The ligands exhibit keto-enol tautomerism and containing donor atoms like N, O are important to prepare metal complexes which shows biological activity. The presence of functional group, usually hydroxyl, azomethine, sufficiently near the site of coordination in the hydrazone ligands, gives a five or six membered chelate ring on reaction with metal ion, which shows structural variations depending upon the type of substituent present on aromatic ring².

EXPERIMENTAL

Materials and Methods

All the chemicals used were of the analytical grade (AR) and of highest purity. The 2-hydroxy benzoylhydrazide was prepared by the method reported³ in the Vogel. The ester like methylsalicylate and hydrazine hydrate were obtained from HIMEDIA, while aldehydes such as benzaldehyde, *p*-methoxybenzaldehyde, *p*-methylbenzaldehyde, *p*-bromobenzaldehyde, α -naphthaldehyde and vanadyl sulphate were obtained from THOMAS BAKER. Solvents like ethanol whenever used were distilled and purified according to standard procedures³.

Melting point of ligands was taken in open capillary and was uncorrected. The UV-Vis spectra were recorded on Chemito uv 2600 Double Beam UV-Vis spectrophotometer. IR spectra of all the ligands were recorded in KBr on a Perkin-Elmer Precisely Spectrum 100 FT-IR Spectrometer in the region 4000-400 cm⁻¹. ¹H-NMR spectra was recorded in DMSO-d₆ on a Bruker 300MHz Spectrometer, Mass spectra were recorded on a GC-MS at the Shivaji University, Kolhapur.

The 10⁻³ M solution in water of each of the complexes was prepared to measure molar conductance using EQUIP-TRONICS conductivity meter model no. EQ-660A with a dip-type conductivity cell fitted with platinum electrode (cell constant =1.0 cm⁻¹). The magnetic susceptibility at room temperature were measured using Gouy's method and diamagnetic corrections for the ligand component applied using Pascal's constant to calculate effective magnetic moments⁴. The Rigaku Thermo Plus-8120 TG-DTA instrument was used for TG-DTA analysis of vanadium complexes.

Preparation of 2-hydroxy benzoylhydrazide from corresponding ester

A mixture of methyl salicylate (1.3 ml, 10 mmol) and hydrazine hydrate 80% (1.2 ml, 20 mmol) were refluxed in ethanol for 3hrs on water bath. The resulting reaction mixture was allowed to cool to room temperature. The separated product was filtered washed with ethanol and purified by recrystallisation from ethanol (yield 85%).

Synthesis of hydrazones with various aldehydes

The solution (0.01 M) of 2-hydroxy benzoyl hydrazide in ethanol was taken in a two neck round bottom flask fitted with water condenser. Stirred for 10 min and heated gently on heating mantle till clear solution obtained. The solution of substituted aromatic aldehyde (0.01 M) in ethanol was added slowly to this stirred solution. This reaction mixture was further reflux on water bath for 3hrs. When this solution was cooled to room temperature, precipitate formed was separated by filtration and purified by recrystallisation from ethanol (yield 80%).

Synthesis of Vanadium complexes

To a hot suspension of ligand (0.01M) in ethanol, an ethanolic solution (0.01M) of the metal salt vanadyl sulphate was added drop wise with constant stirring with the help of rotameter and refluxed for 3hrs. The resulting reaction mixture was cooled to room temperature and maintained at pH 7.8 to 7.9 by adding ammonia then refluxed further for 30 min. The resultant product was filtered, repeatedly washed with ethanol and dried at room temperature.

RESULTS AND DISCUSSION

All complexes were obtained as green solids, soluble in water. The complexes are non-hygroscopic and thermally

stable indicating a strong metal-ligand bonding. The elemental analysis data of the metal complexes is shown in table 1. The value observed for molar conductance of all vanadium metal complexes fall between 0.0008 to 0.0013 mhos.cm²mol⁻¹ in 10⁻³ M aq solution indicate the complexes are non-electrolytic in nature.

Table 1: Physical and analytical data of the complexes:

| 2-hydroxy benzoylhydrazide; Aldehydes; Vanadyl sulphate; characterization. | Molecular Formula (Formula Wt.) | Yield % | Colour | % Elemental analysis Found (calculated) | | | | μ_{eff} (B.M.) |
|--|---|---------|--------|---|------------------|----------------|------------------|---------------------------|
| | | | | V | C | H | N | |
| V1 | [C ₃₀ H ₂₆ O ₇ N ₄ V] (605.498) | 74 | Green | 8.40 (8.41) | 59.49 (59.51) | 4.31 (4.33) | 9.24 (9.25) | 1.73 |
| V2 | [C ₂₈ H ₂₂ O ₅ N ₄ V] (545.445) | 72 | Green | 9.33 (9.34) | 61.64 (61.66) | 4.04 (4.06) | 10.25 (10.27) | 1.71 |
| V3 | [C ₃₀ H ₂₆ O ₅ N ₄ V] (573.499) | 73 | Green | 8.86 (8.88) | 62.81 (62.83) | 4.58 (4.57) | 9.79 (9.77) | 1.72 |
| V4 | [C ₂₈ H ₂₀ O ₅ N ₄ Br ₂ V] (703.237) | 71 | Green | 7.26 (7.24) | 47.81 (47.82) | 2.84 (2.87) | 7.98 (7.97) | 1.74 |
| V5 | [C ₃₆ H ₂₆ O ₅ N ₄ V] (645.565) | 72 | Green | 7.89 (7.88) | 66.98 (66.95) | 4.06 (4.10) | 8.68 (8.70) | 1.72 |

Magnetic Susceptibility Measurement

The magnetic susceptibility for all the vanadium complexes at room temperature were recorded by the Gouy's method using Hg[Co(SCN)₄] as a calibrant. The effective magnetic moments were calculated after applying diamagnetic corrections for the ligand components using Pascal's constants⁴. The room temperature μ_{eff} value for the vanadium complexes were found in the range 1.71-1.74 B.M. The magnetic susceptibilities of the complexes are consistent with square-pyramidal geometry around the central metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

Infrared Spectra

The FTIR spectra of the metal complexes were recorded in KBr over the range 4000-400 cm⁻¹. The FTIR spectrum of the free ligands shown four characteristics bands at around 3404, 3260-3300, 1653 and 1607 cm⁻¹ assignable to free (-O-H) stretching phenolic moiety, (-N-H), amide carbonyl (-C=O) and azomethine (-C=N), stretching mode respectively. The absence of a weak broad band in 3260-3300 cm⁻¹ region, noted in the spectra of the metal complexes indicates deprotonation of bonded (-NH) group during complex formation and subsequent coordination of the oxygen of amide carbonyl to metal ion. The ν (C=N) band in complexes is shifted to lower wavenumber with respect to free ligand, indicating that the nitrogen of azomethine group is coordinated to the metal ion, which was further confirmed by observation of the red shift in the ν (N-N) stretching frequency from 849 to 975 cm⁻¹ region. New bands observed in the complexes at 1653 and 1687 cm⁻¹ are attributed to the >C=N-N=C< group. The spectra of metal complexes showed a new band at 512 cm⁻¹ and 438 cm⁻¹ for ν (M-O) and ν (M-N) vibrations respectively. The presence of strong band at 975 cm⁻¹ in the spectra of complexes is assigned to ν (M=O) stretching mode. Hence, coordination takes place via oxygen of amide and nitrogen of azomethine group of ligand molecule.

Table 2: Important IR spectral bands (cm⁻¹) of the complexes

| Inference | V1 | V2 | V3 | V4 | V5 |
|---------------|------|------|------|------|------|
| ν (C=N) | 1590 | 1580 | 1580 | 1592 | 1585 |
| ν (N=C-O) | 1109 | 1108 | 1111 | 1110 | 1122 |
| ν (M-O) | 512 | 512 | 520 | 513 | 512 |
| ν (M-N) | 438 | 432 | 431 | 435 | 437 |
| ν (M=O) | 975 | 971 | 975 | 970 | 971 |

Electronic spectra

The electronic spectra of the metal complexes in water (10⁻⁴ M) was recorded. The electronic spectra of vanadium

metal complexes exhibit low intensities d-d bands in the ranges 12820-12987 cm⁻¹, 16667-17391cm⁻¹ and 27397-27932 cm⁻¹ due to $2t_{2g} \rightarrow 2e_g$, $2t_{2g} \rightarrow 2b_{1g}$ and $2t_{2g} \rightarrow 2a_{1g}$ transitions respectively, characteristic of a square pyramidal ligand field around V(IV). The electronic spectra also exhibit a fourth high energy band around 29585-30211cm⁻¹, which can be assigned⁵ as a ligand to metal charge transfer transition which is consistent with square pyramidal geometry around the VO(IV) ion.

Thermal measurements

The simultaneous TG-DTA studies of the complexes was recorded in nitrogen atmosphere on Rigaku Thermo Plus-8120 TG-DTA instrument by increasing the temperature from room temperature upto 900°C at the heating rate of 10°C/min. All the complexes investigated shows similar behavior in their thermogram which exhibit three steps. The complexes are stable upto 200°C after which in the first step the complexes losses some moiety C₇H₇CHON in the temperature range between 200 to 360°C. The complexes losses another moiety in the second step in the temperature ranges between 360 to 540°C which could be attributed due to loss of C₇H₅O₂N. Further decomposition occurs in the temperature range of 560 to 680°C corresponds to the final residue as vanadium oxide the ultimate product of heating.

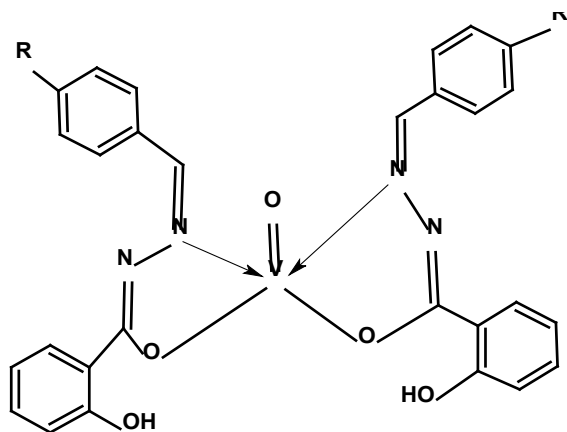
Table 3: Thermal data for vanadium metal complexes

| Complex | Temperature Range (°C) | % Weight loss | | Decomposition product |
|---|------------------------|---------------|------------|---|
| | | Found | Calculated | |
| V1 [C ₃₀ H ₂₆ O ₇ N ₄ V] | 200-360 | 44.29 | 44.31 | C ₇ H ₇ CHON |
| | 360-540 | 44.61 | 44.63 | C ₇ H ₅ NO ₂ |
| | 560-680 | 11.10 | 11.06 | VO |
| V2 [C ₂₈ H ₂₂ O ₅ N ₄ V] | 200-360 | 38.21 | 38.18 | C ₆ H ₅ CHN |
| | 360-540 | 49.53 | 49.55 | C ₇ H ₅ NO ₂ |
| | 560-680 | 12.26 | 12.27 | VO |
| V3 [C ₃₀ H ₂₆ O ₅ N ₄ V] | 200-360 | 41.23 | 41.21 | C ₇ H ₇ CHN |
| | 360-540 | 47.13 | 47.12 | C ₇ H ₅ NO ₂ |
| | 560-680 | 11.64 | 11.67 | VO |

| | | | | |
|---|---------|-------|-------|---|
| V4 | 200-360 | 52.02 | 52.05 | C ₆ H ₄ NCHBr |
| [C ₂₈ H ₂₀ O ₅ N- 4Br ₂ V] | 360-540 | 38.44 | 38.43 | C ₇ H ₅ NO ₂ |
| | 560-680 | 9.54 | 9.52 | VO |
| V5 | 200-360 | 47.76 | 47.77 | C ₁₀ H ₇ CHN |
| [C ₃₆ H ₂₆ O ₅ N ₄ V] | 360-540 | 41.88 | 41.86 | C ₇ H ₅ NO ₂ |
| | 560-680 | 10.36 | 10.37 | VO |

Conclusion

Based on the above results the following conclusion may be drawn. The higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively. Room temperature magnetic studies are indicative of paramagnetic nature and an square pyramidal geometry of the VO(IV) complexes which is supported by the electronic spectra. The IR spectra shows bonding of the metal through N- and O- donor atoms of the two ligands.



Structure of the vanadium metal complexes (R = - H, CH₃, OCH₃, Br, Ph)

REFERENCES

1. S. K. Patil, V. M. Naik and N. B. Mallur, J. Chem. Pharm. Res., 4(4),2029(2012).
2. R. M. Patil and N. V. Thakkar, Synth. React. Inorg. Met.-Org.Chem., 30(6), 1159(2000).
3. Furnis B S, Hannaford A J, Smith P W G and Tatchell A R, Vogel Text-book of Practical Organic Chemistry, 5th Ed. ELBS Longman London, (1989).
4. R. L. Datta and A. Syamal, Elements of mgnetochemistry, 2nd Ed. Affiliated East-West Press, Pvt. Ltd., New Delhi, (2004).
5. R. C Maury, D. D. Mishra and V. Pillai., Synth. React. Inorg. Met-org. Chem., 25, 1123(1995).