Synthesis, Characterization and Catalytic Activity of Oxovanadium(IV) Complexes of Heterocyclic Acid Hydrazones

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Two acid hydrazones, furan-2-carbaldehyde nicotinic hydrazone (L_1) and furan-2-carbaldehyde benzhydrazone (L_2) have been synthesized and they are characterized by elemental analysis, IR, NMR and UV spectral analysis. Oxovanadium(IV) complexes of these two hydrazones were synthesized and characterized by elemental analysis, IR, UV, EPR, molar conductivity and magnetic susceptibility measurements. Conductivity measurements reveal that the complexes are non-electrolytes. Spectral data indicates the square pyramidal geometry for the monomeric five coordinated oxovanadium(IV) complexes with the general formula $[VO(L)(OCH_3)]$. The complex was studied for its catalytic activity and was found to be a good catalyst in quinoxaline synthesis.

Keywords: Acid hydrazones, Oxovanadium complexes, EPR spectrum, Square pyramidal, Catalytic activity.

INTRODUCTION

Schiff base ligands such as hydrazones are widely studied for their applications in pharmaceutical and industrial fields[1-3]. Over the past few decades, a great deal of attention has been focused on the complexes formed by transition metal ions with hydrazones due to their widespread applications and interesting coordination capability with transition metal ions[4-6]. The transition metal complexes of hydrazones have potential applications as active materials in non-linear optics[7], catalysts[8], innovative magnetic materials[9], luminescent probes[10] and molecular sensors[11].

Introduction of a >C=O group in the hydrazide part increases the electron delocalization and denticity of the hydrazone and the resulting compound is known as acid hydrazone. Further, the number of coordination sites can be increased by suitable substitution on the hydrazone framework. If a hetero ring is attached to the hydrazone framework, the hetero atom can also coordinate to the metal center thus increasing the denticity[12]. Another possibility is that if the hydrazide part of hydrazones contains a hetero atom, it can also involve in bonding. This unusual coordination can evidently change the way the complexes are formed[13]. In the case of complexes with ONO donor hydrazones we can incorporate heterocyclic bases to the central metal structure[14]. We report here the synthesis and structural studies of some oxovanadium(IV) complexes of heterocyclic acid hydrazones.

EXPERIMENTAL

All the chemicals used of AR grade. The solvents were purified before use by standard procedures. Elemental analysis for carbon, hydrogen and nitrogen were performed on a Vario EL III CHNS instrument. The molar conductivity of the complexes in DMF solution (10^{-3} M) at room temperature was measured using a direct reading conductivity meter. The IR spectrum was recorded on Bruker α T instrument as KBr pellets in the range 4000-400 cm^{-1}.The ^{1}H NMR spectra were recorded using Bruker 400 MHz Spectrometer, with CDCl$_3$ as solvent and TMS as standard. X-band EPR spectra of the complexes were recorded in the DMF at LNT using JES-FA200 ESR spectrometer. The magnetic susceptibility measurements were done on powdered samples at room temperature, using VSM. The electronic spectrum was recorded by using Shimadzu UV-visible spectrophotometer instrument.

Preparation of acid hydrazones: Nicotinic hydrazide/ benzhydrazide dissolved in methanol and refluxed with furan-2-carbaldehyde in the presence of few drops of acetic acid for 6 h. Product was filtered off, washed with methanol and dried. Compound recrystallized from methanol. The results of the spectroscopic and composition analyses are as follows.

Furan-2-carbaldehyde nicotinic hydrazone (L_1): Colourless crystalline solid, Yield: 70 %, m.w.: 215 m.f.: $C_{11}H_9N_3O_2$, Anal. calcd. (%): C, 61.39; H, 4.18; N, 19.53. Found, (%): C, 61.7; H, 4.27; N, 19.56. IR (KBr, v_{max}, cm^{-1}): 3213 ν(NH),

165 2 ν(C=O), 1564 ν(C=N),^{1}H NMR (δ, ppm): 9.1 (NH), 8.7 (C-H, azomethine), 6-8 (Ar-H). UV-visible (DMF, 10^{-5} M, cm^{-1}): 31250 (n$\rightarrow$$\pi$*), 45450 ($\pi$$\rightarrow$$\pi$*).

Furan-2-carbaldehyde benzhydrazone (L$_2$): Colourless needle-like crystalline solid, Yield: 72 %, m.w.: 214, m.f.: C$_{12}$H$_{10}$N$_2$O$_2$, Anal. calcd. (%): C, 67.29; H, 4.67; N 13.08. Found (%): C, 67.0 2; H 4.57; N 12.94. IR (KBr, ν_{max}, cm^{-1}): 3 244 ν(NH), 1644 ν(C=O), 1563 ν(C=N),^{1}H NMR (δ, ppm): 9.2 (NH), 8.5 (C-H, azomethine), 6-8 (Ar-H). UV-visible (DMF, 10^{-5} M, cm^{-1}): 31750 (n$\rightarrow$$\pi$*), 45454 ($\pi$$\rightarrow$$\pi$*).

Preparation of the oxovanadium(IV) complexes: To a solution of furan-2-carbaldehyde nicotinic hydrazone/furan-2-carbaldehyde benzhydrazone (1 mmol) in methanol (20 mL), vanadylacetylacetonate (1 mmol) solution in methanol (20 mL) was added. Mixture was stirred in magnetic stirrer for 5 h. The resulting solution was allowed to stand at room temperature for slow evaporation. The precipitate that separated out was filtered, washed with methanol and dried over P$_4$O$_{10}$.

Oxovanadium(IV) complex VOL$_1$(OCH$_3$)]: m.w.: 312, Yield: 55 %, Colour: Dark brown, $\mu_{eff.}$ (B.M.): 1.87, Anal. calcd. (%): C, 46.15; H, 3.52; N, 13.46. Found (%): C, 46.83; H, 3.66; N, 13.33, IR (KBr, ν_{max}, cm^{-1}): 1520 ν(C=N), 1582 ν(C=N (new)), 1374 ν(C-O), 959 ν(V=O); UV-visible (DMF, 10^{-5} M, cm^{-1}): 31746 (n$\rightarrow$$\pi$*), 46200 ($\pi$$\rightarrow$$\pi$*); EPR spectra parameters: g$_\parallel$ = 1.94, g$_\perp$ =1.99, A$_\parallel$ (cm^{-1}) = 181.11 × 10^{-4}, A$_\perp$ (cm^{-1}) = 46.44 × 10^{-4}.

Oxovanadium(IV) complex VOL$_2$(OCH$_3$).H$_2$O]: m.w.: 329, Yield: 56 %, Colour: Dark brown, $\mu_{eff.}$ (B.M.): 1.88, Anal. calcd. (%): C, 47.41; H, 3.05; N, 7.95. Found (%): C, 47; H, 3.59; N, 7.47; IR (KBr, ν_{max}, cm^{-1}): 1520 ν(C=N), 1594 ν(C=N (new)), 1366 ν(C-O), 988 ν(V=O); UV-visible (DMF, 10^{-5} M, cm^{-1}): 31820 (n$\rightarrow$$\pi$*), 45600 ($\pi$$\rightarrow$$\pi$*); EPR spectra parameters: g$_\parallel$ = 1.87, g$_\perp$ = 1.98, A$_\parallel$ (cm^{-1}) = 174.58 × 10^{-4}, A$_\perp$ (cm^{-1}) = 44.36 × 10^{-4}.

RESULTS AND DISCUSSION

In ligand (L$_1$) strong bands due to the ν(NH) and ν(C=O) modes at 3213 cm^{-1} and 1652 cm^{-1} while in ligand (L$_2$) at 3244 cm^{-1} and 1644 cm^{-1} are observed. It suggested that both the hydrazone exists in the amido form in the solid state[15]. A prominent band at 1564 cm^{-1} due to azomethine ν(C=N) linkage is observed indicating that condensation between carbonyl compound and that of the hydrazide has taken place[16]. In both the complexes absence of strong bands due to (NH) and (C=O) modes indicated that the ligand coordinates to the metal in enolate form. A downward shift of the band (C=N) of azomethine group suggesting coordination of azomethine nitrogen to the metal centre[17]. The band observed at 959 cm^{-1} and 988 cm^{-1} are due to the V=O stretching[18].

The bands attributed to the transitions of the n$\rightarrow$$\pi$* and $\pi$$\rightarrow$$\pi$* of uncomplexed hydrazones are slightly shifted upon complexation. The bands related to *d-d* transitions in the VO^{2+} complex could not be visualized in solution spectrum. However, the diffuse reflectance spectrum of the complex could exhibit bands characteristics of a square pyramidal oxovanadium complex, due to the high concentration of the complex in the solid state[19].

The complexes were formulated from the analytical data, magnetic measurements and molar conductance data. They

support the suggested formulae. Methanol and ethanol solvents used as reaction media can act as co-ligands during the preparation of the complexes. As the literature suggests the coordinated methanol in [VO(L)(MeOH)] can be deprotonated to yield a methoxy derivative, [VO(L)(OMe)][20,21]. The molar conductivity measurements in 10^{-3} M DMF solutions indicated that both the complexes are non-electrolytic in nature. The values of magnetic moment were found to be close to the spin only value 1.73 B.M. which indicate the presence of one unpaired electron. It also proved that there is no interaction between oxovanadium-oxovanadium moiety.

In V(IV) complexes value of g is below the value for free electron. The spin of ^{51}V nucleus is I = 7/2. In mononuclear V(IV) complexes the EPR signals are split into eight hyperfine lines. VO^{2+} is one of the most stable diatomic cation and its paramagnetism is almost due to spin angular momentum. EPR spectra were recorded in DMF solution at 77K. In frozen DMF, tumbling motions of the molecules are restricted which results in anisotropic spectrum. Corresponding parameters are characteristics of square pyramidal oxovanadium(IV) complexes with C$_{4V}$ symmetry, the V=O bond along z and the other four donor atoms are along the x, y axes, exhibiting two g (g$_\parallel$, g$_\perp$) and two A (A$_\parallel$, A$_\perp$) values.The g$_\parallel$ < g$_\perp$ and A$_\parallel$ > A$_\perp$ values are characteristic of an axially compressed system with unpaired electron in d$_{xy}$ orbital[22,23].

Based on the above data obtained, the following tentative structures have been proposed for the present complexes.

[VOL$_1$(OCH$_3$)]   [VOL$_2$(OCH$_3$)]·H$_2$O
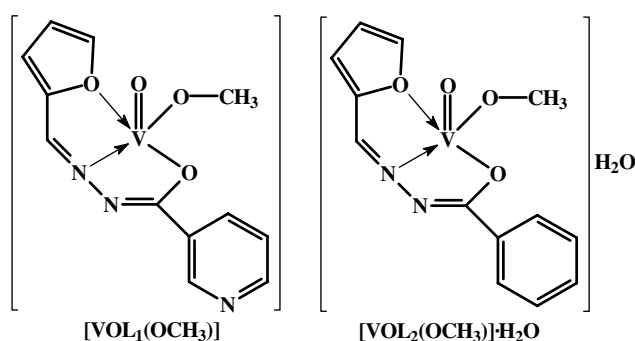
Catalytic activity studies: We studied the synthesis of quinaxaline derivatives using oxovanadium complex [VOL$_1$(OCH$_3$)]. Quinoxaline derivatives are nitrogen-containing heterocycles, which are important in the fields of medicine as antitumor, anticonvulsant, antimalarial, anti-inflammatory, antiamoebic, antioxidant, antidepressant *etc.*[24-26]. The classic method for quinoxaline preparation is the condensation of a 1,2-dicarbonylic compound with a 1,2-diamino compound. In general, this procedure needs high temperature, the use of a strong acid catalyst and long reaction times. The salient features of the present catalytic activity studies were high yields, short reaction times, mild reaction conditions and operational simplicity. Synthesis of quinoxaline derivatives were done by using benzil and different diamines. Benzil (1 mmol) and *o*-phenylene-diamine/4-nitro-*o*-phenylenediamine (1 mmol) dissolved in 3 mL of methanol/acetonitrile and stirred in room temperature in the presence of 0.02 g of oxovanadium complex. The progress of the reaction was monitored by TLC. On cooling, the crystals of quinoxaline were separated out. It was

then dried over P_4O_{10}. The compounds were recrystallized from methanol and acetonitrile (Table-1) and characterized by spectral methods.

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TABLE-1
EFFECT OF SOLVENT ON SYNTHESIS OF QUINOXALINE

Compound	Solvent	Time (min)	Yield (%)
2,3-Diphenyl quinoxaline	MeOH	2	96
2,3-Diphenyl quinoxaline	Acetonitrile	3	92
6-Nitro-2,3-diphenyl quinoxaline	MeOH	180	92

2,3-Diphenyl quinoxaline: White solid, m.p.: 125-128 °C, m.f.: $C_{20}H_{14}N_2$, m.w.: 282, IR (KBr, ν_{max}, cm^{-1}): 3055, 1620, 1577, ^{1}H NMR (CdCl$_3$) δ (ppm): 7.3 (m, 6H), 7.5 (d, 4H), 8.6 (d, 2H), 7.75 (t, 2H).

6-Nitro,2,3-diphenyl quinoxaline: White solid, m.p.: 193-194 °C, m.f.: $C_{20}H_{13}N_3O_2$, m.w.: 327, IR (KBr, ν_{max}, cm^{-1}): 3055, 1600, 1570, 1370.

Conclusion

We carried out the experiment without catalyst under identical conditions. Only very low amount of substrate was converted in the reaction (below 80 %) and took 3 h for first derivative and 24 h for the second derivative suggesting that our complex is functioning as a catalyst for quinoxaline synthesis. It proved that oxovanadium complexes have the advantages of high activity and short reaction times as a catalyst for the synthesis of quinoxaline.

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