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Synthesis and spectral characterization of ternary complexes of oxovanadium(IV) containing some acid hydrazones and 2,2'-bipyridine

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Abstract

An interesting series of heterocyclic base adducts of oxovanadium(IV) complexes have been synthesized by the reaction of vanadium(IV) oxide acetylacetonate with some hydrazones (H₂L) in the presence of a heterocyclic base 2,2'-bipyridine. The compounds were characterized by analytical and different physico-chemical techniques like IR, electron paramagnetic resonance (EPR) and UV-Vis spectral studies and magnetic studies. The EPR spectra indicate that the free electron is in the d_{xy} orbital. The coordination geometry around oxovanadium(IV) in all complexes is octahedral, with one dibasic tridentate ligand L²⁻, and one bidentate heterocyclic base. The IR spectra suggest that coordination takes place through azomethine nitrogen and enolate oxygen from the hydrazide moiety and phenolate oxygen. The pyridyl nitrogens of the hydrazones, H₂L² and H₂L⁴ are not involved in the coordination. The molar conductivities show that all the complexes are non-electrolytes. All electronic transitions were assigned. All the compounds are paramagnetic. EPR studies of all compounds suggest axial symmetry. The calculated bonding parameters indicate that in-plane σ bonding is more covalent than in-plane π bonding. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrazones; Oxovanadium(IV); Hydrazonate complexes; 2,2'-Bipyridine; EPR

1. Introduction

The synthesis and structural investigation and reaction of transition metal Schiff's bases have received a renewed attention in recent years, because of their biological activities as antitumoral, antifungal and antiviral activities. A lot of Schiff's bases such as thiosemicarbazones have been reported [1,2]. Most of the thiosemicarbazones contain NNS donor atoms. However, very little information is available for hydrazones containing ONO or NNO donor atoms. Copper(II) complex of salicylaldehyde benzoylhydrazone was shown to be a potent inhibitor of DNA synthesis and cell growth. This hydrazone also has mild bacteriostatic activity and a range of analogues has been investigated as potential oral iron chelating drugs for genetic disorders such as thalassemia [3].

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The coordination chemistry of vanadium has received considerable attention since the discovery of vanadium in enzymes like bromoperoxide and azetobactorvinelandii [4]. Its biological significance is further exemplified by its incorporation in natural products (amavadin in mushroom), in blood of sessile marine organism and enzyme in potent inhibitor of phosphoryl transfer [5]. Several vanadium compounds have recently been investigated in animal model systems as treatment for diabetes [6]. Studies are ongoing in clinical trial in human beings with transition metal complexes [7]. In addition, studies with vanadate in human beings have recently been reported [8].

In this paper, we report syntheses, analytical and spectral characterizations of some oxovanadium(IV) complexes with four different aroyl hydrazones, derived from acid hydrazides namely, benzoic acid hydrazide, nicotinic acid hydrazide and 4-hydroxybenzoic acid hydrazide. The aldehyde/ketone used are salicylaldehyde and 2-hydroxyacetophenone. A bidentate base 2,2'-bipyridine was used as auxiliary ligand for coordination with oxovanadium(IV).

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2. Experimental

2.1. Materials

Salicylaldehyde (BDH), 2-hydroxyacetophenone (BDH), benzoic acid hydrazide (Fluka), 4-hydroxybenzoic acid hydrazide (Fluka), nicotinic acid hydrazide (Fluka), 2,2'-bipyridine (S.D. Fine Chem. Ltd.) and vanadium(IV) oxide acetylacetonate (Merk) were of Analar grade and used without further purification. All the solvents were dried using standard methods before use.

2.2. Physical measurements

Elemental analyses were carried out using a Heraeus Elemental Analyzer at Regional Sophisticated Instrumentation Center, Center Drug Research Institute, Lucknow, India. IR spectra in the range of $4000-400 \,\mathrm{cm}^{-1}$ were recorded on a Shimadzu DR 8001 series FTIR instrument as KBr pellets. Far IR spectra were recorded in polyethylene matrix on IFS 66 V FT-IR spectrometer in the range of $500-50 \text{ cm}^{-1}$. The ¹H NMR spectra were recorded by using Bruker DRX500, using DMSO-d₆ as solvent and TMS as standard at Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India. Magnetic studies were done using vibrating sample magnetometer at IIT, Roorkee, India. Electron paramagnetic resonance (EPR) spectra were recorded in a Varian E-112 spectrometer at X-band, using TCNE as the standard at Regional Sophisticated Instrumentation Center, Indian Institute of Technology, Bombay, India. Frozen solution spectra were simulated with computer programs. Solid state reflectance were measured using Ocean Optics Inc., SD-2000 Fiber Optic Spectrometer.

2.3. Syntheses of ligands

Acid hydrazides (1 mmol) dissolved in methanol was refluxed with methanolic solutions of salicylaldehyde or 2-hydroxyacetophenone (1 mmol), in presence of a few drops of glacial acetic acid for 6 h (Fig. 1). On cooling the reactant media, crystals of hydrazones were separated out. All the compounds (Fig. 2) were recrystallised from methanol and characterized by analytical and different spectral methods.

2.4. Syntheses of complexes

All the complexes were synthesized using the following general method. Vanadium(IV) oxide acetylacetonate



Fig. 3. Scheme of the synthesis of the complexes.

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(1 mmol) was dissolved in dichloromethane. To a stirred ethanolic solution of hydrazone (1 mmol) and 2,2'-bipyridine (1 mmol), under dinitrogen atmosphere vanadyl solution was added. Resultant homogeneous brown solution was stirred for 3 h (Fig. 3). Reddish orange products formed were filtered and washed with cold ethanol, followed by



Fig. 1. Scheme of synthesis of H_2L^4 .

ether, and dried in vacuo. Unfortunately, we are unable to grow single crystals suitable for single crystal XRD for any of these complexes.

3. Results and discussion

3.1. Syntheses of the ligand and oxovanadium(IV) complexes

The ¹H NMR spectral assignments of all the ligands were made on the basis of previous reports [9–12]. All the spectra show two singlets corresponding to phenolic –OH and –NH. The singlet at $\delta = \sim 13$ ppm and $\delta = \sim 11$ ppm represent –OH and –NH, respectively. The signal for –OH is obtained at a down field due to possibility of the formation of intramolecular hydrogen bonding with azomethine nitrogen. The ligands do not show any peak attributed to enolic –OH proton indicating that they exist in keto forms. Upon addition of D₂O the intensities of both OH and NH protons significantly decrease. This supports the assignment. The aromatic protons appear as multiplets at 6.9–7.9 ppm.

The ligands were found to coordinate as dianionic L^{2-} on complexation to oxovanadium(IV). The complexes were found to be readily formed from vanadium(IV) oxide acetylacetonate solution in ethanol by H₂L in presence of heterocyclic base, 2,2'-bipyridine. The elemental analyses (Table 1) of the complexes are in agreement with the formula (VO)L(bipy). All compounds are found to be sparingly soluble in water, ethanol and methanol and soluble in DMF and DMSO. Conductivity measurements in DMF show the complexes to be nonconductors.

The magnetic moment obtained at 298 K for the complexes are in the range of 1.57–1.91 BM The values correspond to spin only value of systems having one electron. These are magnetically diluted complexes in which metal ion is not involved in magnetic exchange with the neighboring metal ion [13].

3.2. Electronic spectral analysis

The solid state visible spectra show the characteristic series of absorption bands common to vanadyl systems in

Table 1

Colors a	nd el	lemental	analyses	the	ligands	and	complexes
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Table 2 Electronic spectral assignments (cm⁻¹)

Compound	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$	LMCT	$n-\pi^*$	$^2B_2 \rightarrow {}^2E$
(VO)L ¹ (bipy)	18,518	20,560	25,125	33,333	14,705
(VO)L ² (bipy)	18,450	20,408	23,809	34,722, 31,520	14,306
(VO)L ³ (bipy) (VO)L ⁴ (bipy)	18,398 18,248	20,320 19,230	25,120 24,390	30,769 34,482	14,520 14,285



Fig. 4. Solution state EPR spectrum of (VO)L¹(bipy) at 77 K.

terms of Ballhausen and Gray model for the one electron transitions [14]. Accordingly, the first absorption band at ~14,300 cm⁻¹ region can be assigned to the electronic transition ${}^{2}B_{2} \rightarrow {}^{2}E (d_{xy} \rightarrow d_{xz}, d_{yz})$, the second signal ~18,200 cm⁻¹ due to ${}^{2}B_{2} \rightarrow {}^{2}B_{1} \rightarrow {}^{2}B_{1} (d_{xy} \rightarrow d_{x^{2}-y^{2}})$ and the third one due to ${}^{2}B_{2} \rightarrow {}^{2}A_{1} (d_{xy} \rightarrow d_{z^{2}})$ (Table 2). These values are consistent with distorted octahedral structure for oxovanadium(IV) [15].

3.3. Electron paramagnetic resonance spectral studies

The EPR spectra (Table 3) of the all the complexes were recorded in DMF solution at 77 K and the representative spectrum is presented in the Fig. 4.

Compound	Color	Analytical data found (calculated)				
		C (%)	H (%)	N (%)		
H ₂ L ¹	Pale yellow	69.74 (70.00)	5.19 (5.00)	11.51 (11.66)		
(VO)L ¹ (bipy)	Reddish orange	63.17 (62.58)	4.06 (3.93)	12.19 (12.14)		
H_2L^2	Pale yellow	66.12 (65.85)	5.24 (5.13)	16.95 (16.46)		
(VO)L ² (bipy)	Reddish orange	60.47 (60.51)	4.13 (4.02)	14.55 (14.70)		
H_2L^3	Pale yellow	66.66 (66.70)	5.22 (5.26)	10.36 (10.43)		
(VO) L ³ (bipy)	Reddish orange	61.34 (61.11)	4.23 (4.10)	11.24 (11.4)		
H_2L^4	Pale yellow	60.70 (60.23)	4.83 (4.60)	16.55 (16.21)		
(VO)L ⁴ (bipy)	Reddish orange	59.19 (59.79)	3.84 (3.71)	14.64 (15.15)		

Table 3				
EPR and	bonding	parameters	of the	complexes

	(VO)L ¹ (bipy)	(VO)L ² (bipy)	(VO)L ³ (bipy)	(VO)L ⁴ (bipy) 1.61	
μ (BM)	1.90	1.67	1.60		
811	1.960	1.963	1.964	1.956	
g_{\perp}	1.992	1.994	1.998	1.986	
gav/iso	1.981	1.981	1.986	1.979	
$A_{ }$ (cm ⁻¹)	145.99×10^{-4}	147.65×10^{-4}	146.97×10^{-4}	141.54×10^{-4}	
A_{\perp} (cm ⁻¹)	46.38×10^{-4}	49.13×10^{-4}	52.51×10^{-4}	50.99×10^{-4}	
$A_{\rm av/iso}$ (cm ⁻¹)	79.96×10^{-4}	82.2×10^{-4}	84.34×10^{-4}	82.00×10^{-4}	
α^2	0.616	0.589	0.578	0.704	
β^2	0.947	0.939	0.902	0.869	





Table 4 Selected IR frequencies (cm⁻¹) of ligands and complexes

Compound	$v_{\rm C=N}$	v _{N-C}	v _{C-O}	$v_{V=O}$	$v_{\rm V-O}$	$v_{ m V-N}$	$v_{ m bipy}$
$\begin{array}{c} \hline \\ H_2L^1 \\ (VO)L^1(bipy) \end{array}$	1620 1600	- 1536	- 1344, 1469	_ 955	- 518	_ 455, 419	_ 1438, 712, 616
H_2L^2 (VO)L ² (bipy)	1603 1589	- 1528	_ 1366, 1471	_ 963	- 510	_ 443, 417	_ 1436, 722, 628
H ₂ L ³ (VO)L ³ (bipy)	1610	- 1535	_ 1347, 1458	_ 470	-	- 451, 418	_ 1440, 718, 619
H ₂ L ⁴ (VO)L ⁴ (bipy)	1609 1595	- 1522	_ 1352, 1469	_ 957	520	- 458, 418	_ 1439, 722, 621

Axially anisotropic spectra are obtained with two sets of eight line pattern with $g_{||} < g_{\perp}$ and $A_{||} \gg A_{\perp}$ relationship is characteristics of an axially compressed d_{xy}^{-1} configuration [16,17].

The spectra show two type of resonance components, one set is due to parallel features and other set due to perpendicular features, which indicate axially symmetric anisotropy with sixteen line hyperfine splitting, characteristic of interaction between the electron and vanadium nuclear spins. The g_0 and A_0 values are remarkably constant for all complexes. Ligand nitrogen or hydrogen superhyperfine splittings are not observed on vanadium line. This indicates the unpaired electrons to be in b_{2g} orbital (d_{xy} , 2B_2 ground state) localized in metal, thus excluding the possibility of its interaction with ligands [18–22].

The spectra show signals characteristic of mononuclear VO^{2+} species. The isotropic parameters g_0 and A_0 are ~ 1.98 and ~ 88 G, respectively. These values are in range of typical for VO^{2+} distorted octahedral complexes [23–25]. It is reported the g and A values are very sensitive to the vana-

dium coordination environment and may be used to distinguish between the species with different coordination environment. In the present case, A and g values for all the complexes are almost same and therefore no appreciable change in the coordination environment.

The molecular orbital coefficient α^2 and β^2 were also calculated for the complexes by using the following equations.

$$\alpha^2 = \frac{(2.0023 - g_{||})E}{8\lambda\beta^2}$$
$$\beta^2 = \frac{7}{6} \left[\left(-\frac{A_{||}}{P} \right) + \left(\frac{A_{\perp}}{P} \right) + \left(g_{||} - \frac{5}{14}g_{\perp} \right) - \frac{9}{14}g_e \right]$$

where $P = 128 \times 10^{-4} \text{ cm}^{-1}$, $\lambda = 135 \text{ cm}^{-1}$ and *E* is the electronic transition energy of ${}^{2}\text{B}_{2} \rightarrow {}^{2}\text{E}$. The lower values for α^{2} compared to β^{2} indicated that in-plane σ bonding is more covalent than in-plane π bonding [26].

The in-plane π bonding parameter β^2 observed are consistent with those observed for McGarvey and Kilvelson for vanadyl complexes of acetylacetone.



Fig. 6. Far IR spectrum of the of (VO)L⁴(bipy).

3.4. Infrared spectral studies

Infrared spectral results are presented in Table 4 and representative spectra are shown in Figs. 5 and 6. Compound H_2L^1 , H_2L^2 , H_2L^3 and H_2L^4 show a band around 3400 and $3200 \,\mathrm{cm}^{-1}$, which are due to OH streching mode and NH streching mode of free OH and NH groups, respectively. These bands are absent in complexes, which suggests deprotonation of the phenolic group indicating the coordination though phenolic oxygen, and enolisation of the carbonyl group, followed by deprotonation. IR spectra of complexes show sharp band at $1536-1510 \text{ cm}^{-1}$ due to newly formed N=C bond indicating the coordination of hydrazones take place in the form of enol rather than as keto form. The lowering of the band at $\sim 1610 \,\mathrm{cm^{-1}}$ of ν (C=N) by 20–13 cm⁻¹, is explicit evidence for coordination of the hydrazone through the azomethine nitrogen. The spectrum of the complexes exhibit a symmetric shift in the position of the band in the region $1600-1350 \,\mathrm{cm}^{-1}$ due to C=C and C=N vibrational modes and their mixing patterns are different from those present in ligands spectra. Coordination of heterocyclic base is indicated by weak bands in the region of $455-443 \text{ cm}^{-1}$, are due to V–N stretching vibrations. Weak bands in the region $520-510 \text{ cm}^{-1}$ indicate V-O (aryl) bond, resulting from the coordination of phenolic oxygen. A very sharp peak at $970-955 \text{ cm}^{-1}$ suggests the presence of V=O bond in complexes. The frequency range observed in complexes indicates that V=O bond is weakened by strong σ and π electron donation by enolate and phenoxy groups to the antibonding orbital of the V=O group [27,28]. The variation in frequency suggests that the $d\pi - p\pi$ overlap between vanadium and oxygen atom is influenced by substituents and coligands [16,29,30].

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