



Synthesis and spectral characterization of ternary mixed-vanadyl β -diketonate complexes with Schiff bases

Balram Prasad Baranwal*, Kiran Tripathi, Alok Kumar Singh, Saurabh Tripathi

Coordination Chemistry Research Laboratory, Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273 009, India

ARTICLE INFO

Article history:

Received 5 December 2011

Received in revised form 27 January 2012

Accepted 3 February 2012

Keywords:

Oxovanadium(IV)

Mixed-ligand complexes

Schiff bases

β -Diketones

ABSTRACT

A new method to synthesize some mononuclear ternary oxovanadium(IV) complexes of the general formula $[\text{VO}(\beta\text{-dike})(\text{SB})]$ (where $\text{H}\beta\text{-dike}$ = acetylacetonone; benzoylacetonone or dibenzoylmethane, HSB = Schiff bases) has been explored by stepwise substitutions of acetylacetonate ion of $\text{VO}(\text{acac})_2$ with Schiff bases. The substituted acetylacetonone could be fractionated out with *p*-xylene as an azeotrope. The complexes were characterized by elemental analyses, molecular weight determinations, spectral (electronic, infrared, ^1H NMR, EPR and powder XRD) studies, magnetic susceptibility measurements and cyclic voltammetry. Molar conductance measurements indicated the complexes to be non-electrolytes in nitrobenzene. Bidentate chelating nature of β -diketonates and Schiff base anions in the complexes was established by infrared and NMR spectra. Molecular weight determinations confirmed mononuclear nature of the complexes. The EPR spectra illustrated coupling of the unpaired electron with ^{51}V nucleus ($I=7/2$). Cyclic voltammograms of all the complexes displayed two-step oxidation processes. The oxidation peak potential corresponded to the quasireversible one-electron oxidation process of the metal center, yielding V(V) species. Transmission electron microscopy (TEM) indicated spherical particles of ~ 200 nm diameter. The synthesized complexes are mixed-ligand complexes showing a considerable hydrolytic stability in which vanadium is having coordination number 5. A square pyramidal geometry around vanadium has been assigned in all the complexes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Current interest in the mononuclear metal β -diketonates assemblies of the general composition $[\text{VO}(\beta\text{-dike})(\text{SB})]$ is mainly because of these complexes possess anticancer and insulin mimetic activity [1–5], specially with β -diketonate ligands [6,7]. In the past decade, Bohm's catalysts, namely, $\text{VO}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$ /Schiff base systems [8–10] have received considerable attention. The advantages of this catalyst system include good-to-high activity and enantioselectivity as well as easy modification of Schiff base ligands. In higher oxidation states (IV and V), vanadium is a hard metal ion which forms fairly stable complexes with O-donor ligands, but it binds weakly to N- or S-donor atoms [11]. Furthermore, the lability and stability of the vanadium complexes and the nuclearity of its compounds affect their biological response [12,13]. An extensive work has been done on $\text{VO}(\text{acac})_2$ and its adducts with various O- and N-donor ligands [14]. However, the substitution reaction of vanadyl acetylacetonate has not been done so far.

Keeping in view of these objectives, we have explored a new and easier method of synthesis for mixed-ligand ternary vanadium(IV)

complexes with multidentate ligands like β -diketonates and Schiff bases. The complexes were characterized by spectral methods and their redox behavior was discussed. Particle size of the complexes was obtained in the nano-range from powder XRD and TEM. These were showing a considerable hydrolytic stability.

2. Experimental

2.1. Materials and analytical methods

Organic solvents (Qualigens) were purified before use by standard methods [15]. $\text{VO}(\text{acac})_2$, benzoylacetonone and dibenzoylmethane from Aldrich were used as received after checking their melting points. Vanadium and chlorine were estimated gravimetrically as silver vanadate and silver chloride, respectively [16]. Acetylacetonone in the collected azeotrope was estimated colorimetrically with ferric alum according to the method described by Bonner and Thorne [17].

2.2. Physico-chemical measurements

The instruments employed for recording the magnetic susceptibility, conductivity measurements, IR, ^1H NMR, TEM and elemental analyses (C, H and N) are as reported earlier [18]. Electronic spectra

* Corresponding author. Tel.: +91 551 2203459.

E-mail address: drbbaranwal@gmail.com (B.P. Baranwal).

were recorded on a Cary 2390 spectrophotometer in Nujol. Powder XRD data were collected on a Bruker D8 Advance diffractometer with Ni filtered Cu K α radiation with a scan speed of 1 s and scan step of 0.05°. EPR spectra were recorded on E-112 ESR spectrometer (Varian, USA). The spectrometer was operated at X-band (9.5 GHz) with sensitivity of $5 \times 10^{10} \Delta H$ spins. Cyclic voltammetric experiments were carried out using CHI – 620C electrochemical analyzer. A three-electrode setup was used for measurement consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and a Ag/Ag⁺ reference electrode. Tetrabutyl ammonium

perchlorate was used as a supporting electrolyte and the solution concentration was taken 10^{-3} M.

Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) using thermistor sensing device with the help of which the changes in boiling points were recorded by the change in resistance of the thermistor. The following formula was applied for the determination of the molecular weights:

$$M = \frac{KW}{\Delta R}$$

where M is the molecular weight of the unknown sample, W is the weight of solute, ΔR is the change in resistance due to addition of solute (W). The thermistor constant (K) for benzene was evaluated by using naphthalene as a standard solute. In each experiment, 15–20 mL of benzene was employed.

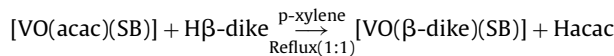
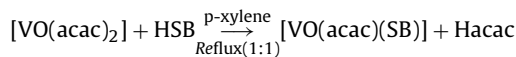
2.3. Synthesis of oxovanadium complexes

In a typical synthesis for [VO(bzac)(SB-1)] (**2**) first step is to prepare Schiff bases by condensation of salicylaldehyde with aniline or p-chloroaniline [18,19]. A solution of HSB-1 (3.16 g, 13.63 mmol) in 20 mL p-xylene was slowly added to VO(acac)₂ (3.61 g, 13.63 mmol) in 50 mL p-xylene with constant stirring. The reaction mixture was refluxed for 10 h with slow and continuous azeotropic fractionation of liberated acetylacetone and p-xylene (b.p. 122 °C). The progress of the reaction was followed by estimation of acetylacetone content in the collected azeotrope colorimetrically. A clear brown solution was resulted when the reaction was completed. Excess solvent was removed *in vacuo* and a brown colored solid, [VO(acac)(SB-1)] (**1**) was obtained (results of elemental analyses are given in Table 1). A solution of benzoylacetone (1.25 g, 7.71 mmol) in 20 mL p-xylene was slowly added to the solution of complex **1** (3.06 g, 7.71 mmol) in 50 mL p-xylene with constant stirring. The reaction mixture was refluxed for 12 h with slow and continuous fractionation of liberated acetylacetone and p-xylene. Excess solvent was removed under reduced pressure and the product was reprecipitated from benzene-diethylether mixture (1:4 ratio). A similar procedure was adopted to synthesize other oxovanadium(IV) complexes by taking different reactants in equimolar ratios and details of analytical results are given in Table 1.

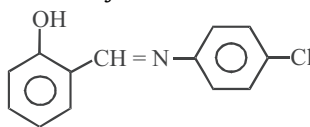
3. Results and discussion

Some mixed-ligand complexes of vanadium(IV) were synthesized by stepwise substitution reactions carried out in p-xylene. p-Xylene was a suitable choice in these reactions as it forms an azeotrope with the liberated acetylacetone, which could be

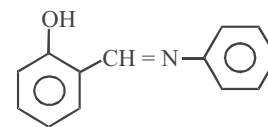
fractionated out to push the reaction in the forward direction. The reactions are given below:



where Hacac = acetylacetone; H β -dike = benzoylacetone or dibenzoylmethane and HSB = HSB-1 or HSB-2



HSB-1



HSB-2

All the synthesized complexes are non-volatile colored solids which are soluble in non-polar organic solvents including benzene, toluene, chloroform, dichloromethane *etc.* The molar conductance of complexes at 10^{-2} – 10^{-3} molar concentrations in nitrobenzene was obtained in the range 7–8 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ which indicated them to be non-electrolytes [20]. Ebullioscopic method of molecular weight determinations showed that all the complexes were monomeric in refluxing benzene (Table 1).

3.1. Hydrolytic stability of the complexes

VO(acac)₂ is a moisture sensitive compound which forms adduct with water. This is checked while replacement of acetylacetonate anion with the ligands used in the present investigation. This hydrolytic stability is tested by addition of 1% water in benzene solution of the complexes. Even after refluxing the contents for ~12 h, no change was observed. The complexes, after removing the excess solvent under vacuum, corresponded to the initial composition.

3.2. Infrared spectra

In infrared spectra of all the complexes O–H stretching vibrations of β -diketones and Schiff bases were found absent in the region 3600–3200 cm^{-1} . No band was found in 1600–1700 cm^{-1} region indicating the CO group of β -diketones was not free in the complexes. Two splitted new bands observed at 1595–1565 cm^{-1} ($\nu_{\text{C}=\text{O}}$) and 1517–1496 cm^{-1} ($\nu_{\text{C}=\text{C}}$) indicated the chelating nature of β -diketonate ion in the complexes [21]. The $\nu_{\text{C-O}}$ (phenolic) bands appeared in the region 1280–1263 cm^{-1} in free Schiff bases were shifted to higher wave number ($\sim 20 \text{ cm}^{-1}$) which may be due to bond formation from oxygen to the metal after deprotonation. The infrared spectra of all the free Schiff bases exhibited a strong and sharp band in the region 1631–1620 cm^{-1} are shifted to lower frequencies ($\sim 15 \text{ cm}^{-1}$) in complexes indicating coordination through azomethine nitrogen. A band at $\sim 485 \text{ cm}^{-1}$ and one at $\sim 588 \text{ cm}^{-1}$ were assigned to V–N and V–O vibrations, respectively [22]. A strong band, observed at $\sim 954 \text{ cm}^{-1}$, was assigned to $\nu(\text{V}=\text{O})$ [22] in all the complexes.

3.3. Electronic spectra

The electronic spectra of the oxovanadium(IV) complexes exhibited three bands at 12,055, 16,750 and 25,900 cm^{-1} . First two bands ($\sim 12,000$ and $\sim 16,750 \text{ cm}^{-1}$) may be assigned due to ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ and ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ transition. The third band at $\sim 26,000 \text{ cm}^{-1}$ was an intense charge transfer band due to ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transition. These transitions were characteristic of square pyramidal geometry around vanadium atom in these complexes [23,24].

Download English Version:

<https://daneshyari.com/en/article/1233029>

Download Persian Version:

<https://daneshyari.com/article/1233029>

[Daneshyari.com](https://daneshyari.com)