



Ultrasound assisted synthesis, characterization and electrochemical study of a tetradentate oxovanadium diazomethine complex



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ABSTRACT

The oxovanadium (IV) complex "VOL" of a tetradentate Schiff base ligand derived from the condensation of diaminoethane and 2-hydroxy-1-naphthaldehyde was efficiently prepared via ultrasound irradiation and the template effect of VO(acac)₂.

The resulting product was characterized by elemental analysis, infrared, electronic absorption and molar conductance measurement. Single X-ray structure analysis showed that the complex is a monomeric five-coordinate with a distorted square pyramidal geometry. It crystallizes in monoclinic system having unit cell parameters $a = 8.3960(5) \text{ \AA}$; $b = 12.5533(8) \text{ \AA}$ and $c = 18.7804(11) \text{ \AA}$; $\alpha = \gamma = 90^\circ$; $\beta = 104.843^\circ(2)$, with $P 2_1/c$ space group.

Cyclic voltammetry of the complex, carried out on a glassy carbon (GC) electrode in DMF, showed reversible cyclic voltammograms response in the potential range 0.15–0.60 V involving a single electron redox wave V^V/V^{IV} , the diffusion coefficient is determined using GC rotating disk electrode. The Levich plot $I_{lim} = f(\omega^{1/2})$, was used to calculate the diffusion-convection controlled currents.

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1. Introduction

Schiff base ligands (SB) derived from diamines and phenolic aldehydes have proven to be a class of versatile ligands for many transition metals including vanadium (IV) [1–3]. Recently, the coordination chemistry of vanadyl complexes has extraordinary developed in various directions due to their interesting structural features [4–6], catalytic applications [7] potential roles in a variety of biorelated processes, such as insulin mimics [8,9], as well as antimicrobial or anti-leukemia effects [10,11]. The presence of different heterocyclic moieties in some oxovanadium SB complexes has been linked to their antitumoral properties conferring them a promising future in treatment of cancers [12].

The majority of oxovanadium (IV) SB complexes exhibiting N₂O₂ coordination and reported in the literature are green. Their structure is generally well established as monomers with five-coordinate square-pyramidal geometry [5,6] but in rare cases, trigonal bipyramidal or distorted octahedral geometries have been

observed [13–15]. Heterogeneous oxovanadium SB complexes catalysts, immobilized in microspheres, have been successfully used in the aerobic selective oxidation of ethyl benzene to acetophenone and exhibit high catalytic activity and excellent selectivity [16].

Electrochemical study and structural properties of oxovanadium complexes with tetradentate SB ligands attract particular attention because of their reversible one-electron redox behavior [17,18]. However, oxovanadium complexes with a large number of tetradentate SB ligands have been widely reported [19,20].

Electrochemical study and structural properties of oxovanadium complexes bearing tetradentate SB ligands have attracted particular attention owing to their two successive one electron redox couple [17,18] and oxovanadium complexes with a large number of tetradentate SB ligands have been widely reported [19,20]. Over the last decades considerable efforts have been aiming at the development of new synthetic procedures including the solvent-free method [21], microwave assisted synthesis approach [22], electrosynthesis [23] and ultrasound assisted synthesis [24]. Ultrasound irradiation is considered as a green and efficient technique for the activation of reagents in the synthesis of organic [25,26] and inorganic compounds [27]. The formation of several metal

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complexes bearing azo ligands, like Schiff bases [28,29], porphyrins [30] and quinolones [31], have been enhanced under ultrasound. The significant features of the ultrasound approach are the formation of pure products in prominent yields [32], the improved rate of reactions and the easier handling of reagents and products. The ultrasound synthesis technique is thus highly adapted to green chemistry approaches in coordination chemistry [33].

Considering the importance of oxovanadium SB complexes, we wish to report in this work a safe procedure without solvent under ultrasound irradiation for the synthesis of an oxovanadium complex by template method, previously prepared by F.C. Anson [34] using a conventional procedure. The complex has been characterized by single crystal X-ray diffraction and the electrochemical properties of this complex have been investigated by cyclic voltammetry at a glassy carbon (GC) electrode in DMF solvent. The diffusion coefficient has been determined using the Levich plot on a GC rotating disk electrode.

2. Experimental

2.1. Materials and measurements

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. Sonication was performed on an US-bath with frequency of 50–60 Hz and a nominal power (720 W). Elemental analyses were performed on an Elementar-Vario EL III CHNS analyzer. Infrared spectra were obtained using potassium bromide (KBr) pellets ($4000\text{--}400\text{ cm}^{-1}$) on a Shimadzu FTIR spectrophotometer. Electronic spectra in the 200–900 nm range were recorded using a Shimadzu UV-1800 spectrophotometer using DMF as solvent. Molar conductance of VOL complex was determined in DMF (10^{-3} M) at room temperature using MeterLab CDM-210 conductivity meter. Melting point of the complex was determined on a Kofler Bank 7779 apparatus.

Electrochemical experiments were performed on a PGZ 301 potentiostat, cyclic voltammograms (CV) and rotating disk Electrode (RDE) measurements were recorded at room temperature in DMF solutions containing 0.1 M LiClO_4 as supporting electrolyte, using a glassy carbon (GC) as working electrode, platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Prior to the experiments the working electrode was polished and rinsed thoroughly with distilled water and acetone. The polished electrode was placed in 0.5 M H_2SO_4 solution and the electrochemical activation of the electrodes were performed by continuous potential cycling from -500 to 1800 mV at a sweep rate of 100 mV s^{-1} until a stable voltammogram is obtained [35]. Before each electrochemical investigation, the electrolyte was purged with nitrogen during 15 min.

Cyclic voltammogram measurements were performed in the range $-2200\text{--}1600\text{ mV}$ versus SCE in which the electrochemical redox couple of $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ is observed in the positive window of the scan. Under identical conditions, the ferrocene/ferricinium (Fc/Fc^+) couple is observed at 455 mV .

2.2. Synthesis procedures

2.2.1. Ultrasonication method

A reaction flask containing 0.344 g (2 mmol) of 2-hydroxy-1-naphthaldehyde, $66.8\text{ }\mu\text{l}$ (1 mmol) of 1,2-diaminoethane and 0.265 g (1 mmol) of bis(acetylacetonato) oxovanadium (Scheme 1), mixed in a mortar, was immersed in an ultrasonic bath at a temperature of $50\text{ }^\circ\text{C}$. The reaction mixture was exposed to ultrasound irradiation for 40 min. Upon reaction completion shown by TLC analysis (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 9.5/0.5, V/V). The obtained solid

was filtered and washed several times with methanol and diethylether, successively and dried over night in vacuum. Single crystals, suitable for X-ray diffraction, were obtained after 2 days of crystallization from DMSO/MeOH. Color: green, Yield: 95.4%, mp $>270^\circ$.

2.2.2. Conventional method

To a solution of 0.344 g (2 mmol) of 2-hydroxy-1-naphthaldehyde in 8 ml of methanol was added $66.8\text{ }\mu\text{l}$ (1 mmol) of 1,2-diaminoethane in 5 ml of methanol. 0.265 g (1 mmol) of bis(acetylacetonato) oxovanadium dissolved in 15 ml of methanol was added drop wise. The reaction was stirred and refluxed for 3 h under nitrogen atmosphere. Reaction complete, based on TLC analysis, the resulting compound was filtered and washed with methanol and diethylether to afford pure desired product yielding 77.6%. S.A. Amer [36], N. Choudhary [37] and F.C. Anson [34–38] have reported the synthesis of this complex yielding 70–90%.

Both oxovanadium complexes gave satisfactory elemental analysis, in good agreement with calculated values. Analysis calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_3\text{V}$, prepared under ultrasound irradiation: C: 66.52%, H: 4.19%, N: 6.46%; found: C: 66.83%; H: 4.35%; N: 6.32%; IR (KBr pellets $\nu\text{ cm}^{-1}$) 1618 (C=N), 1340–1360 (C–O), 1542 (C=C), 983 (V=O); UV–Vis: DMF, $\lambda\text{ nm}$, [$\epsilon\text{ M}^{-1}\text{ cm}^{-1}$]: 323 [7722], 380 [4166], 610 [83].

2.3. X-ray crystallography

Suitable single crystals of the oxovanadium complex (VOL) were grown by slow layer diffusion of DMSO into a MeOH solution at room temperature. A green plate single crystal of dimensions $0.25 \times 0.18 \times 0.12\text{ mm}^3$ suitable for X-ray analysis was used for data collection at 173 (2) K on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid device, using Mo/ $K\alpha$ radiation ($\alpha = 0.71073\text{ \AA}$). The crystal-detector distance was 38 mm.

The cell parameters were determined (APEX2 software) [39] from reflections taken from three sets of 12 frames, each at 10s exposure. The structure was solved by direct methods using the program SHELXS-97 [40]. The refinement and all further calculations were carried out using SHELXL-2013 [41]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . A semi-empirical absorption correction was applied using SADABS in APEX2 [39]; transmission factors: $T_{\text{min}}/T_{\text{max}} = 0.6157/0.7456$.

2.4. Results and discussion

2.4.1. Molar conductance

The molar conductance of 10^{-3} M of VOL complex in DMF as solvent is $\Lambda = 1.74\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, this very low value indicating that the title complex is electrically neutral [42,43].

2.4.2. Crystal structure of VOL complex

The crystal structure of the complex, depicted in Fig. 1, consists of one molecule in the asymmetric unit. The compound crystallizes in the monoclinic system with space group P21/c and the cell dimensions $a = 8.3960(5)$; $b = 12.5533(8)$; $c = 18.7804(11)\text{ \AA}$; $\alpha = \gamma = 90^\circ$; $\beta = 104.843^\circ(2)$.

Parameters for data collection and refinement are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

The structure of the VOL complex has a slightly distorted square pyramidal coordination geometry. The basal square plane is formed by the N,N'-bis(2-hydroxy-naphthalideno)-diaminoethane molecule, which acts as a tetradentate ligand through its two N

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