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Chemistry of molecular and supramolecular structures of vanadium(IV) and dioxygen-bridged V(V) complexes incorporating tridentate hydrazone ligands

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ABSTRACT

Four hydrazone ligands: 2-benzoylpyridine benzoyl hydrazone (HBPB), di-2-pyridyl ketone nicotinoyl hydrazone (HDKN), quinoline-2-carbaldehyde benzoyl hydrazone (HQCB), and quinoline-2-carbaldehyde nicotinoyl hydrazone (HQCN) and four of their complexes with vanadyl salts have been synthesized and characterized. Single crystals of HBPB and complexes $[VO(BPB)(\mu_2\text{-}O)]_2$ (**1**) and $[VO(DKN)(\mu_2\text{-}O)]_2\cdot½H_2O$ (**2**) were isolated and characterized by X-ray crystallography. Each of the complexes exhibits a binuclear structure where two vanadium(V) atoms are bridged by two oxygen atoms to form distorted octahedral structures within *cis*-N_2O_4 donor sets. In most complexes, the uninegative anions function as tridentate ligands, coordinating through the pyridyl- and azomethine-nitrogen atoms and enolic oxygen whereas in complex $[VO(HQCN)(SO_4)]SO_4\cdot4H_2O$ (**4**) the ligand is coordinated in the keto form. Complexes $[VO(QCB)(OMe)]\cdot1.5H_2O$ (**3**) and **4** are found to be EPR active and showed well-resolved axial anisotropy with two sets of eight line pattern.

1. Introduction

Interest in coordination chemistry of aroylhydrazones has been a subject of enthusiastic research since they show a wide range of catalytic properties, especially those examples derived from heterocyclic aldehydes or ketones [1]. The heightened interest in vanadium coordination complexes stems from its importance in biological systems, which is only now beginning to be fully appreciated [2]. Vanadium may or may not play an essential role in normal mammalian metabolism [2]. However, at pharmacological concentrations, some species are potential therapeutic agents [3,4]. Thus, the insulin-enhancing, insulin mimetic properties of oxovanadium(V) complexes, their use as model complexes for the active site of vanadoenzymes, and their use as catalysts in biological and industrial processes have been reported [5–9]. Furthermore, these compounds exhibit potential as anti-tumour agents by inhibiting growth of malignant cell lines by induction of cell-cycle arrest and/or cytotoxic effects [10]. Although most known insulin-like complexes contain vanadium in oxidation state +IV, vanadium(V) compounds have also been found to have insulin-like properties [11]. Depending on the number and type of donor atoms, and the nature of substitution in these oligodentate ligands, a variety of mononuclear and polynuclear oxo-, dioxo-vanadium(V) complexes and complex clusters have been reported [12–14]. The metal centres in oxovanadium(V) monomers with a N_2O_3 chromophore usually exhibit square pyramidal or trigonal bipyramidal geometries. The two five coordinate vanadium(V) centres often dimerise into octahedral bis(μ-oxo)-bridged complexes *via* (L)V=O–V=O(L) intermolecular interactions with highly asymmetric metal-(μ-O) distances.

In view of importance of vanadium complexes, we present here the synthesis, spectroscopic characterization of VO^{2+} and VO_2^+ complexes of some aroyl hydrazones and crystal structure determinations of two representative binuclear (μ_2-oxo)-bridged vanadium species.

2. Experimental

2.1. Materials

Di-2-pyridylketone (Aldrich), 2-benzoylpyridine (Aldrich), quinoline-2-carbaldehyde (Aldrich), Benzhydrazide (Aldrich), and nicotinic hydrazide (Aldrich), vanadyl sulfate (Aldrich) and $VO(acac)_2$ (E-Merck) were used as received. Solvents were purified by standard procedures before use.

2.2. Syntheses of ligands

All the hydrazone ligands were synthesized by adapting the earlier reported procedure, namely via condensation between

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appropriate aldehyde/ketone with the respective acid hydrazide as described below [15]. The chemical structures and abbreviations for the ligands are given in Fig. 1.

2.2.1. Synthesis of 2-benzoylpyridine benzoyl hydrazone (HBPB)

A methanol solution of benzoic hydrazide (0.136 g, 1 mmol) was refluxed with 2-benzoylpyridine (0.183 g, 1 mmol) continuously for 4 h after adding a few drops of glacial acetic acid. There was no immediate formation of the product. Then the reaction mixture was kept aside for slow evaporation at room temperature. After 3–4 days, colourless block-shaped crystals suitable for single crystal analyses were formed which were carefully separated (Scheme 1). Yield: 79%, m.p.: 128–130 °C. Elemental *Anal.* Calc.: C, 75.73; H, 5.02; N, 13.94. Found: C, 75.46; H, 5.23; N, 13.98%.

Selected IR (cm^{-1}) bands: ν(N–H) 3063; ν(C=O) 1678; ν(C=N) 1571.

Electronic absorption bands (MeCN) λ_{max} (nm): 233, 271, 322.

2.2.2. Synthesis of di-2-pyridyl ketone nicotinoyl hydrazone hemihydrate (HDKN·0.5H$_2$O)

Colourless HDKN·0.5H_2O was synthesized from di-2-pyridyl ketone and nicotinoyl hydrazide by a procedure similar to that described for HBPB. Yield: 84%, m.p.: 158–160 °C. Elemental *Anal.* Calc. for HDKN·0.5H_2O: C, 65.37; H, 4.52; N, 22.42. Found: C, 65.94; H, 4.26; N, 22.47%.

Selected IR (cm^{-1}) bands: ν(N–H) 2928; ν(C=O) 1689; ν(C=N) 1579.

Electronic absorption bands (MeCN) λ_{max} (nm): 223, 269, 318.

2.2.3. Synthesis of quinoline-2-carbaldehyde benzoyl hydrazone sesquihydrate (HQCB·1.5H$_2$O)

Pale-yellow HQCB·1.5H_2O was synthesized from quinoline-2-carbaldehyde and benzoic hydrazide. Yield: 89%, m.p.: 143–145 °C. Elemental *Anal.* Calc. for HQCB·1.5H_2O: C, 67.54; H, 5.33; N, 13.90. Found: C, 67.81; H, 4.86; N, 14.40%.

Selected IR (cm^{-1}) bands: ν(N–H) 3191; ν(C=O) 1655; ν(C=N) 1593.

Electronic absorption bands (MeCN) λ_{max} (nm): 240, 277, 326.

2.2.4. Synthesis of quinoline-2-carbaldehyde nicotinoyl hydrazone sesquihydrate (HQCN·1.5H$_2$O)

Colourless HQCN·1.5H_2O was prepared in the same way as for HDKN except quinoline-2-carbaldehyde was used instead of di-2-pyridyl ketone. Yield: 84%, m.p.: 140–142 °C. Elemental *Anal.* Calc. for HQCN·1.5H_2O: C, 63.36; H, 4.98; N, 18.47. Found: C, 63.16; H, 4.59; N, 18.58%.

Selected IR (cm^{-1}) bands: ν(N–H) 3173; ν(C=O) 1656; ν(C=N) 1591.

Electronic absorption bands (MeCN) λ_{max} (nm): 241, 279, 315.

2.3. Syntheses of complexes

2.3.1. Syntheses of [VO(BPB)(μ_2-O)]$_2$ (**1**)

Complex **1** was prepared by refluxing a methanolic solution of HBPB (1 mmol, 0.301 g) and vanadyl sulfate (1 mmol, 0.163 g) for 5 h. The resulting solution was allowed to stand at room temperature and after slow evaporation, yellow crystals of complex **1** were separated, filtered and washed with ether and dried over P_4O_{10} *in vacuo.*

[VO(BPB)(μ_2-O)]$_2$: Yield: 63%, m.p.: 225–227 °C. λ_m (DMF): 6 $ohm^{-1}\ cm^2\ mol^{-1}$. Elemental *Anal.* Calc.: C, 60.01; H, 3.87; N, 10.77. Found: C, 59.86; H, 4.28; N, 11.31%.

2.3.2. Synthesis of [VO(DKN)(μ_2-O)]$_2$·2H$_2$O (**2**)

To a solution of HDKN (1 mmol, 0.312 g) in methanol, a DMF–methanol mixture of VO(acac)$_2$ (1 mmol, 0.265 g) was added. The resulting solution was refluxed for 5 h. and then kept at room temperature. The pale-yellow crystals of **2** that separated out were filtered, washed with ether and dried over P_4O_{10} *in vacuo.*

[VO(DKN)(μ_2-O)]$_2$·2H_2O: Yield: 83%, m.p.: 182–184 °C. λ_m (DMF): 8 $ohm^{-1}\ cm^2\ mol^{-1}$. Elemental *Anal.* Calc. for [VO(DKN)(μ_2-O)]$_2$·2H_2O: C, 51.23; H, 3.69; N, 17.07. Found: C, 51.65; H, 3.23; N, 17.71%.

2.3.3. Synthesis of [VO(QCB)(OMe)]·1.5H$_2$O (**3**)

Complex **3** was prepared in similar manner as complex **2** by refluxing methanol solutions of HQCB (1 mmol, 0.303 g) and VO(acac)$_2$ (1 mmol, 0.265 g) for 5 h. A green crystalline precipitate was filtered, washed with ether and dried over P_4O_{10} *in vacuo.*

[VO(QCB)(OMe)]·1.5H_2O: Yield: 89%, m.p.: >300 °C. λ_m (DMF): 20 $ohm^{-1}\ cm^2\ mol^{-1}$. Elemental *Anal.* Calc. for [VO(QCB)(OMe)]·1.5H_2O: C, 54.14; H, 4.54; N, 10.52. Found: C, 53.73; H, 4.41; N, 10.63%.

2.3.4. Synthesis of [VO(HQCN)(SO$_4$)]SO$_4$·4H$_2$O (**4**)

Complex **4** was prepared in similar manner as complex **1** refluxing methanol solutions of HQCN (1 mmol, 0.303 g) and vanadyl

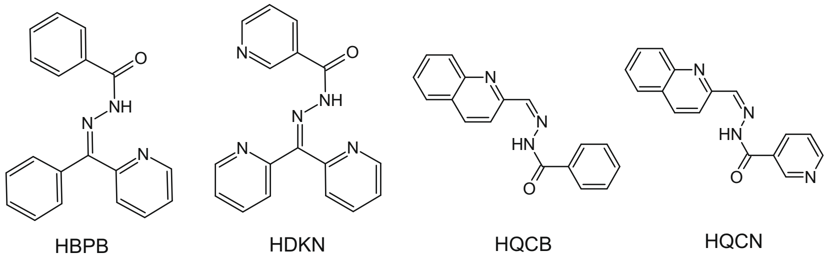
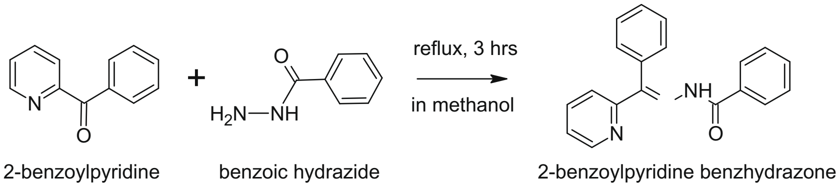


Fig. 1. Chemical structures of hydrazone ligands and their abbreviations.



Scheme 1. Synthesis of 2-benzoylpyridine benzoyl hydrazone.