

# Poster Presentations

## [MS37-P10] A Crystallographic and Kinetic Study of *O,O'* Bidentate Vanadium Complexes Carla Pretorius,<sup>a</sup> Johan A. Venter, Andreas Roodt

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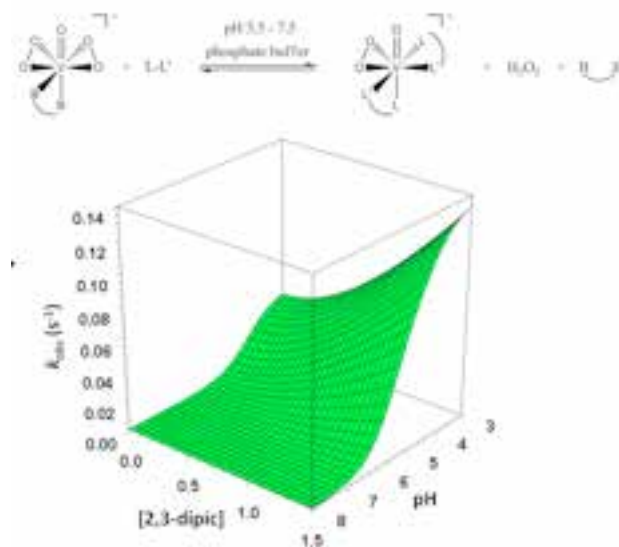
[VO(acac)<sub>2</sub>] (acac= acetylacetonate) and related complexes have been successfully synthesized and reported during the past few decades. Recent research has shown that vanadium β-diketonates are effective insulin mimicking agents with [VO(acac)<sub>2</sub>] and [VO(Et-acac)<sub>2</sub>] (Et-acac= 3-ethyl-2,4-pentanedionate) in particular showing excellent activity [1-2]. This discovery, along with other industrial and medical applications, has been the key driving force for research into new frontiers of vanadium coordination chemistry.

This study is concerned with the coordinative and structural properties of vanadium complexes in the +4 and +5 oxidation states containing primarily *O,O'* bidentate ligands. In addition, different ancillary ligands were selected and coordinated to the vanadium centre to evaluate their structural influence utilizing single crystal X-ray diffraction studies (XRD) in combination with infrared spectroscopy (IR). This has resulted in a new understanding of the solid state characteristics of these novel complexes and the effect of altering the electronic environment around the vanadium centre on structural properties. One such structure, [VO(dbm)<sub>2</sub>(MeOH)] (dbm= dibenzoylmethane) showed the importance of hydrogen bonding in the crystal lattice to expand into a novel 3-dimensional network of linked molecules. [3] A unique polymorph was also reported in this study and was compared to the published structure of [VO(dbm)<sub>2</sub>(pyr)] (pyr= pyridine).

A kinetic investigation of the substitution reaction of [VO(O<sub>2</sub>)<sub>2</sub>bpy] and 2,3-pyridine dicarboxylate (2,3-dipic) was integrated with

the study (see scheme). The complex solution chemistry of vanadium necessitated a wide array of experiments to evaluate the effects of not only ligand concentration on reaction rates, but also pH dependence of certain species in solution. Additionally, <sup>51</sup>V NMR experiments revealed important information regarding product formation and the identification of an intermediate, [VO(O<sub>2</sub>)(2,3-dipic)]<sup>2-</sup>, in the reaction. This culminated in a proposed reaction mechanism and rate law that accounts for various pH, pKa and concentration effects. Figure 1 illustrates the dependence of the pseudo first-order rate constant on pH and entering ligand concentration.

**Figure 1:** Three-dimensional plot showing the dependence of the pseudo first-order rate constant on pH and [2,3-dipic].



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