

# A Journey through a Vanadium Trail: Some Retrospection

By

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## Abstract:

This lecture consists of two parts. The first part deals with the chemistry of  $\mu$ -oxo divanadium compounds containing  $[\text{V}_2\text{O}_3]^{n+}$  ( $n = 4, 3$  and  $2$ ) cores. Compounds containing such cores have been widely studied in recent time because of their high thermodynamic stability and ease of synthesis. In literature at least thirty such compounds have been reported for which the crystal structures are known. All these compounds have symmetrical structures involving identical ligand molecules attached to both the vanadium centers. The purpose of the work presented in this part is to develop synthetic protocols to introduce ligand asymmetry in to the  $[\text{V}_2\text{O}_3]^{n+}$  cores and to study the influence of this asymmetry on the structural and spectroscopic behaviors of these compounds. The methodology developed has been extended to synthesize hetero-dinuclear compounds containing discrete V-O-M ( $\text{M} = \text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ ) cores.

The second part centers around a single crystal-to-single crystal (SCSC) transformation observed with a binuclear alcoholato-vanadium(V) compound to an oligomeric aldehyde-coordinated vanadium(IV) product. This irreversible transformation is triggered by photo-induced generation of phenoxyl radical that initiates an internal redox process where vanadium(V) is reduced to vanadium(IV) at the expense of a two-electron ligand-based oxidation from an alcoholate to an aldehyde. Such solid-state SCSC reactions impose severe demands on the structural similarity between the reactant and the product and are consequently quite rare. Attempts will be made to establish the mechanism of this internal redox process based on extensive X-ray diffraction study, IR and EPR spectroscopy.

## References:

1. M. Chaudhury et al. *Inorg. Chem.* **2008**, *47*, 4891.
2. M. Chaudhury et al. *Inorg. Chem.* **2007**, *46*, 5483.