

Synthesis of a novel vanadium(IV)-iron(III) heterometallic alkoxide: Aiming at low-nuclearity Single-Molecule Magnets

Danilo Stinghen^{1*}, Ronny R. Ribeiro¹, Siddhartha O. K. Giese¹, Giovana G. Nunes¹, Jaísa F. Soares¹

¹*Departamento de Química, Universidade Federal do Paraná, Curitiba, Brazil*

*e-mail: danilostinghen@gmail.com

Since the advent of the first single-molecule magnets, efforts have been driven towards the synthesis of molecules with both high magnetic anisotropy and a high total spin angular momentum quantum number. However, in more recent years it has been perceived that even low-nuclearity molecules may display SMM behaviour,¹ provided that the magnetic building blocks have high individual anisotropy. Along those lines, our research group has become interested in the use of building blocks containing non-oxo vanadium(IV) for this sort of molecules, since early investigations on homometallic dimers (Figure 1) containing this metal ion have afforded evidence of a consistent orbital contribution to the susceptibility, an important source of magnetic anisotropy.²

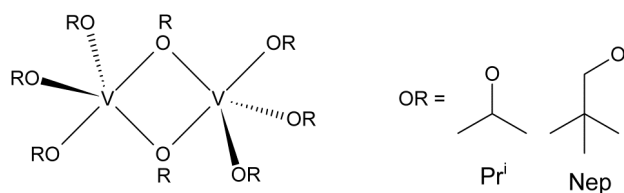


Figure 1 – Representation of the structure of the vanadium(IV) dimers employed as precursors

The objective of the present work is therefore to employ non-oxo vanadium(IV), despite its low number of unpaired electrons, together with other potentially anisotropic metal centres, to obtain low nuclearity molecules displaying slow relaxation of the magnetisation.

In this context, the reaction between the vanadium(IV) binuclear complex $[V_2(OR)_8]$ (R = neopentoxide) and an iron(III) precursor, $[Fe_2(\mu-OMe)_2(dpm)_4]$, dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate, produced brownish-red platelets of **1**, in small yields. EPR spectroscopy has afforded evidence that the product of the reaction is a heterometallic complex. In the solid state and in solution with non-coordinating solvents, the spectrum has a complex set of lines attributable to a mixed metal compound, while in solution of coordinating solvents, mononuclear vanadium(IV) and iron(III) signals are prevalent, suggesting that the heterometallic structure is present in the solid state, but breaks down in the presence of coordinating solvents. FTIR and preliminary single-crystal X-ray diffractometry studies have confirmed the formation of a product containing both the dpm^- and $^-\text{ONep}$ ligands, as was initially intended. CHN content analysis is consistent with a formulation $[FeV(ONep)_5(dpm)_2]$. The reaction between the iron(III) precursor and $[V_2(OPr^i)_8]$ is also underway, and so far the isolated product has displayed similar spectroscopic features to **1**, suggesting that the OPr^i ligand may also be suitable for the synthesis of heterometallic compounds.

- 1 Gomez-Coca, S. *et al. J. Am. Chem. Soc.* **2013**, 135, 7010.
- 2 Westrup, K. C. M. *et al. Dalton Trans.* **2011**, 40, 3192.
- 3 Nunes, G. G. *et al. Inorg. Chem. Comm.* **2003**, 6, 1278.

CNPq, CAPES, Fundação Araucária, UFPR.