Synthesis and characterization of decavanadate with Rhodamine B as a counterion

Viktor K. Boell[1*], Juliana M. Missina[1], Kahoana Postal[1], Francielli Santana[1], Siddhartha O. K. Giese[1], David L. Hughes[2], André L. Rüdiger[1], Jaísa F. Soares[1], Giovana G. Nunes[1]

[1]Departamento de Química, UFPR, Curitiba-PR, Brazil, [2] School of Chemistry, University of East Anglia, Norwich, UK.

*e-mail: boellviktor@gmail.com

The polyoxoanion decavanadate $[V_{10}O_{28}]^{6-}$ is widely used in biological, pharmacological, and medical areas, mainly because of its enzyme inhibition properties.[1]

Recently, fluorescent molecules, such as rhodamine B, have been associated with inorganic compounds in order to obtain cellular markers, which help visualize the intracellular target.[2] The purpose of this work was to synthesize and characterize the decavanadate with rhodamine B (RhodB) as a counterion. The reaction was carried out layering an aqueous solution of rhodamine B onto a decavanadate solution, freshly prepared by acidifying an aqueous solution of $NaVO_3$ until pH = 4. After complete diffusion of both phases, a violet powder was isolated along with dark green crystals (**A**, 61% yield of the crystalline product based on vanadium). The IR spectrum of **A** showed characteristic bands of the rhodamine B cation, as well as signals related to ν(V=O) at 956 cm^{-1}, ν_s and ν_{as}(V–O–V) at 823 and 756 cm^{-1}, typical of decavanadate. Elemental and single crystal XRD analyses of **A** confirmed the expected formulation $(RhodB)_6[V_{10}O_{28}]\cdot 8H_2O$, whose structure is under refinement. The characterization of **A** in solution was performed by ^1H and ^{51}V NMR analyses. The former showed chemical shifts consistent with the nine non-equivalent hydrogens of rhodamine B. The ^{51}V NMR spectrum evidenced partial breakage of the polyoxoanion, displaying a signal with δ = -560 ppm correspondent to the species $H_2VO_4^-$. Three signals of low intensity were observed with δ = -424, -500 and -515 ppm, which correspond to the three coordination environments of vanadium in decavanadate. The first decavanadate signal is generally of lower intensity, making it difficult to identify in diluted solutions. In the case of **A**, the decavanadate concentration was reduced by partial breakage of the aggregate. Thermogravimetric analysis showed a continuous weight loss from 20 to 500 °C, corresponding to the loss of water and organic cations. In this work, the association of decavanadate with a fluorescent molecule was successfully achieved in good yield. In future steps, the cytotoxicity and the fluorescence properties of **A** will be investigated.

[1.] Aureliano, M.; Fraqueza, G.; Ohlin, C. A. *Dalton Trans.* **2013**, *42*, 11770.
[2.] Mottram, L. F.; Forber, S.; Ackley, B. D.; Peterson, B. R. *Beilstein J. Org. Chem.* **2012**, *8*, 2156.

UFPR, CAPES / PVE A099/2013, CNPq, Fundação Araucária.