Techntetium derivatives of Dawson Heteropolyanions: Redox properties and α_1/α_2 Relative Stability

XavierLópez, Susanna Romo, Israël-Martyr Mbomekallé, Donna McGregor, Lynn Francesconi, Josep M. Poblet

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·li Domingo s/n, 43007 Tarragona, Spain

Javier.lopez@urv.cat

This work analyzes the differences in the redox behavior between the well-known α_1 and α_2 positional isomers of the technetium-monosubstituted Dawson anion, $[P_2W_{17}TcO_{62}]^{n-}$ [1]. The results, based on cyclic voltammetry (CV) measurements and density functional (DFT) calculations, show these two isomers' relative stability upon the number of electrons that the Tc ion carries. The α_1 form gains relative stability as the systems gets reduced from d^0 for Tc(VII) to d^3 for Tc(IV). The most stable oxidation state observed for technetium is Tc(V). In this case, the α_1 isomer is computed 4.0 kcal mol^{-1} more stable than α_2, whereas in fully oxidized form, Tc(VII), α_2 is more stable by –3.6 kcal mol^{-1}. This gain in stability for α_1 correlates with Tc orbital energies obtained with DFT calculations [2]. The first unoccupied molecular orbital of the α_1 isomer lays lower than its α_2 homologue, traducing into a more exothermic reduction process for α_1. The same stabilization of α_1 vs. the number of d electrons added has been observed in other $P_2W_{17}MO_{62}$ systems (M = V, Mo, Re). CVs also show, and DFT calculations explain, why isomer α_1 can not be oxidized to Tc(VII) in aqueous media, whereas it is possible for the α_2 isomer. Such a general behavior can be applied to systems containing other M ions. The pH influence on the reduction potentials has also been investigated. As in other polyoxometalate systems, increasing the pH shifts the reduction potentials towards more negative values. In addition, one-electron waves that appear close (or as a single two-electron one) to each other at low pH values split as pH is increased, although isomer α_1 and α_2 also show differences in this issue. At high pH, both isomers feature a pH-independent first reduction wave.

References:

[1] Howell, R. C.; Nilges, M. J.; Mbomekallé, I. M.; Lukens, Jr., W. W.; McGregor, D.; Belford R. L.; Francesconi, L. C. *Inorg. Chem.,* submitted to publication.

[2] López, X.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **124** (**2002**) 12574.

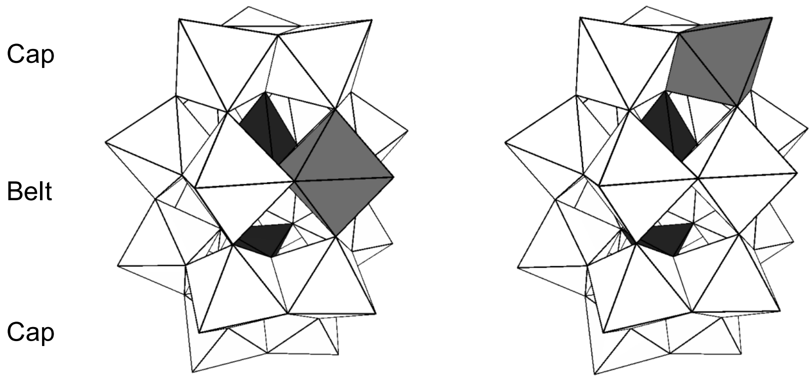

Figure 1. α_1 (left) and α_2 forms of the $P_2MW_{17}O_{62}$ Dawson anion. White and gray octahedra are WO_6 and MO_6 units, respectively. Black tetrahedra are PO_4 moieties.

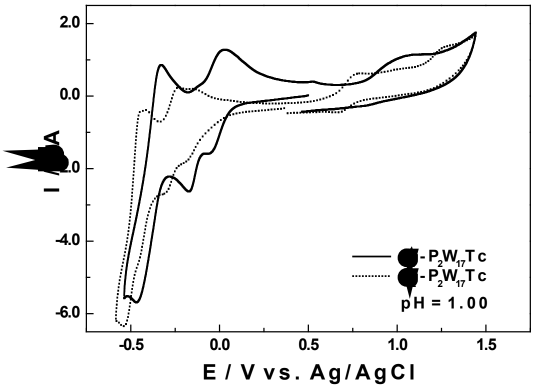

Figure 2. Cyclic voltammograms of **1** (solid line) and **2** (dotted line) in 0.2M Na_2SO_4 + H_2SO_4 pH 1. Working electrode: glassy carbon; reference electrode: Ag/AgCl; Scan rate: 10 mV.s^{-1}; polyoxometalate concentration: 0.2 mM.