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Unusual redox neighborhood in technetium compounds

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Techetium has a great number of oxidation states (usually we say 9 but in fact much more) and is evidently one of the elements with the most complicated chemistry. This is due its position in the center of 4d elements row with 7 electrones available for chemical bonding. One of the very special options complicating technetium chemistry is its ability to cluster formation and especially the possibility for Tc cluster to be reduced by consequtive addition of electrones one by one. So the oxidation states of Tc in hydrochloric acid could be 4+ (in K2TcCl6), 3+ (in [Bu4N]2Tc2Cl8), 2.5+ (in K3Tc2Cl8), 2+ (in K2Tc2Cl6), 11/6+ (in [Me4N]3Tc6Cl14 and 10/6+ (in [Me4N]2Tc6Cl12). We could imagine the number of hydroxides that could be formed sturting from these compounds. Another option is the presence of Tc atoms in different oxidation states within the same compound (p.e. Tc2Ac42 where Tc3+ and Tc7+ coexist in the one compound. New example is the red pertechnic acid. According to new synthesis and X ray structure study it contains 4 TcO6 octahedra with Tc6+, that is usually considered extremely unstable and 16 Tc(VII) tetrahedra aranged in a joint compund [TcVI 4TcVII 1668]·16H2O: a = 11.1743(6), b = 12.8839(6), c = 14.0661(6) Å, $\alpha = 71.128(2)$, $\beta = 69.015(2)$, $\gamma = 74.340(2)\circ$

, P-1, Z = 1. Of next extreme interest is

new Pu(III)(DMSO)6[TcO4]3 compound where reducing and oxidizing parts coexist.

Summary

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