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► **To cite this version:**

A. Thevenet, C. Marie, Dominique Guillaumont, V. Amendola, Philippe Guilbaud. Perrhenate and pertechnetate azacryptates in nitric acid solution. IUPAC 2019- 47th IUPAC World Chemistry Congress, Jul 2019, Paris, France. cea-02972120

**HAL Id: cea-02972120**

**<https://hal-cea.archives-ouvertes.fr/cea-02972120>**

Submitted on 20 Oct 2020

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# Perrhenate and pertechnetate azacryptates in nitric acid solution

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## Abstract

Technetium is an artificial element produced after fission of uranium in nuclear reactors<sup>[1]</sup>. <sup>99</sup>Tc is one of the most important fission product found in dissolution solutions of used nuclear fuel<sup>[2]</sup>. In nitric acid medium, technetium is found at +VII oxidation state as pertechnetate anion TcO<sub>4</sub><sup>-</sup>. Due to the large amounts of <sup>99</sup>Tc produced by nuclear fission and to the long half-life of this radionuclide (2.1 x 10<sup>5</sup> years), technetium is an element of particular importance in nuclear waste management<sup>[3]</sup>. In this work, technetium cryptands in nitric acid medium are studied. The large size and low charge density of the oxoanion make selective recognition in aqueous solution a great challenge.

For this purpose, a “polyammonium cage” ligand<sup>[4,5]</sup> was studied for the pertechnetate anion recognition in nitric acid solution. Coordination studies were performed with its inactive surrogate, the perrhenate anion (ReO<sub>4</sub><sup>-</sup>), by Infrared and RAMAN spectroscopies, single crystal XRD (Figure 1) and DFT calculations. As shown in Figure 1, the ligand conformation adapts itself to let one perrhenate anion enter the cavity (cage size expansion, hydrogens of the protonated amines directed towards the inside of the cavity). The complex stabilization is achieved by direct hydrogen bonds formation between the azacryptand and the perrhenate anion.

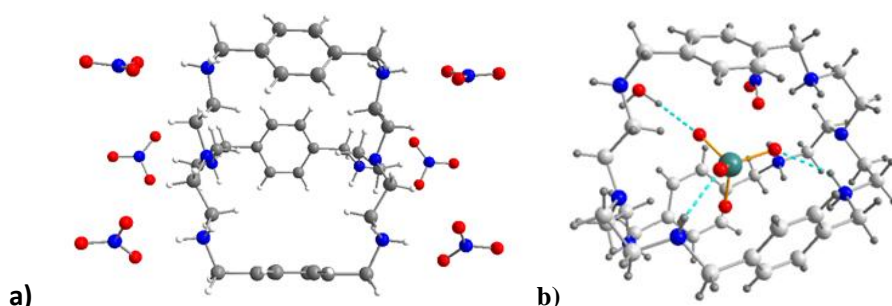


Figure 1 : Crystallographic structures a) free ligand H<sub>6</sub>L and b) complex  
[(ReO<sub>4</sub>)(H<sub>6</sub>L)].(ReO<sub>4</sub>)<sub>1.5</sub>(NO<sub>3</sub>)<sub>3.5</sub>(H<sub>2</sub>O)<sub>3</sub>

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