# EXAFS studies of technetium and rhenium complexes with relevance to radiopharmaceutical chemistry

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<th>Date of experiment:</th>
<th>Date of report:</th>
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<td>Christoph Hennig</td>
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## Report:
In radiopharmaceutical chemistry, the most frequently used technetium compounds are complexes of the oxo ion [Tc=O]³⁺. The applicability of such Tc(V) complexes is limited because of a possible instability and strong influence of the [Tc=O]³⁺ unit on the biobehaviour. Thus, there is a considerable interest in alternative chelate systems that offer lower polarity and enhanced in vivo stability. We created a new type of Tc(III) chelate that should fulfill these requirements. We synthesized e.g. Tc1 and Tc2 as prototypic representatives of this novel class of Tc(III) compounds [1]. EXAFS analyses should be compared with results of single-crystal X-ray diffraction analyses. The detection of non-coordinated carbon atoms of the chelate ligand should be studied. Investigations of Tc and Re carbonyl chemistry has led to an organometallic M(I) aqua ion, [M(CO)₃(H₂O)₃]⁺, (M = Tc, Re), as a precursor for the preparation of complexes containing the small [M(CO)₃]⁺ moiety. Tc(I) and Re(I) tricarbonyl complexes represent also a new and promising approach to low valent, non-polar and inert compounds [2]. Structural parameters of the precursor complexes Tc3 and Re1 which are available only in aqueous solution should be determined by EXAFS measurements.

![Tc1](image1.png)  ![Tc2](image2.png)  ![Tc3](image3.png)  ![Re1](image4.png)

Due to the extremely small concentration of the radionuclide present in the radiopharmaceutical preparation, XAS studies as well as most of chemical investigations employ the long-lived isotopes ⁹⁹Tc or inactive ¹⁸⁵/¹⁸⁷Re.

We applied Tc K-edge (21.044 keV) and Re L₃-edge (10.535 keV) EXAFS measurements (transmission mode, room temperature, two or three scans averaged; Tc₁, Tc₂: solid, each sample contained 4 mg metal pressed into Teflon powder; Tc₃, Re₁: concentration ~ 0.01 to 0.02 M, 2 cm sample thickness;). The data
were evaluated using the EXAFSPAK software. Effective scattering amplitude and wave phase-shift functions were calculated using FEFF6.

For Tc1 atomic distances of 2.22 Å (averaged distances for Tc-N and Tc-S), 1.94 Å (Tc-CN) and 3.13 Å (Tc-N\(_{CN}\)) were estimated. For the six carbon atoms included in the chelate system a Tc-C distance of 3.12 Å and a coordination number of 5.3 with a high standard deviation of ± 1.7 was obtained. For Tc2 atomic distances of 2.24 Å (averaged distances for Tc-N and Tc-S), 2.31 Å (Tc-P) and 3.19 Å (Tc-C, averaged value for six carbon atoms of the chelate system and two carbon atoms bound to phosphorous) were estimated. For the carbon coordination shell a coordination number of 7.4 was obtained but also with a high standard deviation of ± 1.6. The estimated distances and coordination numbers for Tc1 and Tc2 are consistent with the data from X-ray crystal-structure analyses. The difference between the bond distances Tc-N and Tc-S obtained from X-ray crystal-structure data is distinct smaller than the expected resolution in distance of the EXAFS analysis, therefore only an averaged value was obtained. To get a satisfactory evaluation of the EXAFS spectra, nearly linear multiple-scattering paths along the isocyanide group were taken into account.

The estimated atomic distances for Tc3 are 1.89 Å (Tc-C), 2.21 Å (Tc-O\(_{aq}\)) and 3.05 Å (Tc-O\(_{CO}\)) and for Re1 1.91 Å (Tc-C), 2.19 Å (Tc-O\(_{aq}\)) and 3.07 Å (Tc-O\(_{CO}\)). Thus no differences between the atomic distances of the analogous complexes were observed assuming an uncertainty of ± 0.02 Å. The estimated coordination numbers agree with the expected values. To obtain a satisfactory evaluation of the EXAFS spectra multiple-scattering paths to model the oxygen atom of the carbon monoxide had to be included.

References: