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Exploring EPR Parameters of ^{99}Tc Complexes for Designing new MRI Probes: Coordination Environment, Solvent, and Thermal Effects on the Spectroscopic Properties

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Currently, cancer is one of the most serious health problems. Studies have shown that this disease has increased in last years, including a growing number of deaths. Among the types of cancer, the breast cancer is the most common. Generally this type of cancer is diagnosed in advanced stages, thereby some modern techniques, such as tomography and Magnetic Resonance Imaging (MRI), which allow the diagnosis in early stages, have been used for breast cancer diagnosis. The MRI is a noninvasive technique for diagnosis because it is based on the magnetic properties of the ^{1}H and ^{17}O nuclei, which are the most abundant elements in the human body [1]. However, with only the natural relaxation of the water molecules in the body, it is often not possible to obtain clear MRI images. Thus, contrast agents (CAs) are used for improving the MRI image resolution. The CAs are paramagnetic compounds able to decrease longitudinal and transverse relaxation times of water molecules in the proximity of their structure, thus facilitating breast cancer diagnosis. Based on this context, it is necessary to understand the relaxation mechanisms of water molecules and the influence of paramagnetic effects on the ^{1}H and ^{17}O hyperfine coupling constant (A_{iso}) values [2].

In this study, the solvent and thermal effects on spectroscopic parameters of ^{99}Tc complexes coordinated to explicit water molecules were evaluated. Molecular dynamics simulations were performed followed by hyperfine coupling constant calculations (A_{iso}) and the QTAIM method was used to probe hydrogen bonds between the studied complex and water solvent molecules. In order to validate our calculation strategy for ^{1}H and ^{17}O hyperfine coupling constant values, the complex $[Mn(H_2O)_6]^{2+}$ was used.

The results showed a small difference between the explicit and explicit/implicit solvent for A_{iso} calculations on complexes 1 and 2 (figure 1). This small difference between the explicit and explicit/implicit solvent found was expected, which shows that the number of water molecules added during the A_{iso} calculation describes the system well. It can be noted also that thermal effect greatly influence the system. It is important to observe that the Tc coordination environments are different for both complexes, therefore, it is important to know that changes in the coordination environment of Tc complexes can significantly influence the A_{iso} results [3]. The QTAIM methodology is a quantum model considered innovative in studies of chemical bonds but also it is effective in characterizing intramolecular and/or intermolecular interactions. Thus, QTAIM calculations are very important to check the influence of hydrogen bonds in the A_{iso} values. Therefore, QTAIM calculations were performed for evaluating the

interaction between the water molecules and the studied complexes and our results showed a strong interaction between them [4].

Since, it is well-known that the use of gadolinium complexes as MRI contrast agents has generated several problems due to their high toxicity [9]. Our theoretical findings point out that an alternative to this traditional approach is to use technetium complexes as MRI contrast agents, because they present lower toxicity and show good A_{iso} results in solution [4].

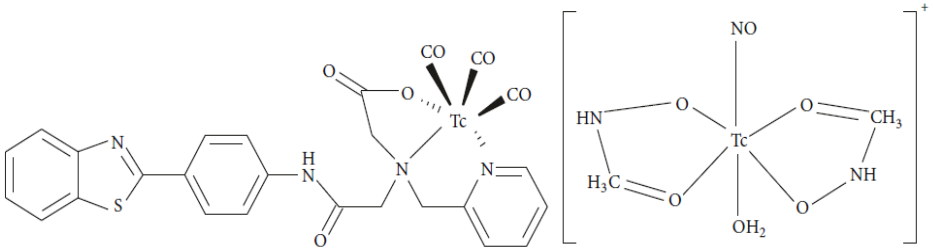

Figure 1: (^{99m}Tc)$(CO)_3$(NNO) conjugated with 2-(4-aminophenyl)benzothiazole(1); oxotechnetium(V) complex with the ligand N(2(1-Hpyrolmethyl).

Key-words: ^{99}Tc; MRI; Contrast Agents; Hyperfine constant.
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