Computational protocol to predict the Tc-99 NMR chemical shift

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Abstract

Tc-99 NMR chemical shift was predicted through models fitted to reproduce experimental data for 24 Tc-complexes.

Introdução

The discovery of new Tc complexes stable under physiological conditions is very important because of your use in ^{99m}Tc imaging or as radiopharmaceuticals. In this context, NMR spectroscopy has played a key role in the characterization of new technetium complexes. The Tc-99 nucleus covers a wide range of chemical shifts (~9000 ppm) and is very sensitive to the nature of the ligands[1].

In this present study, a comprehensive analysis of relevant features involved in the Tc-99 NMR chemical shift predictions are conducted. Non-relativistic and relativistic calculations are employed using distinct computational schemes. In addition, new relativistic NMR-DKH Gaussian basis sets were constructed for Tc atom. The proposed computational protocols were fitted and tested for a initial set of 24 Tc-complexes.

Resultados e Discussão

New all-electrons TZ2P-DKH Gaussian basis set for Tc atom were constructed for use together previous[2] NMR-TZ2P-DKH (H-He, Li-Ne, Na-Ar, K-Ca, Ga-Kr, Rb-Sr, In-Xe and Pt atoms) basis sets.

DFT non-relativistic calculations were carried out by using the GAUSSIAN 09 program Revision D.01. The geometries of all molecules were optimized at B3LYP/Def2-SVP basis set and the solvent effect as also considered in the geometry optimization and NMR chemical shift using the IEF-PCM formalism.

The NMR shielding constant (σ) was calculated using GIAO method at non-relativistic PBEPBE/NMR-TZ2P-DKH level. The Tc-99 NMR chemical shift was predicted through the equation (1), where the parameters “a” and “b” were fitted using a data of 24 Tc-complexes, Figure 1.

$$\delta_{calc} = a \times \sigma + b \qquad (1)$$

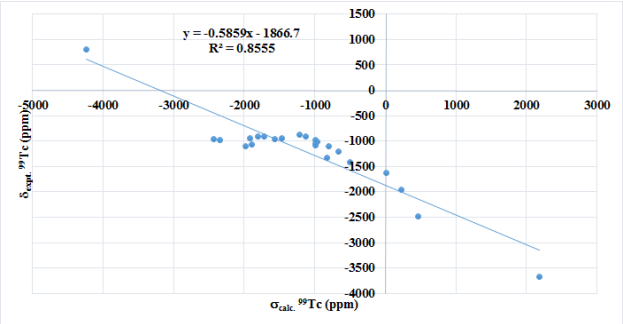

Figure 1. Simple regression linear model (δ_{expt} x σ_{calc}) used to development the model.

For the 24 Tc-complexes used in the present fit, was found a coefficient of determination (R^2) of 0.8555 and a mean absolute deviation for the Tc-99 NMR chemical shift of 245 ppm, showing a good agreement of the model with the experimental data.

Conclusões

The results obtained in the present study showed that the constructed model and the NMR-TZ2P-DKH basis set are a good alternative to predict the Tc-99 NMR chemical shift. In the next step, the model will be improved and more complexes will be considered.

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[1] Franklin, K. J.; Lock, C. J. L.; Sayer, B. G. and Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, 104, 5303.Curtis, M. D.; Shiu, K.; Butler, W. M. e Huffmann, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.
2 Paschoal, D.; De Oliveira, M. A. L.; Ramalho, T. C.; Fonseca-Guerra, C.; Dos Santos, H. F., submitted.