Computational protocol to predict the Pt-195 NMR chemical shift

Diego Paschoal[a] (PQ), Marcone A. L. de Oliveira[a] (PQ), Teodorico C. Ramalho[b] (PQ), Hélio F. Dos Santos[a] (PQ)

[a]*Universidade Federal de Juiz de Fora, Departamento de Química, Campus Universitário Martelos, 36.036-900, Juiz de Fora – Brasil*
[b]*Universidade Federal de Lavras, Departamento de Química, 37.200-000, Lavras – MG, Brasil*

Keywords: Pt-195 chemical shift, Pt(II) complexes, NMR-TZPP-DKH basis sets, NMR spectroscopy

INTRODUCTION

Due the strong development in the last decades, NMR spectroscopy has played a key role in the discovery and design of new drugs. In addition of being widely used in the characterization of new structures, NMR has also been used in the optimization of complexes targets, in the elucidation of reaction mechanism, as well as in the studies of biomarkers and biosensors[1]. In this present study a comprehensive analysis of relevant issues involved on the Pt-195 NMR chemical shift predictions are conducted. Non-relativistic and relativistic calculations are employed in distinct computations schemes to assess the most accurate method to use in a theoretical calculations of Pt-195 NMR. In addition to the existing methods, new relativistic NMR-TZPP-DKH Gaussian basis sets were constructed for H-He, Li-Ne, Na-Ar, K-Kr, Rb-Xe and Pt.

METHODS

DFT non-relativistic calculations were carried out by using the GAUSSIAN 09 program Rev. A.02. Figure 1, present the level of theory models used in this work. The NMR shielding constant was calculated through the GIAO approach and to calculate the δ^{195}Pt, a simple linear regression model (δ_{expt} x σ_{calc}) was used. The calculated chemical shift was given by $\delta_{calc} = a \times \sigma_{calc} + b$. Besides, we have performed NMR relativistic calculations using the ADF 2012.01 program. Finally, 183 Pt(II) complexes were used for the development of models and other 73 Pt(II) complexes were used to validate the methodology.

Models	Level of Theory	NMR	Program
Model 1	PBEPBE/DZP-DKII/TZP-DKII//B3LYP/LANL2DZ/Def2-TZVPP	Linear regression	GAUSSIAN 09 Rev. A.02
Model 2	PBEPBE/SARC-ZORA/TZP-DKII//B3LYP/LANL2DZ/Def2-TZVPP	Linear regression	GAUSSIAN 09 Rev. A.02
Model 3	B3LYP/NMR-TZPP-DKII//B3LYP/LANL2DZ/Def2-TZVPP	Linear regression	GAUSSIAN 09 Rev. A.02
Model 4	PBEPBE/NMR-TZPP-DKII//B3LYP/LANL2DZ/Def2-TZVPP	Linear regression	GAUSSIAN 09 Rev. A.02
Model 5	PBEPBE/NMR-TZPP-DKII//B3LYP/LANL2DZ/Def2-SVP	Linear regression	GAUSSIAN 09 Rev. A.02
Model 6	PBEPBE-ZORA(SO)/TZ2P//B3LYP/LANL2DZ/Def2-TZVPP	Linear regression	ADF 2012.01
Model 7	PBEPBE-ZORA(SO)/TZ2P//B3LYP/LANL2DZ/Def2-TZVPP	$\delta_{calc} = \sigma_{ref} - \sigma_{calc}$	ADF 2012.01

Figure 1. Level of theory models used in this work

RESULTS AND DISCUSSION

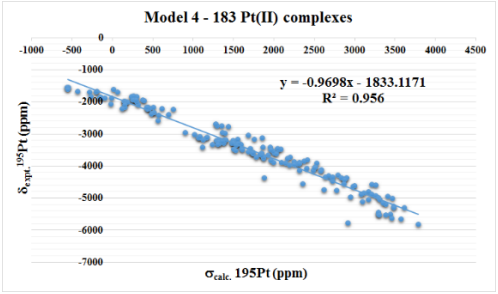

Figure 2. Simple regression linear model (δ_{expt} x σ_{calc}) used to development the Model 4.

Figure 2 present the data to the simple regression linear model used to development (183 Pt(II) complexes) the Model 4. The model 4 showed normal behavior of residues to the confidence interval of 95% (significance above 0.01). After we substitute the calculated shielding constants in the equation and found the calculated δ^{195}Pt. For these 183 Pt(II) complexes an excellent coefficient of determination (R^2) of 0.9564 was obtained. The absolute and relative deviation were of 179 ppm and 6%, respectively. In the next step, other 73 Pt(II) complexes were used to validation the models. For Model 4, the absolute and relative deviation were of 190 ppm and 8%, respectively, showing an excellent agreement with the experimental data.

CONCLUSIONS

The results show that constructed models and the NMR-TZPP-DKH basis sets are an excellent alternative to predict the δ^{195}Pt even for complexes which were not used in the construction thereof.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the FAPEMIG (CEX-BPD-00060-14), CAPES, CNPQ and UFJF.

[1] A. V. Klein and T. W. Hambley, Chem. Rev., 109, 4911, (2009).