

## NMR J-Coupling Constants of Tl–Pt Bonded Metal Complexes in Aqueous Solution: Ab Initio Molecular Dynamics and Localized Orbital Analysis

Lucas C. Ducati,<sup>†</sup> Alex Marchenko,<sup>‡</sup> Jochen Autschbach<sup>‡</sup>

<sup>†</sup>*Department of Fundamental Chemistry Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes 748, São Paulo, SP 05508-000, Brazil*

<sup>‡</sup>*Department of Chemistry University at Buffalo State, University of New York, Buffalo, New York 14260-3000, United States*

**Abstract:** The influence of solvent (water) coordination and dynamics on the electronic structure and nuclear magnetic resonance (NMR) indirect spin–spin coupling (J-coupling) constants in a series of Tl–Pt bonded complexes,  $[(\text{NC})_5\text{Pt-Tl}(\text{CN})_n]^{n-}$ , where  $n = 0, 1, 2, 3$ , and  $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$ , is investigated using Kohn–Sham (KS) Car–Parrinello molecular dynamics (CPMD) and relativistic hybrid KS NMR calculations with and without coordination to water. Coordination of the Tl center by water molecules has a dramatic impact on  $^1\text{J}(\text{Tl-Pt})$  and other J-coupling constants. It is shown that a previous computational study of the same complexes using static optimized structures and nonhybrid functionals was correct about the important role of the solvent but obtained reasonable agreement with experimental NMR data because of a cancellation of substantial errors. For example, the CPMD trajectories show that on average the inner coordination shell of Tl is not saturated, as previously assumed, which leads to poor agreement with experiment when the J-coupling constants are averaged over the CPMD trajectories using NMR calculations with nonhybrid functionals. The combination of CPMD with hybrid KS NMR calculations provides a much more realistic computational model that reproduces the large magnitudes of  $^1\text{J}(\text{Tl-Pt})$  and the correct trends for other coupling constants. An analysis of  $^1\text{J}(\text{Tl-Pt})$  in terms of localized orbitals shows that the presence of coordinating water molecules increases the capacity for covalent interactions between Tl and Pt. There is pronounced multicenter bonding along the metal–metal axis of the complexes.

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