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Solvent Effect on NMR Parameters of Tl(III) Complexes by ab initio Molecular Dynamics and Relativistic KS-DFT Calculations

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Highlights

Relativistic DFT NMR calculations based on AIMD sampling with explicit microsolvation and continuum model solvation reproduce the solvent sensitive NMR experimental parameters of Tl(III) complexes.

Abstract

Thallium(III), a pollutant found in lakes and oceans,[1] forms stable complexes in solution such as $[Tl(CN)_mCl_n]^{\{3-m-n\}}$ where $(m+n \leq 4)$.[2,3] Thallium is rarely studied by NMR although ^{205}Tl is high sensitivity NMR active metal nucleus, because it resonates at a frequency outside the range of most NMR probes. In this sense, it is interesting to evaluate how the solvent effect impacts the stability of these complexes in solution and their NMR properties. Due to the high ^{205}Tl receptivity, these complexes show good quality experimental data, which may guide theoretical studies, and verify the accuracy of the theoretical methods applied. $^1J(^{205}Tl\text{-}^{13}C)$ of $[Tl(CN)]^{2+}$ complex shows pronounced dependence of solvent (Figure 1). The bare form (*) shows a catastrophic value of 237 kHz, while the experimental value is around 14 kHz. Taking into account the implicit solvent for $^1J(^{205}Tl\text{-}^{13}C)$ calculation gives a value around -10 kHz. However, while the explicit microsolvation and continuum model solvation are combined for the NMR calculation, the accuracy increases drastically.

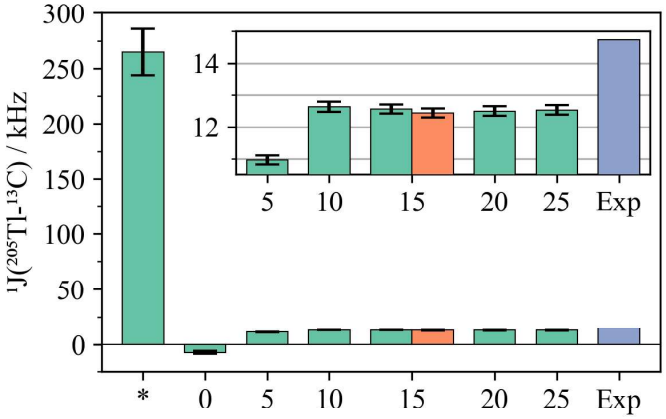

Figure 1. Averaged $^1J(^{205}Tl\text{-}^{13}C)$ on explicit nearest neighbor solvent count. All data are means corresponding to trajectory averages (64 frames) at Scalar-ZORA/PBE0/TZ2P-J. Orange bar corresponds to SO-ZORA/PBE0/TZ2P-J for 15 nearest neighbor solvents. The asterisk corresponds to bare structures (no explicit or implicit solvation), while the remaining counts (0−25) correspond to structures including the given number of explicit nearest solvent molecules and implicit solvation via COSMO. Standard errors (in the means) are given by the solid black lines.

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