Quantum-Chemical Calculations of ^{195}Pt-NMR Chemical Shifts in Platinum(IV) Porphyrins with Axial Ligands (Cl^-, Br^-, I^-, SCN^-)

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Platinum(IV) porphyrin derivatives with two various axial ligands such as halide and thiocyanate anions shown in Figure 1 have been synthesized and their ^{195}Pt-NMR chemical shifts have been also measured by us and others. In this study, we calculated the optimized geometries and the ^{195}Pt-NMR chemical shifts of these complexes. We also confirmed the relativistic effect of the Pt-NMR chemical shifts.

The level of theory is the DFT-ZORA, and the DFT functional is OPBE0. The basis set is TZ2P for Pt and N, TZP for the axial ligand atoms, and DZP for the other atoms. We used abbreviation L-L' for platinum(IV) porphyrin with the two axial ligands L and L' in Figure 1, for example, Cl-Br.

The calculated ^{195}Pt-NMR chemical shifts reproduced well the trend of the observed ones. The contribution of the paramagnetic term (σ^{para}), which is the orbital response term, mainly determines the total chemical shifts in the present complexes. Because we have already known that the correlation between the Hammett substituent constants and the ^{195}Pt-NMR chemical shifts breaks down in SCN-SCN, we showed the relation between the reciprocal orbital-energy difference (ΔE^{-1}) and the paramagnetic contribution (σ^{para}) as an alternative analysis in Figure 2. We found that σ^{para} was linearly correlated with ΔE^{-1}, although on the SCN-SCN and I-I complexes there was significant deviation from the linear correlation.

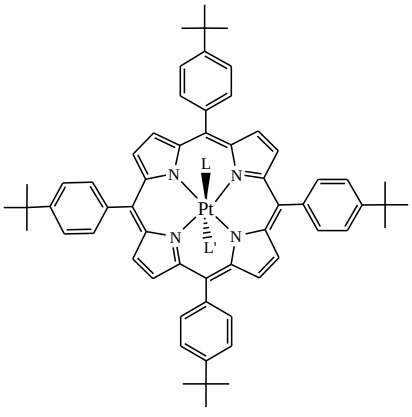

Figure 1. Platinum Porphyrins with axial ligands (Cl^-, Br^-, I^-, SCN^-)

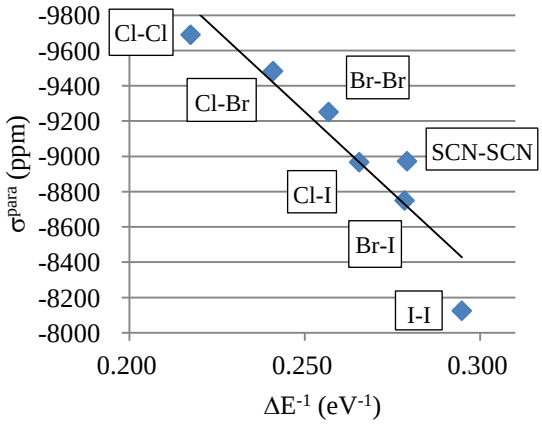

Figure 2. Relation between σ^{para} (ppm) and ΔE^{-1} (eV^{-1})