

## EXPERIMENTAL AND FIRST-PRINCIPLES NMR ANALYSIS OF Pt(II) COMPLEXES WITH O,O'-DIALKYL DITHIOPHOSPHATE LIGANDS

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Square-planar platinum(II) complexes are of interest due to their use in medicine [1], and some dialkyl dithiophosphate transition metal complexes due to their antioxidant [2] and antiwear [3] properties, useful in lubricative oil additives. Ionic O,O'-dialkyl dithiophosphates (dtp) form the main components of commercial flotation reagents, used to extract metals like platinum from ore [4]. Only few Pt(II)-dtp complexes have previously been studied in the crystalline form. Nuclear magnetic resonance (NMR) parameters, such as the chemical shift anisotropy and asymmetry of both  $^{195}\text{Pt}$  and  $^{31}\text{P}$  nuclei, are useful for obtaining precise structural and chemical information, complementing other structural methods such as X-ray diffraction, in particular for surface complexes.

In this work [5], we combine experimental measurements and first-principles calculations to study the NMR parameters of  $^{195}\text{Pt}$  and  $^{31}\text{P}$  in five crystalline Pt-dtp-R complexes, where R is ethyl, *iso*-propyl, *iso*-butyl, *sec*-butyl, or cyclohexyl. Relativistic effects on the electronic structure are treated at the two- and four-component levels of theory. Considering also the contributions due to the ligand field of the crystal, we reach high enough accuracy to confirm the experimental observations, as well as obtain orientational information that is not readily available from experiments, and further analyze the contributions to the calculated properties.

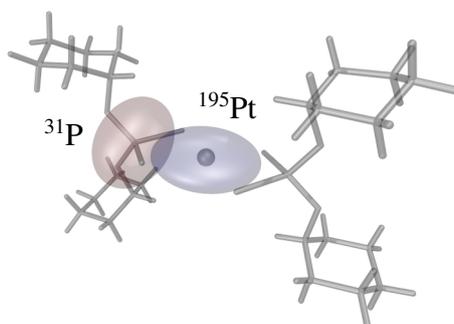


Figure 1:  $^{31}\text{P}$  (red) and  $^{195}\text{Pt}$  (blue) shielding tensors in the Pt-dtp-cyclohexyl complex.

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