

What's in the ^{195}Pt chemical shift of 'simple' platinum complexes? Unique 'fingerprinting' of Pt(IV) using isotope induced shifts at high resolution ^{195}Pt NMR

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^{195}Pt NMR is a powerful tool with which to probe the solution structure as well as solvation shells of Pt(IV) complexes in halide rich aqueous solutions, relevant to large scale separation and refining of this precious metal. It has long been known that the chemical shifts of platinum complexes are extra-ordinarily sensitive to solvent composition, temperature, the oxidation state of the Pt atom, as well as the nature of the donor atoms in the complex, and as will be shown from our recent experiments, also pressure. We are using experimental and computational ^{195}Pt NMR to better understand the fundamental nature of the ^{195}Pt NMR shielding of such 'simple' complexes as well as to gain insight into the nature of species in solution as relevant to industrial process solutions [1-3].

As part of this study, we have been able to generate *inter alia* all possible aquated $[\text{PtCl}_{6-n}(\text{H}_2\text{O})_n]^{2-}$ ($n = 0-5$) complexes in acidified water. At high magnetic field the ^{195}Pt NMR *resonance shapes* of the aquated complexes $[\text{PtCl}_{6-n}(\text{H}_2\text{O})_n]^{2-}$ ($n = 0-5$) are well resolved into the various *isotopomers* for each possible *isotopologue* arising from the $^{35}\text{Cl}/^{37}\text{Cl}$ (and $^{16}\text{O}/^{18}\text{O}$) isotope effects on the ^{195}Pt resonances. The ^{195}Pt resonance of each species can be de-convoluted into a distribution of isotopologues and isotopomers, which thus constitute a unique 'fingerprint' unambiguously identifying each complex species in solution. It is also possible to characterize all geometric isomers which differ only by whether $^{35}\text{Cl}^-$ or $^{37}\text{Cl}^-$ is coordinated *cis* or *trans* to a bound water molecule in *cis/trans* or *fac/mer* isomers of these complexes [4].

Finally we present some of our recent results showing remarkable agreement between calculated by DFT methods and experimental shifts for a series of $[\text{PtX}_6]^{2-}$ ($\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$) complexes in solution. A useful result from our calculations is that the $\delta^{195}\text{Pt}$ for these complex anions is remarkably sensitive to the average Pt-X (ΔL) bond displacement. We find that the $\partial(\delta^{195}\text{Pt})/\partial(\Delta\text{L})$ depends significantly on the nature of the halide-ion coordinated to the Pt(IV), with the calculated $\partial(\delta^{195}\text{Pt})/\partial(\Delta\text{L})$ ranging from 280 ppm per *picometer* bond-displacement for $[\text{PtF}_6]^{2-}$ to 'only' 120 ppm/pm for $[\text{PtI}_6]^{2-}$ [4]. The implications of these results are discussed in the context of preliminary high pressure NMR and temperature effects on the $\delta^{195}\text{Pt}$ shielding.

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