

Measurement of ^{195}Pt Chemical Shift Anisotropy in Two Solid Pt Complexes, $[\text{Me}_3\text{Pt}(\text{acetylacetonato})]_2$ and $[\text{Me}_3\text{Pt}]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. Effect on Solution-state Spin Relaxation

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The anisotropy ($\Delta\sigma$) of the ^{195}Pt chemical shielding for two Pt^{IV} complexes, $[(\text{Me})_3\text{Pt}(\text{acetylacetonato})]_2$ and $[\text{Me}_3\text{Pt}]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, measured by ^1H - ^{195}Pt cross-polarization techniques, is found to be of the order of 10^3 p.p.m. and hence of such a magnitude that a significant contribution of chemical-shift anisotropy relaxation to the ^{195}Pt solution-state relaxation parameters T_1 and T_2 is evident at high magnetic fields.

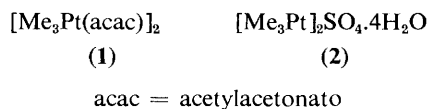
Structural studies on Pt complexes using solution-state n.m.r. spectroscopy are often hampered by the disappearance of J -coupling between ^{195}Pt and other magnetically active nuclei such as ^1H , ^{13}C , and ^{31}P on increasing the magnetic field strength. This is particularly evident for high molecular weight Pt complexes which tumble slowly in solution as witnessed¹ by the lack of observable ^{195}Pt - ^1H splittings in the ^1H n.m.r. spectra of dinucleoside monophosphate- Pt^{II} complexes. In a recent paper Lallemand *et al.*² ascribed this problem to chemical-shift anisotropy (C.S.A.) relaxation becoming more important for the ^{195}Pt nucleus with increasing field strength and decreasing correlation times. From their field-dependent relaxation studies on tetra-co-ordinated $[\text{Bu}^n\text{PPtCl}_2]_2$ they

indirectly estimated that the ^{195}Pt chemical-shift anisotropy ($\Delta\sigma$) was of the order of 900 p.p.m.[†] In this paper we report values of $\Delta\sigma$ for the ^{195}Pt spin in the Pt^{IV} complexes $[\text{Me}_3\text{Pt}(\text{acac})]_2$ (**1**) and $[\text{Me}_3\text{Pt}]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (**2**), measured directly *via* solid state ^{195}Pt n.m.r. spectroscopy.

Table 1. Relaxation parameters for (**1**) (in CDCl_3) and (**2**) (in D_2O) determined at 305 K and 19.3 and 64.4 MHz.

Compound	Resonance frequency/MHz	T_1 /s	T_2 /ms
(1)	19.3	1.6	6.7
	64.4	0.6	3.9
(2)	19.3	2.1	13.0
	64.4	0.6	1.3

[†] The value of $\Delta\sigma$ estimated by Lallemand and the T_1 values used in the calculation appear to be inconsistent for the value of τ_c used. If the reported T_1 values are correct, the estimated $\Delta\sigma$ would be *ca.* 7500 p.p.m. which may be a reasonable estimate for Pt^{II} complexes.



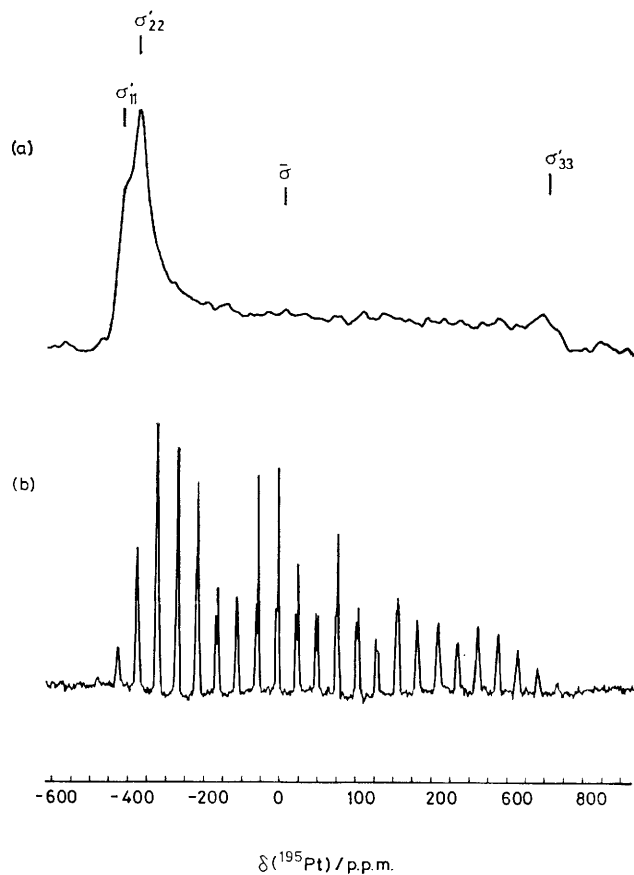


Figure 1. (a) 64.4 MHz solid-state ^1H - ^{195}Pt C.P. powder spectrum of (1). 3×10^4 Pulses were averaged using a spectral width of 100 kHz, matched r.f. fields of 47 G and 10 G for ^{195}Pt and ^1H respectively, and 10 ms contact time. (b) ^1H - ^{195}Pt C.P./M.A.S. spectrum of (1). 10^4 Pulses were averaged as for spectrum (a) but with a spinning speed of 3.4 kHz. $\bar{\sigma}$ is the isotropic shift position which was confirmed by varying the spinning speed.

The 64.4 MHz solid-state ^{195}Pt spectrum of (1) obtained by ^1H - ^{195}Pt cross-polarization (C.P.) techniques \ddagger is shown in Figure 1(a). We note that the powder pattern obtained yields a chemical-shift tensor having principal components σ'_{11} ca. -398, σ'_{22} ca. -355, and σ'_{33} ca. +746 p.p.m. relative to the isotropic chemical shift position. Using the usual definition of $\Delta\sigma = \sigma'_{33} - \frac{1}{2}(\sigma'_{22} + \sigma'_{11})$, we find $\Delta\sigma =$ ca. 1123 p.p.m. For (2) $\Delta\sigma$ is similarly found to be ca. 950 p.p.m. Our results imply therefore that $\Delta\sigma =$ ca. 10^3 p.p.m. is not an unreasonable figure for ^{195}Pt in Pt^{IV} complexes. As pointed out by Lallemand,² $\Delta\sigma$ may be considerably larger for tetra-coordinated Pt^{II} complexes. \ddagger Our measurements were also performed at 19.3 MHz, similar results being obtained except that in both cases σ'_{11} and σ'_{22} were not clearly resolved.

It should be noted that $\Delta\sigma =$ ca. 1100 p.p.m. yields $\Delta\sigma =$ 70.4 kHz at 64.4 MHz. ^{195}Pt spectra obtained with magic-angle spinning at achievable spinning rates are thus composed

\ddagger ^{195}Pt cross-polarization and cross-polarization/magic angle spinning spectra (C.P./M.A.S.) were recorded at 19.3 and 64.4 MHz using Bruker HX-90 and CXP-300 spectrometers and Bruker DR/MAS probes. Samples were contained in delrin Andrewstyp rotors with spinning speeds of 3–5 kHz being used for the M.A.S. experiments. Shielding tensor values, σ_{11} , are relative to the isotropic shift using the convention of positive values corresponding to larger shielding.

of a multitude of spinning sidebands, cf. Figure 1(b). The isotropic shift resonance for (1) and (2) was identified by changing the spinning speed and is clearly not the most intense resonance. In theory, the sideband pattern of Figure 1(b) could be analysed to obtain $\Delta\sigma$.³

These results suggest that the ^{195}Pt relaxation parameters for (1) and (2) will be strongly field dependent. This was confirmed by our studies \S and the results are shown in Table 1.

It is clear from the results that the relaxation parameters are strongly field dependent; however, the magnitude of the dependence is less than the B_0^2 dependence expected.⁴ Simple calculations of T_1 using the measured anisotropies, τ_C ca. 10^{-10} s and the simplified equation for axial symmetry and extreme narrowing⁴ suggest that the C.S.A. contribution to T_1 at 64.4 MHz is comparable with our experimental values. Hence, it would appear reasonable that the T_1 values measured at the lower field are less than expected for C.S.A. relaxation owing to significant contributions from other mechanisms (*i.e.* dipolar and spin-rotation). Preliminary variable-temperature T_1 measurements at 64.4 MHz for (2) indicate that T_1 increases with temperature, which is consistent with either dipolar or C.S.A. mechanisms, with the former being eliminated as a major contributor by the lack of nuclear Overhauser enhancement. It is interesting that T_2 is much shorter than T_1 , a result previously observed but not explained by Pesek and Mason⁵ for both octahedral Pt^{IV} and square-planar Pt^{II} complexes. In both studies, scalar relaxation of the second kind can be eliminated as a mechanism for T_1 except in Pesek and Mason's⁵ study for complexes with direct ^{195}Pt -Br bonding. The most likely cause of the short T_2 values observed for (1) and (2) is the presence of chemical exchange which, under certain conditions, would result in a field dependence. That exchange is occurring in (1) and (2) would not be unexpected and is in fact confirmed for (1) by the observation that in solution the methyl-carbon resonance at 22.6 MHz is broad and weak and at 75.5 MHz is virtually undetectable owing to exchange broadening. By contrast, the 75.5 MHz solid-state ^{13}C C.P./M.A.S. spectrum of (1) exhibits four distinct methyl resonances with clearly resolved ^{195}Pt - ^{13}C couplings.⁶ We are continuing these relaxation studies and a full analysis will be reported elsewhere.

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\S Liquid-state field-dependent relaxation studies were performed on the above instruments using the standard high-resolution probes. A phase-compensated inversion-recovery sequence was used to measure T_1 . T_2 was measured using the CPMG pulse sequence.