Implication of ^{195}Pt Chemical Shift Anisotropy Relaxation in N.M.R. Studies of Platinum Complexes

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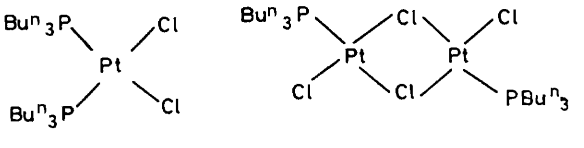
Summary A dominant chemical shift anisotropy relaxation mechanism can account, at high magnetic fields, for the disappearance of some of the ^{195}Pt–^{1}H and ^{195}Pt–^{13}C coupling constants and for the line broadening observed in the ^{195}Pt n.m.r. spectra of Pt^{II} complexes.

WE have observed that in many instances, excluding ligand exchange, the ^{1}H or ^{13}C n.m.r. spectra of platinum complexes display unexpected features such as broadening of the doublets arising from coupling with ^{195}Pt, or disappearance of some small splittings when the spectra are run at high magnetic fields. Accordingly, although ^{195}Pt–^{1}H couplings have been reported at 60 MHz for mono- and bis-nucleoside and nucleotide–Pt^{II} complexes,[1] studies at

100 MHz of similar complexes often do not clearly show such splitting.[2] Furthermore, for several dinucleoside monophosphate Pt$^{\text{II}}$ complexes we have not been able to detect any ^{195}Pt–^{1}H coupling in spectra recorded at 250 MHz.[3]

We have also made some surprising observations when studying various Pt complexes by ^{195}Pt n.m.r.[4] spectroscopy. For example, the ^{195}Pt n.m.r. spectra of compounds (**1**) and (**2**) (Figure 1) exhibit considerable line width differences, *ca.* 2 Hz and *ca.* 15 Hz, when studied at 19·35 MHz, in the absence of any ligand exchange.



(1) (2)

FIGURE 1

This led us to think that chemical shift anisotropy (C.S.A.) relaxation might be efficient in the case of the ^{195}Pt nucleus. This relaxation process is known to be strongly dependent upon the observing magnetic field B_0,[5] and has been reported to be significant in the case of heavy metal ions such as ^{207}Pb.[6] Complex (**2**) was studied as a model compound. Increasing the magnetic field, from 18·8 to 58·7 kG, drastically modifies the ^{195}Pt n.m r. spectrum corresponding to a decrease of the spin–spin relaxation times T_2.† The two external lines of the multiplet, due to Pt–Pt coupling ($J \simeq 190$ Hz),[4,7] which are clearly visible at 18·8 and 21·1 kG, have almost disappeared at 58·7 kG. ^{195}Pt T_1's are also very sensitive to the influence of the magnetic field as indicated by the measurements made at 21·1 and 58·7 kG (Table).

Thus, the enhancement of the relaxation rate observed upon magnetic field increase can only be accounted for by a dominant chemical shift anisotropy (C.S.A.) relaxation mechanism.[8]

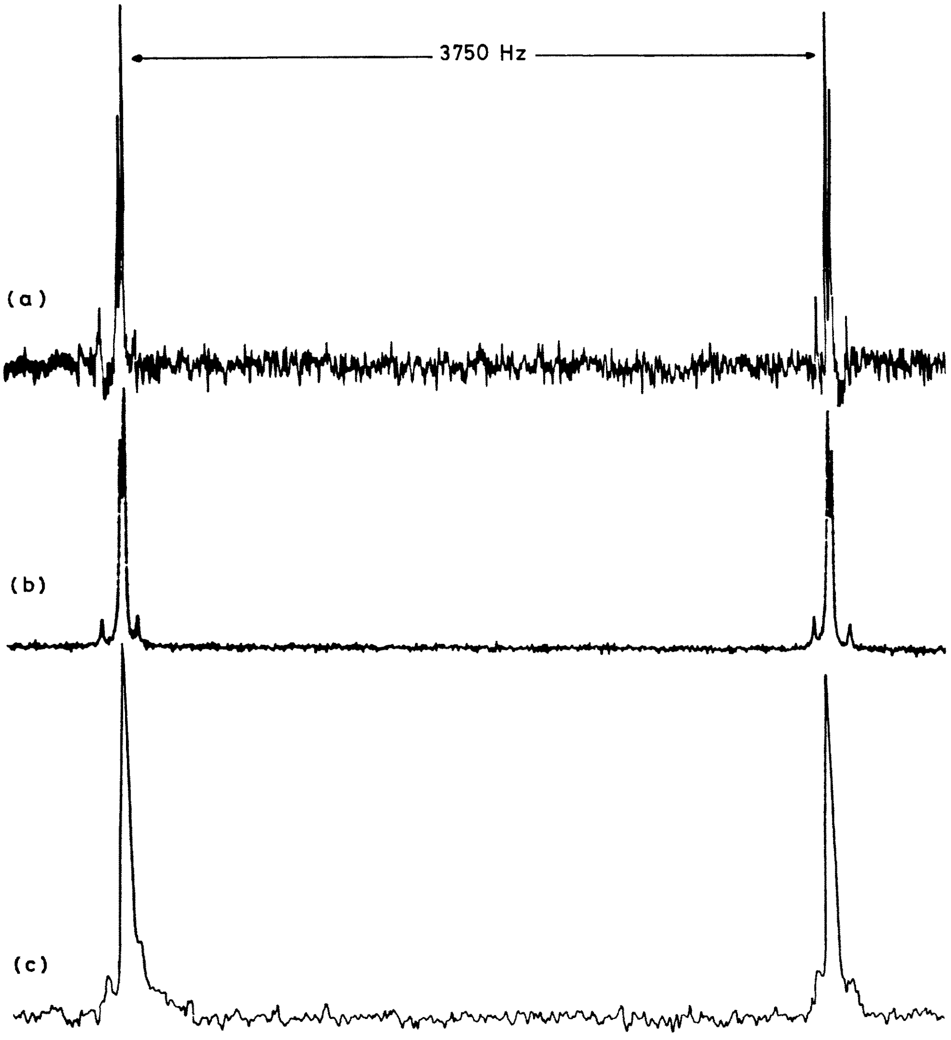


FIGURE 2. ^{195}Pt spectra of compound (**2**) at 18·79 kG (a), 21·14 kG (b), and 58·72 kG (c). Same scale in Hz cm^{-1}.

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† The ^{1}H and ^{31}P n.m.r. spectra of the same sample showed sharp signals indicating that the linewidths observed in the ^{195}Pt n.m.r. spectrum do not result from inhomogeneities of the applied field, and that the extreme narrowing condition ($\omega\tau_c \ll 1$) is satisfied in all cases.

The contribution of C S A to relaxation is given by equations (1) and (2) where $\Delta\sigma$ is an anisotropy term and τ_c the correlation time (in the case of molecules with cylindrical symetry $\Delta\sigma = \sigma_{\|} - \sigma_{\perp}$) At high magnetic fields the T_1/T_2 ratio takes the expected value of 1 2 (Table) In general τ_c is expected to be very anisotropic and to vary with the molecular weight of the compound, the viscosity, and the temperature‡ of the medium and a more complicated formalism has to be used For compound (**2**) a simple calculation using equation (1) gives $\Delta\sigma \simeq 900$ p p m assuming $\tau_c = 10^{-10}$ s It must be noted that much smaller values of $\Delta\sigma$ may be encountered in the case of hexacoordinated platinum complexes which are less anisotropic and for which other relaxation mechanisms may be dominant[9]

$$T_1^{-1}\,(\text{C S A}) = 2/15\,\gamma^2 B_0^2 \Delta\sigma^2 \tau_c \qquad (1)$$

$$T_2^{-1}\,(\text{C S A}) = 7/45\,\gamma^2 B_0^2 \Delta\sigma^2 \tau_c \qquad (2)$$

TABLE ^{195}Pt T_1 values in ms, for complex (**2**), measured at 21 14 kG (19 35 MHz) and 58 72 kG (53 68 MHz) by the 180°–τ–90° method, 200 mg of (**2**) dissolved in 1 5 ml of $CDCl_3$ In all cases spectra were recorded at 27 °C with proton noise decoupling

Complex (**2**)	21 1 kG	58 72 kG
T_1 (^{195}Pt)	*ca* 100 ms	*ca* 10 5 ms[a]
T_1 (^{31}P)	2300 ms[b]	1700 ms
$\Delta\nu_{\frac{1}{2}}$ (^{195}Pt)[c]	11 Hz	40 Hz
calculated T_2[d]	29 ms	7 9 ms

[a] ± 2 ms owing to timing problems in the pulse sequence generator at very short τ [b] T_1 measured on the central line of the ^{31}P spectrum corresponding to the 'isotopomer' containing no ^{195}Pt isotope (J D Kennedy, I J Colquhoun, W McFarlane, and R L Puddephatt, *J Organometal Chem*, 1979, **172** 479) The linewidth at half-height of the main line observed by ^{31}P n m r spectroscopy is 3 Hz [c] Recording of the ^{1}H n m r spectrum of the same sample tube under the same conditions ensured that $\Delta\nu_{\frac{1}{2}}$ (^{195}Pt) was not influenced by B_0 homogeneity [d] $T_2 = 1/\pi\Delta\nu_{\frac{1}{2}}$

The enhancement of relaxation rate due to C S A in square planar platinum(II) complexes may be so large that ^{195}Pt appears to lose its magnetic character (as some quadrupole nuclei) This leads to the disappearance of coupling constants with nuclei such as ^{1}H or ^{13}C and accounts for the absence of ^{195}Pt–^{1}H splitting when studying dinucleoside monophosphate–Pt^{II} complexes such as *cis*-[Pt$(NH_3)_2${guanylyl(3′-5′)guanosine}]$^+$, *cis*-[Pt$(NH_3)_2${inosylyl(3′-5′)inosine}]$^+$, and *cis*-[Pt$(NH_3)_2${adenylyl(3′-5′)-adenosine}]$^+$ [2,3,10]

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‡ We have observed that in several cases ^{195}Pt–^{1}H coupling constants may be restored at higher temperature, owing to an acceleration of the molecular motions leading to shorter τ_c

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