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Natural Abundance ^{195}Pt Nuclear Magnetic Resonance Studies of some Platinum(II) Nitro Complexes

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The direct observation of ^{195}Pt NMR spectra is becoming a useful technique in the structural characterization of platinum complexes [1, 2]. Where coordinated nitrogen ligands are present, relaxation and/or unresolved coupling to ^{14}N can cause broadening of the ^{195}Pt NMR spectra and consequent reduction in its utility. In such cases labeling with ^{15}N often serves to aleviate this problem, while at the same time facilitating the measurement of platinum–nitrogen coupling constants. This is the case with platinum nitro complexes, which have received only scant study by ^{195}Pt NMR spectroscopy [3]. Here we present data obtained by ^{195}Pt NMR spectroscopy for a number of nitro complexes labeled with 99 atom percent NO_2^-.

The ^{195}Pt NMR spectrum of an aqueous solution of $Na_2Pt(^{15}NO_2)_4$ is shown in Fig. 1, trace A. Instead of the broad line seen by Pesek and Mason [3] a well resolved quintet with relative intensities of 1:4:6:4:1 is seen at –2166 ppm (in good agreement with the value of –2159 reported earlier). In our spectrum the line width is 5 Hz. Spectral parameters for this complex and others are compiled in Table I.

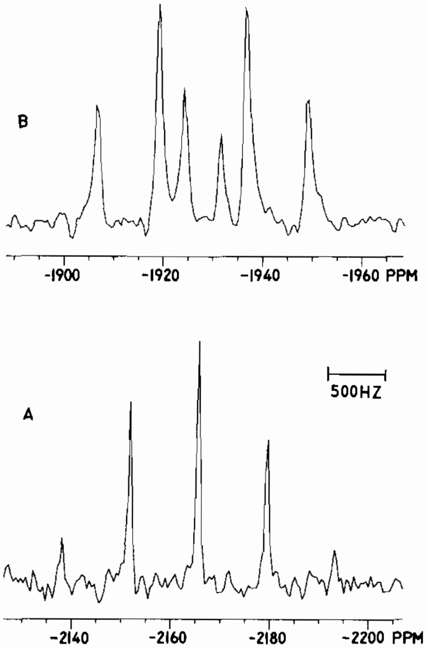

Fig. 1. The 42.9 MHz $^{195}Pt\{^1H\}$ NMR spectrum of A, 0.1 *M* aqueous solution of $K_2Pt(NO_2)_4$ and B, 0.1 *M* aqueous solution of $K(H_2O)Pt(NO_2)_3$ in 12 mm tubes at 25 °C. The spectra were obtained using a 40 KHz spectral width using 5000 scans with a 35 μs pulse (tilt angle 90°) and an acquisition time of 47 millisecond and a 150 millisecond delay. The reference is an external, aqueous Na_2PtCl_6 solution.

The ^{195}Pt NMR spectrum of $H_2OPt(NO_2)_3^-$ which was prepared by the method of Kukushkin and Stefanova (reaction 1) [4, 5] is shown in Fig. 1, trace B.

$$Pt(NO_2)_4^{2-} + NH_2SO_2OH \rightarrow (H_2O)Pt(NO_2)_3^- + N_2 + HSO_4^- \quad (1)$$

TABLE I. ^{195}Pt NMR Data for Platinum Nitro Complexes.

Compound	δ (ppm)[a]	$^1J(^{195}Pt, ^{15}N)$ *trans* to NO_2^-	(Hz)[a] *trans to* O
$Pt(NO_2)_4^{2-}$	–2166	594	
$(H_2O)Pt(NO_2)_3^-$	–1928	531	754
$Pt(NO_2)_3(OH)^{2-}$	–1780	583	626
$Pt(NO_2)_2(C_2O_4)^{2-}$	–1487		748
cis-$(H_2O)_2Pt(NO_2)_2$	–1777		679
trans-$(H_2O)_2Pt(NO_2)_2$	–1780	470	

[a] Recorded from aqueous solutions at 25 °C at 42.9 MHz. All complexes were prepared from 99 atom percent enriched NO_2^-. The reference is external aqueous H_2PtCl_6 and the high frequency positive convention recommended by IUPAC is used in reporting chemical shifts.

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The resonance of the monoanion appears as a doublet of triplets. The unique nitro group, which is *trans* to water, is responsible for the doublet splitting with J(^{195}Pt, ^{15}N) = 754 while the two equivalent nitro groups, which are *trans* to one another, produce the triplet splitting with J(^{195}Pt, ^{15}N) = 531 Hz. The anion $(H_2O)Pt(NO_2)_3^-$ is a weak acid with a pKa of ~-7 [5]. Thus by adjusting the pH of a solution of this anion to 8, $Pt(NO_2)_3OH^{2-}$ becomes the principle species in solution. The ^{195}Pt NMR spectrum of $Pt(NO_2)_3OH^{2-}$, like that of $H_2OPt(NO_2)_3^-$, is a doublet of triplets, and again J(^{195}Pt, ^{15}N) *trans* to a hydroxide ligand is greater than ^{1}J(^{195}Pt, ^{15}N) *trans* to a nitro ligand. The ^{195}Pt NMR spectrum of $Pt(NO_2)_2(O_2C_2O_2)^{2-}$ [6] consists of a triplet due to splitting arising from the presence of the two equivalent nitro groups.

These data indicate that ^{1}J(^{195}Pt, ^{15}N) for nitro complexes, like other one-bond Pt–ligand couplings, is sensitive to the *trans* ligand. The effect of the *trans* ligand on the magnitude of ^{1}J(^{195}Pt, ^{15}N) in this case is $NO_2^- < OH^- < H_2O$, $O_2C_2O_2^{2-}$ and this order is in accord with the usual trend that ligands with a high *trans* influence produce smaller values in ^{1}J(Pt, L) for the *trans* ligand L.

These data are useful in studying the reactions of platinum nitro complexes as the following example shows. The anion $(H_2O)Pt(NO_2)_3^-$ undergoes further substitution as shown in equation 2 [4, 5]. It is expected from kinetic studies that the nitro group

$$(H_2O)Pt(NO_2)_3^- + NH_2SO_2OH \rightarrow (H_2O)_2Pt(NO_2) + N_2 + HSO_4^- \qquad (2)$$

which is *trans* to another nitro group is the one effected by this reaction [5]. Consequently the product is expected to have the *cis* geometry. This prediction is confirmed by ^{195}Pt NMR spectroscopy. The ^{195}Pt NMR spectrum of the freshly formed product is a triplet with ^{1}J(^{195}Pt, ^{15}N) = 679 Hz. This value of ^{1}J is consistent with the presence of the *cis* isomer as the kinetically formed product. However this is not the thermodynamically favored isomer as shown by the fact that the intensity of the triplet at –1777 ppm decreases upon warming the sample to 60 °C. The decay of this triplet is accompanied by the growth of a new triplet centered at –1780 ppm with a much smaller value of ^{1}J(^{195}Pt, ^{15}N) of 470 Hz. We assign this resonance to the *trans* isomer of $(H_2O)_2Pt(NO_2)_2$ and concluded that this is the thermodynamically favored species.

These data demonstrate the utility of ^{195}Pt NMR spectroscopy coupled with ^{15}N labeling in the study platinum nitro complexes. It should be further noted that the magnitudes of ^{1}J(^{195}Pt, ^{15}N) (470–754 Hz) are considerably larger than the coresponding values of ^{1}J(^{195}Pt, ^{15}N) for other nitrogen containing ligands: amines (200–400 Hz) [7], imines (300–500 Hz) [8], N-bound thiocyanate (205–424 Hz) [9] and N-bound cyanate (200–470 Hz) [9]. Consequently the magnitude of ^{1}J(^{195}Pt, ^{15}N) should be diagnostic in detecting the presence of a coordinated nitro group.

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