Solid-State ^{31}P NMR CST in Pt_2 and PtX_2

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Solid-State ^{31}P NMR Chemical Shielding Tensors in Binuclear Platinum Diphosphite Complexes

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The principal elements of the ^{31}P NMR chemical shielding tensors have been determined for three binuclear platinum diphosphite complexes, $K_4[Pt_2(P_2O_5H_2)_4]\cdot2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot2H_2O$ ("Pt_2Cl_2"), and $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot2H_2O$ ("Pt_2Br_2"), by using a Herzfeld-Berger graphical method for interpreting the ^{31}P MAS spectrum. The orientations of ^{31}P chemical shielding tensor relative to the molecular axis system are partially assigned with combination of the longitudinal relaxation study of HPO_3^{2-} and the reference to known tensor orientations of related sites; the most chemical shielding component, δ_{33}, is directed along the P-Pt bond axis. A discussion is given in which the experimental principal elements of the ^{31}P chemical shielding tensor are related with the Pt-Pt bond distances in binuclear platinum diphosphite complexes.

Introduction

Solid-state NMR spectroscopy of S=1/2 nuclei, principally ^{13}C and ^{31}P, has been utilized to yield information concerning the molecular geometry, electronic structure, and motion of molecules in organometallic systems. ^{31}P NMR spectroscopy has been more frequently used than ^{13}C in the organometallic studies, because of the 100% natural abundance and the relatively high sensitivity of the ^{31}P nucleus. ^{31}P chemical shielding tensors have been successfully correlated with the molecular structural parameters such as bond angles and bond distances in phosphido-bridged complexes and phosphates.[1,2] Similarly, the correlation between the ^{31}P isotropic chemical shift and the cation charge of orthophosphates has been investigated.[3] The *cis-trans* isomerization of $(R_3P)_2MCl_2$ (M=Pd, Pt)[4,5] and the determination of NMR parameters in cyclic/acyclic phosphine complexes[6,7] have been studied by ^{31}P CP/MAS NMR spectroscopy. In addition, the effects of molecular motion for solid P_4[8] and phase transition for

P_4S_3[9] on ^{31}P NMR spectra have been investigated. Two-dimensional ^{31}P CP/MAS NMR techniques have been applied to separate the unresolved interactions in the metal phosphine complexes.[10]

Binuclear platinum diphosphite complexes, $K_4[Pt_2(P_2O_5H_2)_4]\cdot2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4X]\cdot2H_2O$ ("Pt_2X"), and $K_4[Pt_2(P_2O_5H_2)_4X_2]\cdot2H_2O$ ("Pt_2X_2"; X=Cl, Br, I), have attracted attention because they can be used to prepare linear chain structures with the electrical properties of a semiconductor.[11~15] The semiconductivity of these complexes have been indirectly investigated by the determination of the intermetallic bond distances from X-ray crystallography. The intermetallic bonding have also been characterized from electronic and vibrational spectroscopic data.[16~18] Herein, three principal elements and the partial orientation of the ^{31}P chemical shielding tensors for Pt_2, Pt_2Cl_2, and Pt_2Br_2 were determined by using the solid-state ^{31}P MAS spectroscopy. Consequently, the NMR results will be related to the Pt-Pt distances in the molecular structures, Pt_2 and Pt_2X_2, to access information about the changes in the Pt-Pt bond that are so important to conduction in the Pt_2X system.

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Experimental

Sample Preparation. $K_4[Pt_2(P_2O_5H_2)_4]\cdot2H_2O$ ("Pt$_2$"), K_4[Pt$_2$(P$_2$O$_5$H$_2$)$_4$Cl$_2$]$\cdot$2H$_2$O ("Pt$_2$Cl$_2$"), and K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$Br$_2$]$\cdot$2 H$_2$O ("Pt$_2$Br$_2$") were prepared by the literature method.[19,20] All chemicals were obtained from Aldrich Chemical Company, Inc.

Solid-State ^{31}P NMR Spectroscopy. Solid-state ^{31}P powder patterns were taken on stationary samples with a Bruker MSL200 solid-state NMR spectrometer operating at 80.98 MHz using a high power probe with a solenoidal coil. The 90° pulse length was 2 μs and the spectra were acquired as simple Bloch decays. The ^{31}P MAS (Magic Angle Spinning) spectra were acquired on Bruker MSL200 and 500 solid-state NMR spectrometers using a 15 kHz CP/MAS probe and a 4 mm ZrO$_2$ rotor with a Kel-F cap. The magic angle was adjusted by examining the ^{79}Br NMR signal of KBr.[21] Powdered samples, 70 to 100 mg, were loosely packed into the rotor along with alumina as an inert filler. At 80.98 MHz resonance frequency (MSL200), the 90° pulse was 5 μs and the spectra were acquired as simple Bloch decays. At 202.46 MHz (MSL500), an 8.9 μs (<90° tip angle) pulse was used. The ^{31}P chemical shift values recorded on the δ-scale are referenced to 85% H$_3$PO$_4$ as external standard. All spectra are exponentially filtered (200 Hz), Fourier transformed, and manually phased.

Solid-State ^{31}P NMR Chemical Shielding Tensors. A Herzfeld-Berger graphical method[22] was used to obtain three principal elements (δ_{11}, δ_{22}, and δ_{33}) of the ^{31}P chemical shielding tensors from the intensities of the spinning sidebands and the isotropic chemical shift, δ_{iso}, in the ^{31}P MAS spectra. The effects of dipolar and J couplings between ^{31}P and ^{195}Pt nuclei on the relative intensities of the ^{31}P MAS peaks[23] were neglected.

Results and Discussion

Shown in Figure 1 are the featureless ^{31}P NMR powder pattern at stationary and well-resolved ^{31}P MAS NMR spectra at three different spinning rates of Pt$_2$. It is difficult to reliably extract the principal elements of the ^{31}P chemical shielding tensor from the powder pattern. In principle, an analysis of the ^{31}P NMR powder patterns can be made by using ^{31}P Zeeman and chemical shielding interactions and dipolar and J coupling interactions between ^{31}P and ^{195}Pt nuclei. However, because the chemical shift anisotropy interaction for the phosphorus site is relatively small with respect to both dipolar and J coupling interactions between ^{31}P and ^{195}Pt nuclei, the ^{31}P powder pattern is featureless at 4.7 Tesla. Thus, the uncertainty in the fit of a simulated ^{31}P powder pattern to the experimental powder pattern is unacceptably large. For this reason, the principal elements of the ^{31}P chemical shielding tensor were acquired from a Herzfeld-Berger graphical analysis of the ^{31}P MAS spectra. In the MAS experiment, it is possible to focus on the spinning sidebands of the S=0 Pt isotopomer; thus the ^{195}Pt (S=1/2) spectral component shown as crosses (+) in Figure 1 is excluded from the analysis. It is usual to analyze below 2-3 kHz slow spinning spectra to obtain the reliable data. However, in this work, above 6 kHz spinning rate spectra have been used
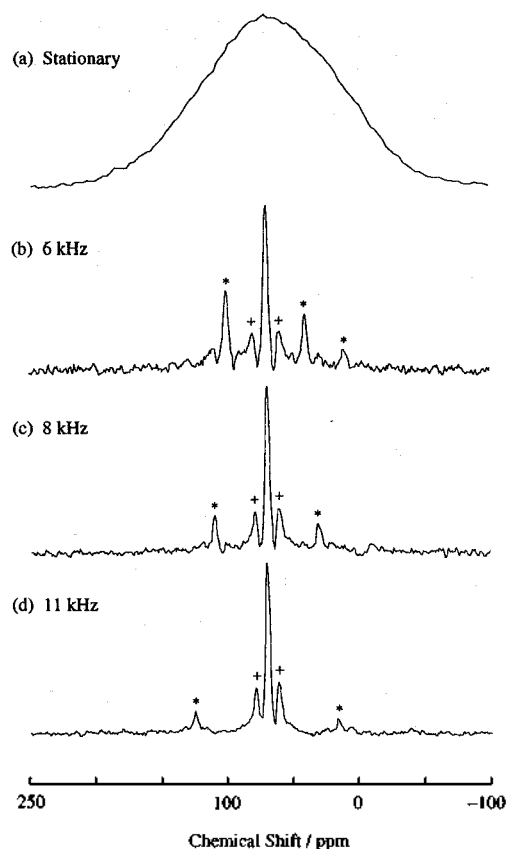
Figures 1. Solid-state ^{31}P powder pattern of K$_4$[Pt$_2$(P$_2$O$_5$H$_2$)$_4$]$\cdot$2 H$_2$O ("Pt$_2$") and ^{31}P MAS spectra at different spin rates, v_r. Asterisks (*) and crosses (+) represent the spinning sidebands and the J coupling peaks to ^{195}Pt, respectively. Experimental parameters are as follows: (a) v_L=80.98 MHz, v_r=0 kHz, NS=30, RD= 120 s; (b) 202.46 MHz, 6 kHz, 16, 100 s; (c) 202.46 MHz, 8 kHz, 8, 100 s; and, (d) 202.46 MHz, 11 kHz, 8, 100 s.

to avoid the overlap between the spinning sidebands of the S=0 Pt isotopomer and the ^{195}Pt (S=1/2) spectral bands. Solid-state ^{31}P chemical shielding tensor for three binuclear platinum diphosphite complexes are listed in Table 1. The values of isotropic ^{31}P chemical shift (δ_{iso}) are essentially the same in solution as in the solid-state; there is an upfield shift going from Pt$_2$ to Pt$_2$Cl$_2$ and Pt$_2$Br$_2$. The values of δ_{11} and δ_{33} show upfield shifts while δ_{22} nearly constant.

The orientation of the ^{31}P chemical shielding tensor elements relative to the molecular axis system cannot be obtained from a Herzfeld-Berger graphical analysis of the S=0 Pt isotopomers. Single crystal NMR studies were attempted for Pt$_2$, but were unsuccessful due to a lack of a large crystal. The ^{31}P chemical shielding tensor orientations have not been determined experimentally in this study, though the most shielded element, δ_{33} is believed to be parallel to the ^{195}Pt-^{31}P bond axis. The ^{31}P chemical shielding tensor orientation assigned partially is shown in Table 1, as is the tensor orientation for a related ^{31}P site in the phosphite anion and the phosphines. In the solution-state ^{31}P NMR study by Farrar and Locker of HPO$_3^{2-}$, the orientation of the ^{31}P chemical shielding tensor elements as shown in Table 1 was determi-

Table 1. Solid-State ^{31}P NMR Chemical Shielding Tensors and Pt-Pt Distances for Binuclear Platinum Diphosphite Complexes

Compound	Solid-State[a]			Orientation	Solid-State		Solution-State[b]		d(Pt-Pt)[c]
	δ_{11}	δ_{22}	δ_{33}		δ_{iso}	J_{Pt-P} (Hz)	δ_{iso}	J_{Pt-P} (Hz)	(Å)
$K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$	138	66	6		69.8	3120	69.4	3095	2.925 (1)
$K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$	92	59	−69		27.5	ca.2460	28.0	2170	2.695 (1)
$K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$	96	60	−71		28.2	2185	24.0	2230	2.723 (4)
	Solution-State								
HPO_3^{2-} [d]	93	93	−30						

[a] Obtained by using a Herzfeld-Berger method. Error limits are ±5 ppm. [b] King, C.; Roundhill, D. M.; Dickson, M. K.; Fronczek, F. R. *J. Chem. Soc. Dalton Trans.* **1987**, 2769. [c] Ref. 12. [d] Ref. 24. Tensor orientation shown in the table based upon 3-fold site symmetry at phosphorus.

ned by the longitudinal relaxation study of the P-H spin system.[24] A single crystal ^{31}P NMR study of chlorotris(triphenylphosphine)rhodium(I) showed that the most shielded element is almost parallel to the Rh-P bond axis.[25] Also, the most shielded elements of the ^{31}P chemical shielding tensor in a number of solid phosphines were taken to lie along the C_3 (or *pseudo* C_3) axis.[26]

In the Ramsey approach,[27,28] the NMR chemical shielding of a nucleus can be decomposed into diamagnetic and paramagnetic contributions, which are generally opposite in sign. Because the coordination at phosphorus is not changed in the series of Pt_2, Pt_2Cl_2, and Pt_2Br_2, the diamagnetic contribution to the chemical shielding tensor elements should remain nearly constant. The range of chemical shift for ^{31}P is quite large. The chemical shifts on the δ-scale for the bare ^{31}P nucleus and free ^{31}P atom are 356 and −605 ppm, respectively, relative to 85% H_3PO_4.[29] In fact, highly shielded tensor elements are relatively rare in ^{31}P NMR, with P_4 (δ_{11} = −190, δ_{22} = −597, and δ_{33} = −597 ppm)[8] and related systems such as P_4S_3 (δ_{11} = 101, δ_{22} = 44, and δ_{33} = −406 ppm)[9] being some of the few examples. The fact that the value of δ_{33} is not close to that for a free ^{31}P atom for any of the binuclear platinum diphosphite complexes listed in Table 1 suggests a large paramagnetic contribution. We speculate that one of the significant changes occurring at the platinum metal center is a change in coordination number from four (Pt_2) to six (Pt_2Cl_2 and Pt_2Br_2), with the higher symmetry of the six-coordinate site affecting the paramagnetic contribution. Also, the increase in the P-Pt distances (and the decrease in the Pt-Pt distances) from Pt_2 to Pt_2Cl_2 and Pt_2Br_2 is an important factor affecting the more paramagnetic chemical shielding at ^{31}P nucleus on the P-Pt bond axis. We have found a good linear relationship between the Pt-Pt distances and the most shielded chemical shielding tensor element, δ_{33}; more shielded δ_{33} value implies more semiconductivity in the linear chain structures.

Figure 2 compares the ^{31}P MAS spectra for Pt_2, Pt_2Cl_2, and Pt_2Br_2. The spectra are similar to solution-state ^{31}P NMR spectra, though the line width, ~430 Hz (FWHH), obscures all but the single bond J coupling between ^{31}P and ^{195}Pt nu-
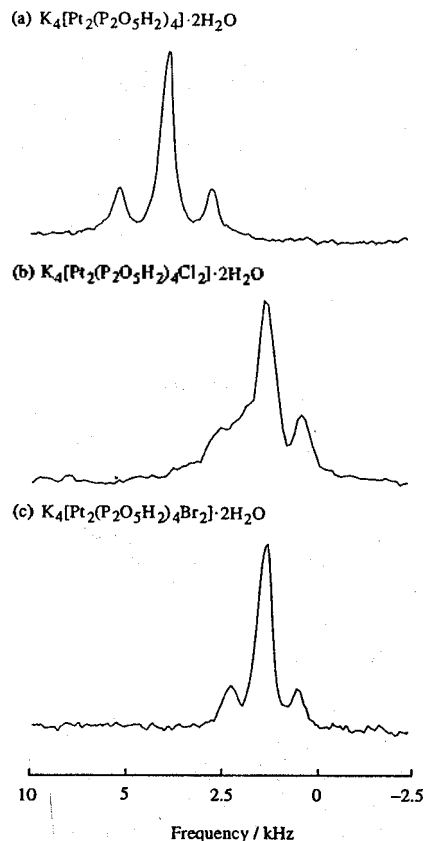
(a) $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$

(b) $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$

(c) $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$

Figure 2. Solid-state ^{31}P MAS spectra of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ ("Pt_2Cl_2"), and $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$ ("Pt_2Br_2") at v_r = 10 kHz and v_L = 80.98 MHz. The spectra show a single peak at the ^{31}P isotropic chemical shift and a doublet due to J coupling between ^{31}P and ^{195}Pt nuclei. Experimental parameters are as follows: (a) $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$, NS=100, RD=30 s; (b) $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$, 250, 30 s; and, (c) $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$, 88, 30 s.

clei. The 33.7% natural abundant ^{195}Pt leads to a doublet in the ^{31}P spectrum which is superimposed upon the ^{31}P

singlet. The isotropic J coupling constants are given in Table 1; the J coupling constants decrease as going from Pt_2 to Pt_2Cl_2 and Pt_2Br_2. A decrease in the value of J (^{31}P-^{195}Pt) may be due to the longer P-Pt bond, with decreased s-orbital character in the P-Pt bonds, which can be explained on the basis of the Pople-Santry equation.[30] The doublet for the ^{31}P-^{195}Pt spin system in Pt_2Cl_2 is noticeably asymmetric in the MAS spectrum. An asymmetry of this type in a ^{31}P powder pattern has been shown to be a result of anisotropies of the ^{31}P chemical shielding and J coupling tensors in (^{31}P-^{195}Pt)[31] and (^{31}P-^{199}Hg) systems.[32,33]

Conclusions

The principal elements and the relative orientations of the ^{31}P chemical shielding tensors have been obtained for Pt_2, Pt_2Cl_2, and Pt_2Br_2 complexes in the solid state. The ^{31}P isotropic chemical shifts and J (^{31}P-^{195}Pt) coupling constants are essentially the same in solution as in the solid state. There is an upfield shift (more negative values on the δ scale) going from Pt_2 to Pt_2Cl_2 and Pt_2Br_2 complexes in $δ_{33}$, which is aligned with the P-Pt bond axis. The paramagnetic contribution to $δ_{33}$ has been discussed based on the structural change at the platinum metal center. The results can be correlated with a decrease in the Pt-Pt distances in the order $Pt_2 > Pt_2Cl_2 ≈ Pt_2Br_2$.

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