

Notes

 ^{31}P Chemical Shift Anisotropy and Structure of Thiophosphates in RbTiPS_5

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Received September 8, 1999

In the course of studying quaternary transition metal thiophosphate compounds, we applied ^{31}P NMR spectroscopic methods to RbTiPS_5 . NMR peak assignment to a specific phosphorous site in the compound brought our attention to the systematic procedure of ^{31}P peak assignment for thiophosphates and orthophosphates. In this work, we correlate ^{31}P chemical shift parameters with structures of PS_4 units in RbTiPS_5 . The possibility of an empirical method to assign the ^{31}P peaks using average P-S bond lengths and average \angle S-P-S deviations from 109.5° ($\Delta\angle$ S-P-S) is discussed.

Experimental Section

Sample preparation procedure and crystal structure of RbTiPS_5 are described in previous reports¹ in detail. All experiments were carried out with the UNITYplus NMR system (Varian Associates Inc., U. S. A.) of 7.05 Tesla and the MSL system (Bruker Analytische GmbH, Germany) of 4.7 Tesla. A MAS rate between 1.4 and 4.2 kHz and 2 μs pulse length were employed. The 90° pulse length was 7.8 and 3.8 μs at 7.05 and 4.7 Tesla, respectively. For static spectra at 4.7 Tesla, a spin echo pulse sequence (90° - τ - 180°) was used with τ of 20 μs . Samples were ground to fine powders before the NMR experiments. Chemical shift was referenced to an external 85% H_3PO_4 aqueous solution and the reading error of center peak chemical shift (δ_{obj}) was within 1 ppm. The ^{31}P MAS spectra were simulated with a home-made simulation program to obtain principal values of the chemical shielding tensor (δ_{11} , δ_{22} , and δ_{33}). The simulation program using the algorithm in the literature^{2,3} takes the input parameters of spinning rate, guessed values of δ_{11} , δ_{22} , and δ_{33} , the spin number of the observing nuclei, and Larmor frequency. The output is the list of peak intensities for spinning sidebands and the center peak. These calculated intensities were compared with the experimental values and the δ_{11} , δ_{22} , and δ_{33} with the minimum deviation were chosen. The step size we used for the chemical shielding tensor variation was 0.1 ppm and the error of each calculated δ_{11} , δ_{22} , and δ_{33} value was within ± 0.2 ppm. Isotropic chemical shift (δ) and chemical shift anisotropy ($\Delta\delta$) were derived from δ_{11} , δ_{22} ,

and δ_{33} values using the following equations,³

$$\delta_i = (1/3)(\delta_{11} + \delta_{22} + \delta_{33})$$

$$\Delta\delta = \delta_{33} - (1/2)(\delta_{11} + \delta_{22})$$

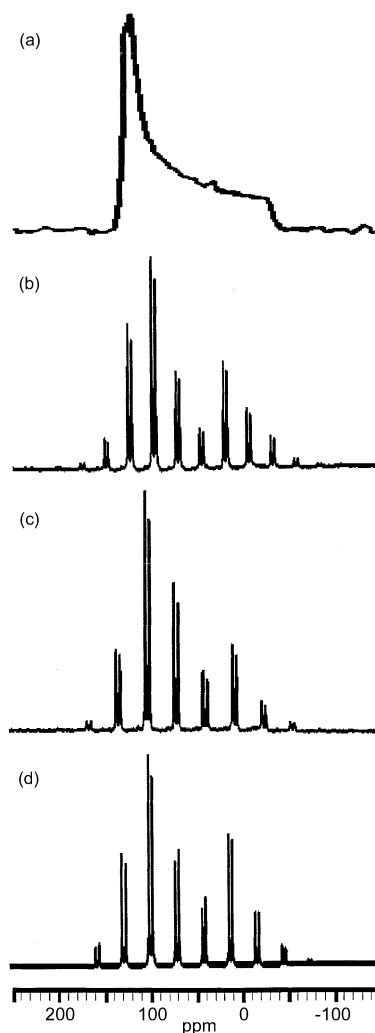


Figure 1. ^{31}P NMR spectra of RbTiPS_5 (A) Static spectrum at 4.7 Tesla. (B) MAS spectrum at 2.0 kHz spinning rate and 4.7 Tesla. (C) MAS spectrum at 3.4 kHz spinning rate and 7.05 Tesla. and (D) simulated spectrum with parameters of 3.4 kHz spinning rate, 121.49 MHz Larmor frequency (7.05 Tesla), $\delta_{11} = 137.7$ ppm, $\delta_{22} = 110.3$ ppm, $\delta_{33} = -37.0$ ppm for a peak pattern and $\delta_{11} = 136.2$ ppm, $\delta_{22} = 120.8$ ppm, $\delta_{33} = -34.2$ ppm for the other, the relative population ratio of 1:1 for two peak patterns, and 50 Hz line broadening.

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Table 1. ^{31}P chemical shift anisotropy parameters of phosphorous sites in RbTiPS_5

P site	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ_i (ppm)	$ \Delta\delta $ (ppm)	δ_{obj} (ppm)
P(1)	137.7	110.3	-37.0	70.3	160.9	70.6
P(2)	136.2	120.8	-34.2	74.3	162.7	74.4

with $|\delta_{33} - \delta_i| \geq |\delta_{11} - \delta_i| \geq \delta_{22} - \delta_i$.

Results and Discussion

The static ^{31}P NMR spectrum (Fig. 1A) of RbTiPS_5 seems to have only one powder pattern. However, MAS NMR spectra (Fig. 1B) shows clearly two sets of peaks. In order to confirm two sets of peaks, a MAS spectrum acquired at a different magnetic field (Fig. 1C) is introduced. The two center peaks did not change their δ_{obj} values in ppm even at different external magnetic field strengths. The two sets of chemical shift parameters were calculated by spectrum simulation at different field strengths and spinning rates. The results are summarized in Table 1 and a representative simulated spectrum is shown in Fig. 1D.

According to a previous report¹ on the crystal structure of RbTiPS_5 , there are two crystallographically different phosphorous sites, and each site resides in different one dimensional chains separated by Rb^+ ions. The one dimensional chains have a common repeating unit of $[\text{Ti}_2(\text{PS}_4)_2\text{S}_2^{2-}]$ although the relative orientation of the chains is different. From the crystallographic data in reference 1, the average P-S bond length and average $\Delta \angle \text{S-P-S}$ were calculated for each P site: $2.079 \pm 0.003 \text{ \AA}$ and 5.453° for P(1) site and 2.084 ± 0.003 and 5.460° for P(2) site.

For orthophosphate ions, a good correlation was obtained between $|\Delta\delta|$ and the average deviation of the O-P-O bond angle from that of a perfect tetrahedron ($109^\circ 28'$): the greater the average deviation of the bond angle, the greater $|\Delta\delta|$.⁴ Also δ_i of an orthophosphate ion was well correlated with the average P-O bond length: the longer the average P-O bond length, the more downfield shifted δ_i .^{4,5} We may apply the same methods used for orthophosphate ions to PS_4 units in our samples; considering the fact that oxygen and sulfur belong to the same Group 16 in the periodic table. Following this argument, the peak pattern with smaller δ_i (70.3 ppm) should be assigned to the P(1) site with smaller average P-S bond length, and the peak pattern with more downfield shifted δ_i (74.3 ppm) to the P(2) site with greater average P-S bond length. If this spectrum interpretation is correct, the relationship between $|\Delta\delta|$ and the average $\Delta \angle \text{S-P-S}$ should hold for the same assignment. Indeed, the P(1) site with a smaller average $\Delta \angle \text{S-P-S}$ than the P(2) site has smaller $|\Delta\delta|$ in the above peak pattern assignment.

The possibility of extending this peak assignment method to other thiophosphate compounds was checked with ^{31}P NMR data of $\text{Nb}_2\text{PS}_{10}$ and $\text{KNb}_2\text{PS}_{10}$ samples.⁶ The plot of $|\Delta\delta|$ and the average $\Delta \angle \text{S-P-S}$ in Figure 2 seems to show relatively a good correlation while the plot of δ_i and the aver-

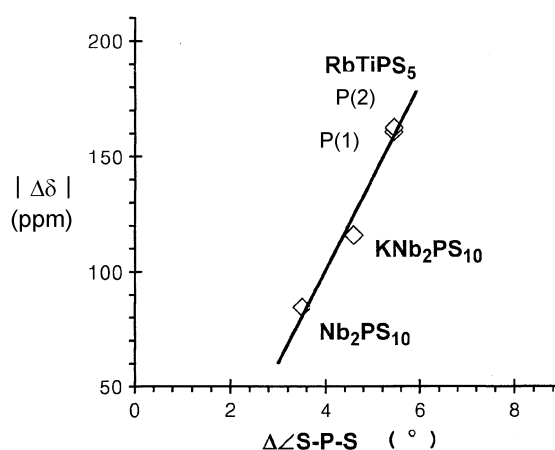


Figure 2. Plot of $|\Delta\delta|$ and the average $\Delta \angle \text{S-P-S}$ deviations from 109.5° ($\Delta \angle \text{S-P-S}$).

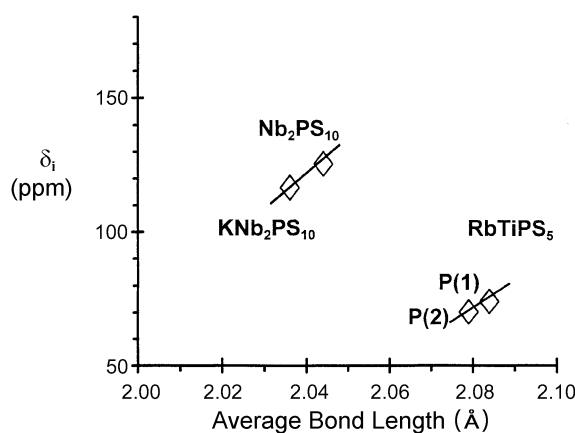


Figure 3. Plot of δ_i and average P-S bond length.

age P-S bond length in Figure 3 does not. The plot in Figure 3 suggests that comparison of δ_i and average P-S bond length may be effective only for the PS_4 units in the compounds with common repeating units; for example, for $\text{Nb}_2\text{PS}_{10}$ and $\text{KNb}_2\text{PS}_{10}$ only or different P sites in RbTiPS_5 only. This result is in contrast with that of orthophosphates. Our results show clearly that $|\Delta\delta|$ of both PO_4 and PS_4 units is mainly governed by the local structure of the units, especially by the deviation of $\angle \text{S-P-S}$ from the ideal tetrahedron angle. On the other hand, δ_i of PS_4 units is sensitive not only to structures of PS_4 units but also to the surrounding environment of the PS_4 units while δ_i of PO_4 units is determined mainly by structures of the PO_4 units. Therefore, correlation of ^{31}P δ_i and average P-S bond length of PS_4 units is useful only for very similar structures. But correlation of $\Delta\delta$ and the average $\Delta \angle \text{S-P-S}$ seems to be universally applicable. It is not certain at this moment why δ_i of PS_4 units is affected by the surrounding environment of the PS_4 units, something not seen in δ_i of PO_4 units. This is a topic worthy of future study.

To estimate the influence of next-nearest-neighbors of phosphorus on δ_i , other correlations were attempted. In Figure 4, ^{31}P δ_i was plotted versus a sum of Z/\sqrt{r} , where Z is the cation charge and r is its ionic radius of the next nearest

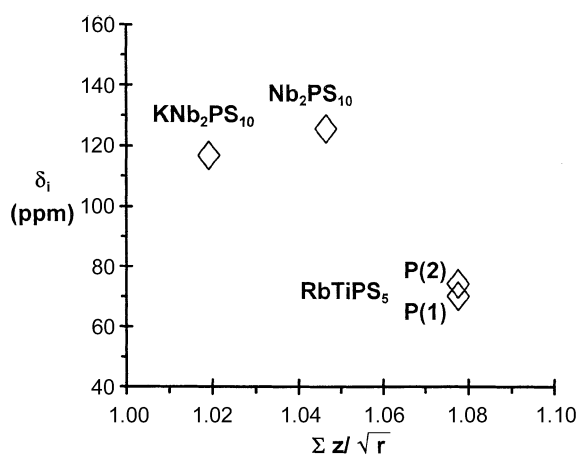


Figure 4. Plot of δ_i and a sum of Z/\sqrt{r} where Z is the cation charge and r is its ionic radius of the next nearest neighbor to phosphorus.

neighbor to phosphorus. Although ^{31}P δ_i is very well correlated with Z/\sqrt{r} for orthophosphates in reference 4, our plot is far from a linear relationship. Bond strength⁷⁻⁹ counting the influence of next-nearest-neighbor atoms systematically might be the best parameter correlated with ^{31}P δ_i of thiophosphates. However, data are not yet abundant enough to reduce bond strength values for thiophosphates. Because bond strength is directly related with bond length⁹ and the influence of next-nearest-neighbor atoms is reflected on P-S bond length to a certain degree, average P-S bond may be

the best choice for ^{31}P peak assignment at present but with the restrictions presented above.

Acknowledgment. We thank Professor Hoseop Yun at Ajou University in Korea for his generous supply of RbTiPS₅ sample. This work is partially supported by MOST (Ministry of Science and Technology in Korea) through the KOYOO project fund endowment at the KBSI (Korea Basic Science Institute). We gratefully acknowledge Dr. K. S. Hong and Ms. Shin Ae Chae at the KBSI for their technical assistance.

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