A Characterization of the Linear P−O−P Bonds in $M^{4+}(P_2O_7)$ Compounds: Bond-Angle Determination by Solid-State NMR

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Abstract: Many compounds of the type $M^{4+}(P_2O_7)$ contain, in their room-temperature structure, both linear and bent pyrophosphate groups. The commonly found packing motif is usually described as a 3 × 3 × 3 cubic superstructure ($Pa\bar{3}$ with $Z = 108$) where 11% of the P−O−P angles are predicted by diffraction methods to be in the unusual linear configuration. Using a novel variant of two-dimensional (2D) exchange NMR spectroscopy, we have measured, in a the cubic room-temperature structure of SiP_2O_7, the angle between the ^{31}P chemical-shift-anisotropy (CSA) tensors in covalently bonded P−O−P unit. The selectivity to covalently bonded pairs is achieved by using the scalar coupling interaction as the driving force for polarization exchange during the mixing time of a two-dimensional exchange experiment. The NMR data show that the "linear" pyrophosphate groups in SiP_2O_7 are in fact linear on the NMR time scale (∼100 μs). A static disorder of "normal" bent units, postulated previously, is clearly excluded.

1. Introduction

Compounds of the type $M^{4+}(P_2O_7)$ have sparked considerable interest because of their peculiar structural properties and the observation of small or negative thermal expansion coefficients.[1] At high temperature, these compounds often conform to a cubic structure of space group $Pa\bar{3}$ with four molecules per unit cell ($Z = 4$). This space group requires all the P−O−P units to be linear, energetically less favorable then a bent configuration. It has been suggested that this unfavorable energetic configuration is stabilized by entropy contributions.[2] In agreement with such a proposition, the linearity of many P−O−P units is in fact lost at ambient temperature where these $M^{4+}(P_2O_7)$ compounds show a 3 × 3 × 3 superstructure with identical space group, but with $Z = 108$, that allows 89% of the P−O−P angles to bend away from 180° (to approximately 145°) while 11% remain linear. This superstructure with 11 crystallographically distinct P nuclei per unit cell has been refined for M = Zr,[2] Si,[3] and Ti.[4]

In principle, the apparent linearity of the P−O−P units in diffraction experiments can have three reasons: (i) a statical disordered arrangement of bent configurations, (ii) a dynamic disorder where the units interconvert between bent structures on a time scale much slower than the (inverse) vibrational frequencies, and (iii) a linear structure, possibly with an extended thermal motion of the oxygen atom. The three experimental studies mentioned above have not resolved the issue; two leave the question open[2,3] while one expresses a preference for a static disorder.[4] By using solid-state NMR, this study shows that the (in diffraction) apparently linear P−O−P in cubic phase SiP_2O_7 are indeed linear on a time scale of a hundred microseconds. A static disorder of bent units (with the same angle as the other bent units) is clearly excluded.

Two-dimensional (2D) exchange NMR spectroscopy[6,7] can measure the angle between the two ^{31}P chemical-shift-anisotropy (CSA) tensors if polarization can be transferred between the two spins involved. By exploiting the knowledge about the orientation of the CSA tensor to the molecular frame, the bond angle can then be evaluated.

In the present context, the magic-angle spinning (MAS) variant[8−10] of 2D exchange spectroscopy must be employed to provide the necessary spectral resolution and resolve the eleven sites per unit cell. The CSA tensor in the evolution and detection periods is characterized by its spinning-sideband pattern.[11,12] During the mixing time, polarization must be transferred between the two spins whose relative orientation is to be characterized. Then, the sideband pattern in the 2D spectrum yields, for a two-spin system, directly the relative orientation (described by three Euler angles) of the two CSA tensors. In the experiments described in refs 7 to 10, the driving force for the polarization transfer in the mixing time was provided by the magnetic dipole−dipole interaction. In a many-

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spin system, like SiP_2O_7, the evaluation of the experimental sideband pattern becomes, however, difficult because cross-peaks between all resonances appear and greatly reduce the individual cross-peak intensity. Furthermore, the partial overlap of cross-peaks makes a quantitative analysis of the cross-peak pattern difficult. Therefore, the scalar *J* couplings are used here as the polarization-transfer mechanism and only the two phosphorus spins within a P−O−P unit exchange polarization. Thus, the unit's relative orientation can selectively be measured. A pulse sequence that leads to *J* polarization transfer in solids is described in ref 13.

Alternatively, a measurement of the electric field gradient at the bridging oxygen site with ^{17}O solid-state NMR could also provide information about the P−O−P angle.[15] This does, however, require isotopically enriched samples. The ^{31}P chemical shifts are not a good measure for the P−O−P angle as is easily seen from the fact that the two ^{31}P within a given P−O−P unit can differ quite substantially in chemical shift (vide infra). Previous solid-state NMR experiments on TiP_2O_7[4] and SiP_2O_7[5] have been carried out, but in these studies extracting the P−O−P angle by NMR was not attempted.

2. Experimental Section

NMR Measurements. The NMR measurements were performed on a Chemagnetics Infinity 400 spectrometer with a 4 mm MAS probehead operating at a ^{31}P frequency of 161.88 MHz. A 2D exchange pulse sequence[6] (top of Figure 1), modified to use the scalar coupling as a polarization-transfer mechanism in the mixing time, was applied. The resulting spectra provide the correlations between covalently bonded nuclei (total through-bond correlation spectroscopy, TOBSY[13]). The first 90° pulse of Figure 1 generates transverse magnetization, and during the following evolution period $\boldsymbol{t_1}$, the spins are free to precess with their chemical-shift frequency. Therefore, the magnetization at the beginning of the mixing time is frequency labeled. During mixing, the five pulse WALTZ8[14] sequence $(\pi_{\bar{x}}-2\pi_x-\pi_{\bar{x}}-3\pi/2_x-\pi/2_{\bar{x}})$ is applied to promote exchange between *J*-coupled nuclei. It produces an average Hamiltonian that contains only scalar-coupling terms.[13] A supercycle over two rotor periods where all five phases of the WALTZ8 are inverted in the second rotor period was applied.[13] During detection, the chemical shift is again used to determine the destination of the magnetization that was labeled before mixing. Two TOBSY spectra were acquired. The first had a mixing time consisting of 21 ms with 8 WALTZ8 cycles per rotor period, a MAS frequency of $\omega_r/2\pi = 4.63$ kHz, and a radiofrequency amplitude of $\omega_1/2\pi = 111$ kHz. The second TOBSY spectrum was acquired with a mixing time of 30 ms (10 WALTZ8 cycles per rotor period, $\omega_1/2\pi = 100$ kHz, and $\omega_r/2\pi = 3.33$ kHz). For pure absorption-phase 2D exchange spectra free from "auto-cross-peaks" under MAS conditions,[8] (anti-echo) free induction decay signals where the end of $\boldsymbol{t_1}$ and the beginning of $\boldsymbol{t_2}$ are rotor-synchronous must be combined with the (echo) signals where the beginning of $\boldsymbol{t_1}$ and beginning of $\boldsymbol{t_2}$ is synchronized[8,9] (see also Figure 1). We have employed the phase-cycle of Boender et al.,[16] combined with States-sampling,[17] to acquire the necessary data. Active synchronization was maintained, using the optical signal from the MAS rotor, by a home-built device. To ensure the rotor-synchronous start of the $\boldsymbol{t_2}$ period, the spin-locked magnetization at the end of the WALTZ cycles is converted, by a $\pi/2$ pulse, to *z*-magnetization. Then, as soon as the optical sensor observes the correct rotor position, it is again flipped to the transverse plane and acquisition begins.

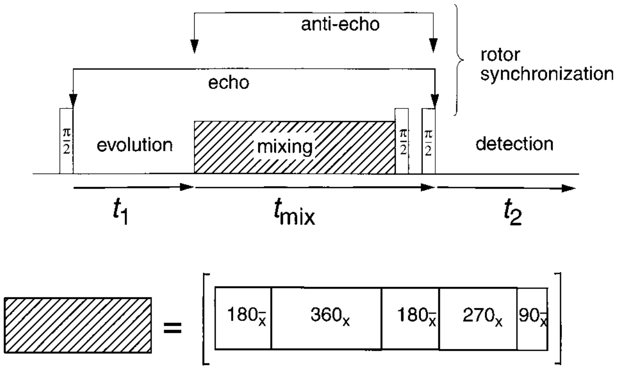

Figure 1. Pulse sequence for rotor-synchronized 2D ^{31}P TOBSY. The top part of the figure describes the synchronization points of the rotor in order to acquire pure absorption phase 2D spectra free from auto-cross-peaks. The mixing period utilizes a WALTZ8 cycle for chemical-shift compensation during the through-bond polarization-transfer period.

Data Analysis. The CSA tensors of the 11 sites were determined by a Herzfeld-Berger analysis[12] from the spinning-sideband intensities in a 1D MAS spectrum with sample spinning at 4.63 kHz. In principle, this analysis is only valid in the absence of dipolar couplings. On the basis of numerical simulations in the framework of the simulation platform GAMMA,[20] we have found that, under the experimental conditions mentioned, the influence of the homonuclear dipolar interaction causes only a minor systematic error (approximately 1 ppm) in the chemical-shift principal values obtained from the Herzfeld-Berger analysis. The dipolar interaction was, therefore, neglected for the analysis. The relative orientation of the CSA tensors was obtained from the experimental cross-peak intensity in the 2D exchange spectra with use of a previously described Fortran program.[8] For the analysis of the 2D data, the CSA principal values as obtained by the Herzfeld-Berger analysis of one-dimensional data were used. The least-squares optimizations were performed with the MATLAB program package.[18]

3. Results and Discussion

The TOBSY spectrum of SiP_2O_7, expanded to show only the centerband (isotropic chemical shift) and the first sideband pattern, is shown in Figure 2. On the diagonal, one observes the eleven centerband resonances, i^0, where the *i* denotes the number of the resonance and the superscript the order of the spinning sideband. The spinning sidebands (on the main diagonal of the 2D spectrum) of order *n* are denoted by i^n. Sidebands up to $n = \pm 2$ were taken into account for the angle determination. The two most shielded resonances, 10 and 11, show considerable overlap. All other resonances are well resolved and their intensity in a one-dimensional spectrum corresponds to the stoichiometry of the unit cell.[19] The cross-peaks between the centerband resonances (i^0-j^0) readily identify the two ^{31}P nuclei that belong to a given P−O−P unit. It becomes obvious that the resonances (1−5), (2−7), (3−6), (8−9), and (10−11) are the diphosphate pairs. Note that the intensity of the signal at i^n-i^m vanishes to excellent approximation for $n \neq m$. These cross-peaks must vanish for a rotor-synchronized experiment and the very low experimental intensity confirms the accurate rotor-synchronization of the experiment.[8] As a consequence, the side diagonals of the two-dimensional spectrum (with signals at i^n-i^m) are empty with the exception of the 10^n-11^m cross-peak, which accidentally appears (almost)

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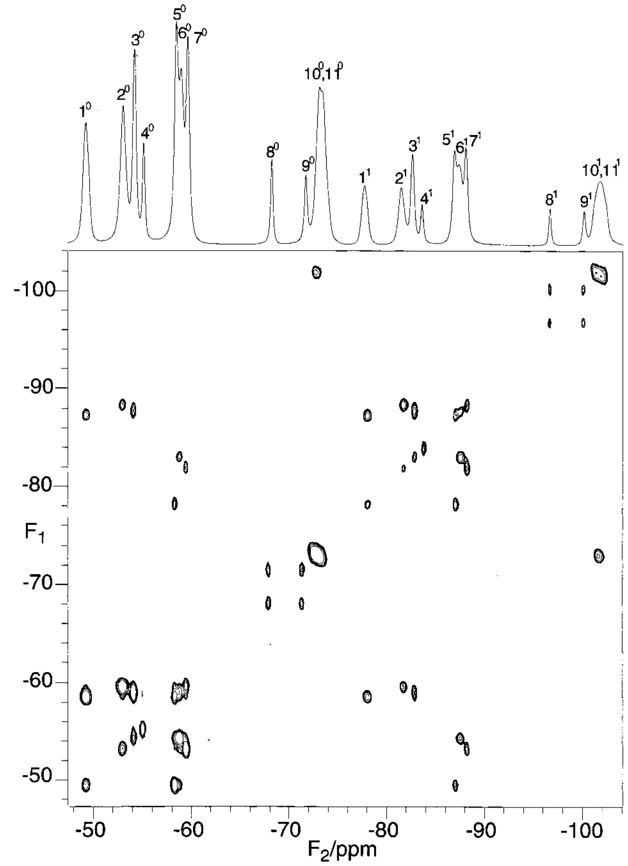

Figure 2. Rotor-synchronized 2D ^{31}P TOBSY spectrum of the cubic phase of SiP_2O_7 recorded with a MAS frequency of 4.63 kHz at a static field of 9.4 T. Only the region showing the centerband and the +1 sideband is reproduced. The pulse sequence of Figure 1 was used. The TOBSY mixing period was set to 21 ms at a radiofrequency field strength of 111 kHz. The ^{31}P ppm scale is referenced externally to phosphoric acid. More experimental details are given in the text.

on a side diagonal because of the almost-degeneracy of resonances 10 and 11. Resonance 4, which has no TOBSY cross-peak, is assigned to the unique ^{31}P nucleus in which the phosphor nuclei in the P−O−P unit are related by a center of inversion.[3] There, the two ^{31}P are magnetically equivalent and the *J* coupling is not expressed in the NMR spectrum.

The angular information is contained in the intensities of the i^n−j^m cross-peaks.[8] From the 2D sideband patterns, two qualitatively different kinds of P−O−P units can be distinguished: the pairs (1−5), (2−7), and (3−6) that show intense sidebands at $n \neq m$ (see Figure 3b) and the pair (8−9) with no significant sideband intensity at these positions (Figure 3a). The latter corresponds to an almost collinear orientation of the two CSA tensors. A difference between these types is also found in the *J* coupling constants as evaluated by polarization-transfer curves;[13] the pairs (1−5), (2−7), and (3−6) yield $J = 23 \pm 1$ Hz, and (8−9) yields $J = 17 \pm 1$ Hz.[13] At the moment, no empirical correlation between *J* and the bond angle is available, but it is conceivable that these values can also be used to determine the angle.

From the 2D sideband pattern, the angle between the CSA tensors of spins *i* and *j* was determined by using the procedure in ref 8. The principal values of the CSA tensors have been determined in a separate set of 1D experiments using the Herzfeld-Berger analysis scheme[12] and are listed in Table 1. Numerical calculations[20] have been used to confirm the approximate validity of the Herzfeld-Berger analysis in the presence of a dipolar coupling in our specific system. The degenerate resonances 10 and 11 have been omitted from the analysis. Because the chemical-shift tensors are found to be close to axially symmetric (see Table 1), only the Euler-angle β can be extracted from the analysis with good accuracy.[21] The introduction of a further Euler angle into the analysis did not lead to a significantly lowered root-mean-square-deviation (rmsd) value and did not change the value of the Euler angle β corresponding to the minimum rmsd by more than 1°. A plot of the rmsd normalized by the noise of the experiment between experimental peak intensities and simulated intensities as a function of β is shown in Figure 4. Experiments were performed at 4.6 and 3.3 kHz MAS frequency. Shown here are the data at a spinning speed of 3.3 kHz, a condition more sensitive to the variation of β around 180°. The results at 4.6 kHz agree well within experimental error. The resonance pairs (1−5), (2−7), and (3−6) yield angles to within 6 degrees

Table 1. ^{31}P Chemical Shift Tensors in Cubic Phase SiP_2O_7

resonance	$\delta_{11}{}^a$	$\delta_{22}{}^b$	$\delta_{33}{}^b$	isotropic shift^c
1	9.4	−73.6	−84.0	−49.5
2	3.3	−74.9	−87.4	−53.1
3	4.8	−78.5	−88.9	−54.2
4	−0.6	−82.3	−82.3	−55.1
5	−2.9	−76.6	−95.6	−58.4
6	3.3	−84.3	−95.5	−58.9
7	−3.8	−82.0	−92.6	−59.5
8	−13.1	−90.1	−100.4	−67.9
9	−10.7	−95.2	−108.0	−71.3
10, 11^d	−13.5	−92.1	−112.9	−72.9

^{a} The estimated uncertainty in δ_{11} is 1 ppm. ^{b} The estimated uncertainty in δ_{22} and δ_{33} is 5 ppm. ^{c} Externally referenced to phosphoric acid. Estimated uncertainty <1 ppm. ^{d} Averaged value.

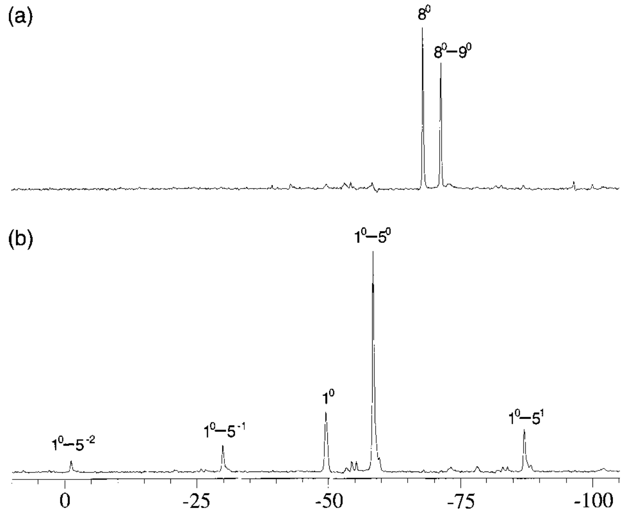

Figure 3. Two cross-sections of the 2D spectrum in Figure 2 at F_1 frequencies corresponding to resonance 8 (a) and resonance 1 (b). The intensity of the cross-peaks i^n−j^m (with $n \neq m$ and $i \neq j$) encodes the P−O−P angle. While no significant intensity is observed for the i^n−j^m cross-peaks in Figure 2a, the significant intensity of these cross-peaks in (b) indicate a bent diphosphate unit for spin pair (1−5). The former suggests a linear P−O−P unit for spin pair (8−9). The high intensity of the cross-peaks compared to the diagonal peak in (b) indicates the high transfer efficiency achievable from TOBSY. The source of the minor additional cross-peaks is the imperfect rotor-synchronization of the mixing time[7] (for i^n−i^m signals) and spurious dipolar polarization transfer for signals of the type i^n−j^m where *n* and *m* are not covalently bonded.

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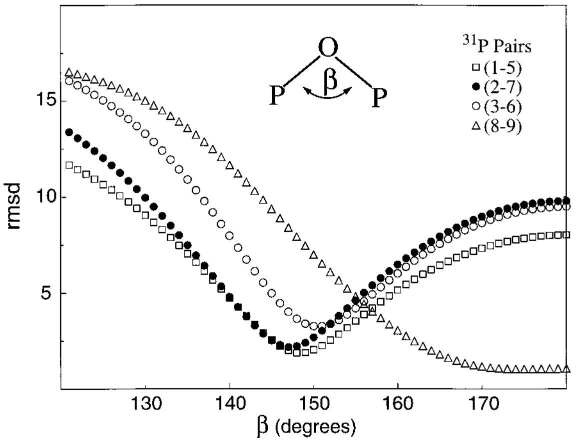

Figure 4. Normalized root-mean-square deviation (rmsd) between the experimental and simulated cross-peak intensities (taken into account were cross-peaks of order $n - m = 0, \pm1, \pm2$) as a function of the angle β for four sets of P−O−P units in cubic SiP_20_7.

Table 2. P−O−P Bond Angles in SiP_2O_7

P−O−P pair	X-ray diffraction bond angle	CSA-CSA β angle
(1−5)	144.4	148 ± 6
(2−7)	143.5	147 ± 5
(3−6)	146.5	150 ± 6
(4−4′)	180[a,b]	180[c]
(8−9)	180[a]	180 ± 18
(10−11)	148.7	bent[c]

[a] Linearity may result from superposition of bent P−O−P units. [b] Inversion symmetry forces 180°. [c] Quantitative analysis not available because of degenerate resonance frequencies.

(statistical error at 95% significance for 24 degrees of freedom) of 148°, 147°, and 150° degrees and in good agreement with the crystallographic values of 144.4°, 143.5°, and 146.5° (see the error surface of Figure 4). The presence of strong cross peaks between different sideband orders of (10−11) indicates that these pairs must be bent. Because the 10^0 and 11^0 resonances overlap, a quantitative evaluation of the angle β with a precision equal to one of the other pairs is, however, not possible. The angle in (8−9) is 180° ± 18° while the angle in (4−4′), where 4′ refers to the spin that is, in the crystal structure, related to 4 by inversion symmetry, must be close to 180° because cross peaks between sideband orders are missing. This finding for (4−4′) is in accordance with the crystallographic symmetry that requires a linear arrangement. The relatively large error of 18° of the angle for the pair (8−9) comes from the relative insensitivity of the cross-peaks intensity on the angle β around 180°. The detailed results are listed in Table 2.

Having determined the angle between the ^{31}P-CSA's within a P−O−P unit, knowledge about the orientation of the principle-axis system of the CSA to the molecular-fixed frame becomes necessary to determine structural information. The local symmetry of the ^{31}P nuclei (taking into account only direct neighbors and neglecting crystal packing effects) would impose an axially symmetric tensor, placing the unique principal axis along the P−O bond. For the (hypothetically) linear P−O−P units, this positioning is exact due to the 3-fold crystallographic symmetry axis.[3] For the bent units, the same relationship between geometry and CSA is still approximately valid. Experimentally it was found that in $Na_4P_2O_7$ and $Cd_2P_2O_7$[22] the least shielded axis, δ_{11}, coincides within 5° of the P−O bond direction. With SiP_2O_7, this relationship is supported by an *ab initio*[23] calculation. Thus, one can identify the angle β directly with the P−O−P bond angle, bearing in mind that a systematic error in the order of 5° can occur for the bent units. The ab initio calculations suggest that the CSA-CSA angle β overestimates the bond angle.

4. Conclusion

This NMR study has revealed the presence of two classes of P−O−P angles in SiP_2O_7. Three coupled pairs (1−5), (2−7), and (3−6) are bent with a P−O−P angle of about 148° while the angle in (8−9) is about 180°. This result excludes that a static disorder of "normal" bent units leads, on average, to a linear structure in the diffraction studies. The 2D NMR results are consistent with either a dynamic disorder with an exchange rate (at ambient temperature) of $k \gg 5000\ s^{-1}$ or a structure that is close to linear, possibly with an extended vibrational motion of the bridging oxygen. Although it cannot be excluded, the explanation by dynamic disorder seems not very likely because a dynamic averaging process would also partially average the anisotropy of the CSA tensors. However, the experimental anisotropy of the tensors of resonances 8 and 9 is just as large as that of the other tensors. A different electronic structure of the linear pair, as compared to the bent pairs, is also reflected in the significant difference of the scalar coupling constant.

The application of rotor-synchronized TOBSY is not restricted to the class of compounds investigated here. It provides a general means to selectively measure chemical bond angles in covalently bound units.

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