Characterization of the Room-Temperature Structure of SnP_2O_7 by ^{31}P Through-Space and Through-Bond NMR Correlation Spectroscopy

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The room-temperature structure of SnP_2O_7 has been investigated using various one- and two-dimensional (1- and 2D) magic-angle spinning (MAS) NMR experiments. We show that ^{31}P homonuclear through-bond and through-space correlation NMR spectroscopies allow us to discriminate between the 12 possible space group symmetries of the structure. In particular, the ^{31}P 2D refocused INADEQUATE experiment allows us to resolve an impressive number of distinct ^{31}P resonances, showing that the asymmetric unit contains at least 49 different P_2O_7 groups with two inequivalent P sites. The results suggest that the symmetry of the SnP_2O_7 room-temperature structure is monoclinic with space group $P2_1$ or Pc.

Introduction

Compounds of the $M^{4+}P_2O_7$ family (M = Si, Ge, Sn, Pb, Ti, Zr, Hf, etc.) have recently generated considerable interest because several members of the family show low or even negative coefficients of thermal expansion over certain temperature ranges.[1−3] At high temperature, these compounds usually have a cubic structure, with $Z = 4$ and space group symmetry $Pa\bar{3}$, which can be described as a network of corner-sharing MO_6 octahedra and PO_4 tetrahedra linked together to form P_2O_7 units (Figure 1).[2] In this ideal cubic structure, the P_2O_7 groups are on 3-fold axes with the P−O−P bridging oxygen atoms at inversion centers and the P−O−P bond angles constrained by symmetry to be 180°.[2] However, the energetically preferred bond angles for these linkages are in the range 130°−160° [2] and at low temperature linear P_2O_7 units are partially or completely avoided by distortion of the ideal cubic structure. The bending of these linear bonds results in a pseudo-cubic structure with a tripled (3 × 3 × 3) unit cell ($Z = 108$). This pseudo-cubic structure, usually described as a 3 × 3 × 3 superstructure relative to the aristotypic structure ($Pa\bar{3}$, $Z = 4$), has been commonly observed at ambient temperature in such systems by various experimental techniques.[3−11]

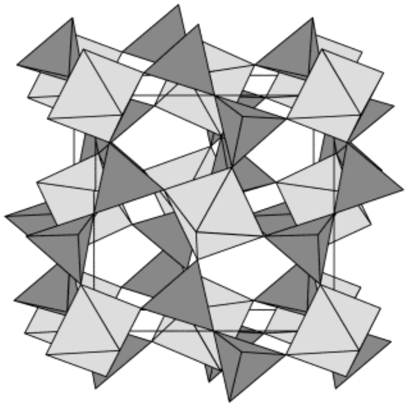

Figure 1. Ideal cubic structure of SnP_2O_7 shown as corner-sharing SnO_6 octahedra and PO_4 tetrahedra.

Although powder and electron diffraction methods give clear evidence of the tripled cell parameters, the exact nature of these room-temperature structures and their space group symmetries is a matter of some debate. Good quality single crystals of these materials can be hard to obtain and the structural complexity makes detailed interpretation of power diffraction patterns difficult. It can be shown that, assuming phase transitions with group−subgroup relationships, the room-temperature structure can adopt 1 of 12 possible

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Table 1. Number of Different Types of $P_2O_7^{4-}$ Groups for the Possible Space Groups Adopted at Room Temperature by AP_2O_7 Materials[a]

	O site symmetry P−O−P geometry						
space group	$\bar{3}$ P_a-O-P_a linear	$\bar{1}$ P_a-O-P_a linear	3 P_a-O-P_b linear	1 P_a-O-P_b bent	no. unique P_2O_7's	no. unique P sites	% linear P_2O_7
$Pa\bar{3}$ (1 × 1 × 1)	1(4)				1	1	100
$Pa\bar{3}$	1(4)		1(8)	4(96)	6	11	11.1
$P2_13$			3(12)	8(96)	11	22	11.1
$R\bar{3}$	1(1)	1(3)	1(2)	17(102)	20	38	5.6
$R3$			3(3)	35(105)	38	76	2.8
$Pbca$		1(4)		13(104)	14	27	3.7
$Pca2_1$				27(108)	27	54	0
$P2_12_12_1$				27(108)	27	54	0
$P2_1/c$		2(4)		26(104)	28	54	3.7
Pc				54(108)	54	108	0
$P2_1$				54(108)	54	108	0
$P\bar{1}$		4(4)		52(104)	58	108	3.7
$P1$				108(108)	108	216	0

[a] The site symmetry adopted by the P−O−P bridging oxygen determines the geometry of each $P_2O_7^{4-}$ unit. For each case the number gives the number of crystallographically unique P_2O_7 groups of a given type and the number in parentheses the total number of such groups in the unit cell. The total cell content is $Zr_{108}(P_2O_7)_{108}$. The total number of unique P sites in the asymmetric unit is given by Σcol1 + col2 + 2*col3 + 2*col4.

space groups derived from the symmetry ($Pa\bar{3}$) of the ideal high-temperature phase.[2] Several members of the family such as SiP_2O_7[6,12] and TiP_2O_7[7,8,13] have been shown to adopt a room-temperature cubic structure with space group $Pa\bar{3}$, which retains the space group of the high-temperature phase but triples each of the cubic cell parameters. Other compounds are known to conform to lower symmetry structures. This was first reported in the case of γ-GeP_2O_7, which has a monoclinic structure with symmetry $P2_1/c$ or lower.[9] For ZrP_2O_7, ^{31}P solid-state NMR experiments have shown that the room-temperature structure is orthorhombic with a $Pbca$ space group.[14] More recently, X-ray, electron, and neutron diffraction studies have shown that room-temperature structure of SnP_2O_7 is pseudo-cubic with symmetry $P2_13$ or lower.[11]

These various space group symmetries give rise to very subtle differences in the reflections observed by powder X-ray diffraction. However, the number of crystallographically distinct phosphorus sites and the number of different types of P_2O_7 groups in the asymmetric unit dramatically increase by lowering the symmetry of the possible space group (see Table 1).[2] In addition, the site symmetry adopted by the P−O−P bridging oxygen atom determines the geometry of each $P_2O_7^{4-}$ unit. For example, $Pa\bar{3}$ symmetry is expected to give rise to 11 crystallographically different P sites forming 6 independent P_2O_7 groups, with 4 in general positions, 1 with the bridging oxygen atom on a 3-fold symmetry site, and 1 with the bridging oxygen atom on a $\bar{3}$ symmetry site (constraining the two P atoms of the P_2O_7 group to be crystallographically equivalent and the P−O−P bond angle to 180°). In contrast, the space group $Pbca$ leads to 27 crystallographically distinct P sites corresponding to 13 P_2O_7 groups in general positions and 1 with the bridging oxygen atom on an inversion center, while for $Pca2_1$ one would expect 54 different P sites forming 27 P_2O_7 groups in general positions.

High-resolution solid-state correlation NMR techniques have proved to be very useful in assigning the space groups of several of these MP_2O_7 compounds[12−14] and other crystalline structure[15−18] since they allow the number of independent P sites in the asymmetric unit and the phosphorus connectivity scheme to be probed. In the following, we have examined the room-temperature structure of SnP_2O_7 using various one- and two-dimensional magic-angle spinning (MAS) NMR experiments. We show that the use of ^{31}P homonuclear through-bond and through-space correlation NMR spectroscopy allows discrimination between the 12 possible space group symmetries of the structure.

Experimental Section

The synthesis of a high-purity crystalline sample of SnP_2O_7 has been described in detail elsewhere.[11] In short, $SnCl_4{:}5H_2O$ and H_3PO_4 were mixed together with a Sn:P ratio of 1:3. The mixture was heated at 2 K/min to 598 K in air at atmospheric pressure and held at this temperature overnight. The resultant powder was reground and heated at 1473 K for 60 h and then air-quenched from the furnace to yield crystalline SnP_2O_7 quantitatively. The high purity of the sample was confirmed by X-ray and neutron powder diffraction.

The solid-state NMR experiments were performed at room temperature on a Bruker DSX 300 spectrometer (7.0 T) with a 4-mm MAS probehead operating at a Larmor frequency of 121.4 MHz for ^{31}P. The one-dimensional (1D) ^{31}P MAS spectra were recorded at 3, 10, and 15 kHz spinning frequencies using single-pulse ($\pi/8$) acquisition with a recycle delay of 200 s to ensure no saturation.

The two-dimensional (2D) ^{31}P through-space single-quantum−double-quantum (SQ−DQ) MAS NMR correlation spectrum was acquired at 10 kHz spinning frequency. We have used the

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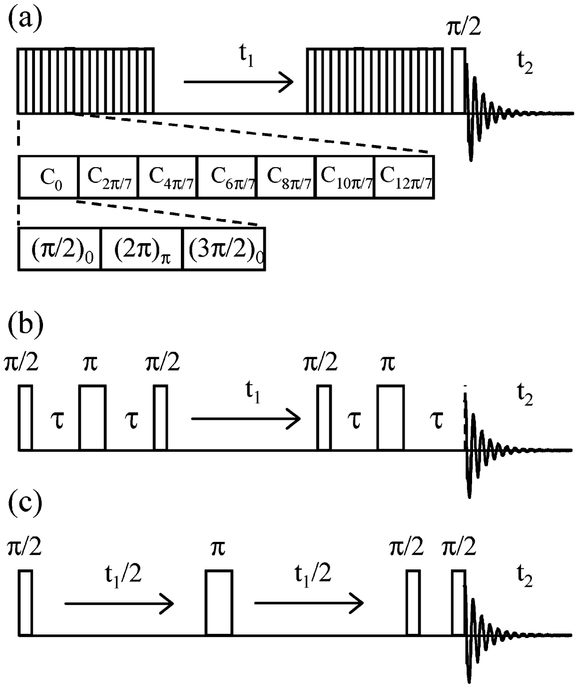

Figure 2. (a) POSTC7[19] pulse sequence used for the 2D through-space SQ−DQ correlation experiment, (b) refocused INADEQUATE pulse sequence[20] used for the 2D through-bond SQ−DQ correlation experiment, and (c) *z*-filtered spin−echo pulse sequence[22] used for the 2D *J*-resolved experiment.

POSTC7 recoupling sequence[19] (Figure 2a) to reintroduce the $^{31}P-^{31}P$ homonuclear dipolar interaction under MAS conditions and to achieve an efficient broadband excitation and reconversion of double quantum coherences ($\omega_{rf}/2\pi = 69.5$ kHz). Short excitation and reconversion periods of 600 μs were used. Sixty-four t_1 increments with 16 transients each were collected. The recycle delay was set to 55 s. A presaturation sequence was applied to ensure equivalent conditions for each transient because of the long ^{31}P longitudinal relaxation rate ($T_1 \sim 700$ s).

The 2D ^{31}P through-bond single-quantum−double-quantum (SQ-DQ) MAS NMR correlation spectrum was acquired while spinning at 10 kHz using the refocused INADEQUATE sequence[20] (shown in Figure 2b). The $\pi/2$ pulse length was 2.3 μs and the delay τ in the excitation and reconversion periods was set to 9 ms. Eighty t_1 increments with 32 transients each were collected using a presaturation sequence and a recycle delay of 55 s.

The 2D homonuclear *J*-resolved spectrum was recorded at a 15 kHz spinning frequency using a *z*-filtered spin−echo sequence (Figure 2c) to obtain pure absorption-mode line shapes.[21,22] The $\pi/2$ pulse length was 2.3 μs. Seventy t_1 increments with 32 scans each were collected using a presaturation sequence and a recycle delay of 20 s.

All the two-dimensional pure absorption phase spectra were obtained using a hypercomplex acquisition.[23] To avoid spinning sidebands in the ω_1 dimension, the t_1 time increment was synchronized with the rotor period. The spinning frequency was stabilized to ±10 Hz for all experiments. ^{31}P chemical shifts were referenced relative to 85% H_3PO_4 aqueous solution using the deshielding convention. Simulations of the 1D MAS and 2D MAS correlation spectra were performed using the dmfit software.[24]

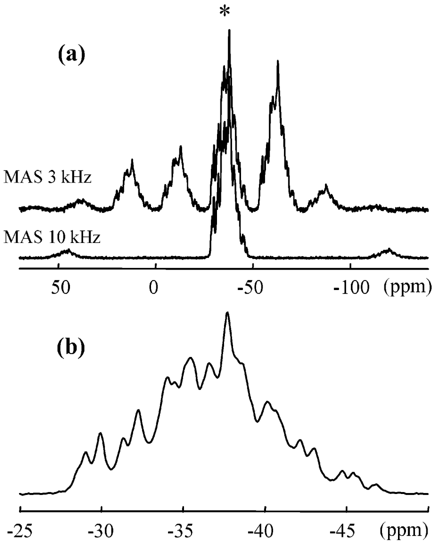

Figure 3. (a) ^{31}P 1D MAS NMR spectra of SnP_2O_7 recorded at 3 and 10 kHz spinning frequencies. The asterisk marks the center band region. (b) Expansion of the center band region (10 kHz spinning frequency).

The use of a moderate principal magnetic field (7.0 T) allows an efficient averaging of the ^{31}P chemical shift anisotropy using MAS spinning frequencies of 10−15 kHz with a large amount of sample. Without the need of ^1H decoupling for this inorganic sample, these spinning frequencies make the rotary resonance condition of the POSTC7 sequence[19] ($\omega_{rf} = 7\omega_{rot}$) easy to achieve. In addition, the line widths of the ^{31}P individual resonances in the SnP_2O_7 sample are mainly due to a small distribution of chemical shift as evidenced from the 2D *J*-resolved experiment and, consequently, the 1D MAS and 2D MAS correlation spectra recorded using a higher magnetic field (9.4 T) did not show any significant increase of the spectral resolution.

Results and Discussion

The ^{31}P 1D MAS NMR spectra of SnP_2O_7 recorded at 3 and 10 kHz spinning frequencies are depicted in Figure 3. The center band of these spectra (isotropic chemical shift) shows a complex line shape that can be seen to contain more than 17 overlapping ^{31}P isotropic resonances, indicating the presence of at least 17 crystallographically different ^{31}P sites in the asymmetric unit of SnP_2O_7. In addition to these isotropic resonances, an intense spinning sideband pattern, reflecting the ^{31}P chemical shift anisotropy, is observed at low spinning frequency. The average ^{31}P chemical shift anisotropy, determined from the spinning sideband intensities,[25] is characteristic of the distorted PO_4 tetrahedra involved in P_2O_7 groups. In agreement with a previous electron diffraction study, these 1D MAS spectra clearly indicate the exclusion of the possibility of a cubic symmetry with $Pa\bar{3}$ space group, for which only 11 independent phosphorus sites are expected. The distinction between the 11 remaining possible space groups containing between 22 ($P2_13$) and 216 ($P1$) individual P sites is more difficult

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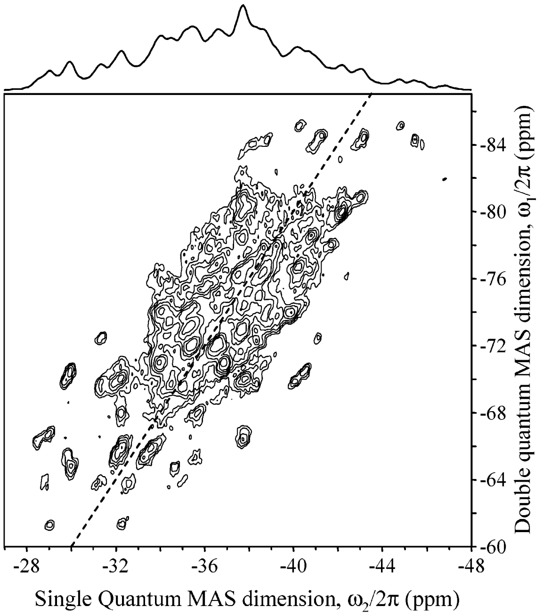

Figure 4. ^{31}P 2D through-space SQ−DQ MAS correlation spectrum of SnP_2O_7 obtained using the POSTC7[19] sequence and a spinning frequency of 10 kHz. The dashed line indicates the diagonal of the spectrum. The 1D MAS spectrum is shown above the 2D spectrum.

due to the large spectral overlap in this 1D MAS NMR spectrum. However, it should be mentioned that the integrated intensities of the resolved ^{31}P resonances located at about −28.9 and −46.8 ppm correspond to approximately 4 and 1% of the total integrated intensity, respectively. Assuming each P site gives rise to approximately the same intensity contribution to the overall envelope of peaks, this suggests the presence of a very large number of P sites in the asymmetric unit and a corresponding low space group symmetry. However, additional experimental information is needed before excluding any of the possible space groups.

As well as the number of individual ^{31}P sites, the number of unique P_2O_7 groups in the asymmetric unit can be used for space group assignment. To characterize the number of unique P_2O_7 groups in the SnP_2O_7 structure, we have used the ^{31}P 2D through-space SQ−DQ correlation MAS NMR experiment. In this experiment, the coherence transfer between coupled nuclei is driven by the $^{31}P-^{31}P$ through-space dipolar interactions leading to the observation of nearest-neighbor spatial proximities. In inorganic pyrophosphates, the intra-P_2O_7 phosphorus−phosphorus interatomic distances are typically 0.3 nm while the inter-P_2O_7 P−P distances are in the range 0.4−0.5 nm. The use of short double-quantum excitation and reconversion periods allows one to differentiate intra-P_2O_7 dipolar coupling and weaker long-range inter-P_2O_7 dipolar interactions and thus to identify the P−O−P connectivity scheme. This has been previously shown in the case of TiP_2O_7,[13] ZrP_2O_7,[14] and other crystalline pyrophosphates.[26,27] The ^{31}P 2D through-space correlation MAS spectrum of SnP_2O_7 obtained using the POSTC7[19] sequence is shown in Figure 4. In this SQ−DQ correlation spectrum, the resonances of two coupled phosphorus atoms occur at a common double-quantum frequency in the ω_1 indirect dimension and are correlated with the single-quantum frequency of each peak in the ω_2 dimension. This leads to the resolution of at least 27 pairs of cross-correlation peaks with various intensities that almost completely overlap in the 1D MAS spectrum. While a large number of these correlation peaks would likely be attributed to the through-space intra-P_2O_7 dipolar connectivities, the presence of additional inter-P_2O_7 longer range dipolar interactions makes the determination of the number of P_2O_7 units in the structure difficult. In this complex case, the observation of the inter-P_2O_7 correlation peaks that reflect the spatial proximity of the different P_2O_7 units damages the spectral resolution of the through-space correlation spectrum. Nevertheless, at least 38 of the 54 resolved resonances (27 pairs) show significantly different ^{31}P isotropic chemical shifts in the single-quantum dimension of the 2D spectrum. This suggests that the asymmetric unit contains at least 38 crystallographically different P sites, ruling out the space groups with <38 independent P sites.

A more convenient approach to determine the through-bond P−O−P connectivities and the number of distinct P_2O_7 groups in the structure would be to use the through-bond scalar *J* coupling, as routinely done in liquid-state NMR spectroscopy. In rigid solids, the isotropic *J*-coupling is usually much smaller than the dipolar interactions and the chemical shift anisotropy. Nevertheless, ^{31}P, ^{13}C, or ^{29}Si homonuclear though-bond correlation spectra have already been obtained in solids,[12,13,20,28,29] and recently, we have shown that the refocused-INADEQUATE experiment allows an unambiguous determination of the through-bond P−O−P connectivity scheme in crystalline and disordered phosphates.[30] The 2D ^{31}P through-bond SQ−DQ correlation MAS spectrum of SnP_2O_7, obtained using the refocused INADEQUATE sequence,[20] is depicted in Figure 5. It clearly shows a spectacular gain in resolution relative to the 1D MAS and 2D through-space dipolar correlation spectra. This 2D spectrum exhibits 46 different pairs of resolved cross-correlation peaks that reflect the through-bond intra-P_2O_7 connectivity. In addition, 3 of the 46 paired correlation peaks display an asymmetric line shape, suggesting the presence of at least two overlapping contributions. To reduce the number of fitting parameters, the experimental SQ−DQ correlation spectrum was sheared along the ω_1 dimension to obtain a symmetric SQ−SQ correlation spectrum with two equivalent dimensions.[21] As shown in Figure 6, a good fit of the experimental refocused INADEQUATE spectrum was obtained with 98 distinct ^{31}P resonances of nearly Lorentzian shape (30% Gaussian admixture) corresponding to 49 P_2O_7 units with two inequivalent P sites. Consequently, all the space groups with <98 independent P sites can be excluded. In the 2D spectrum, the line widths of the individual ^{31}P resonances range between 55 and 90 Hz, suggesting that the broader lines of higher intensity could result from additional peak overlaps. It should be noted that the

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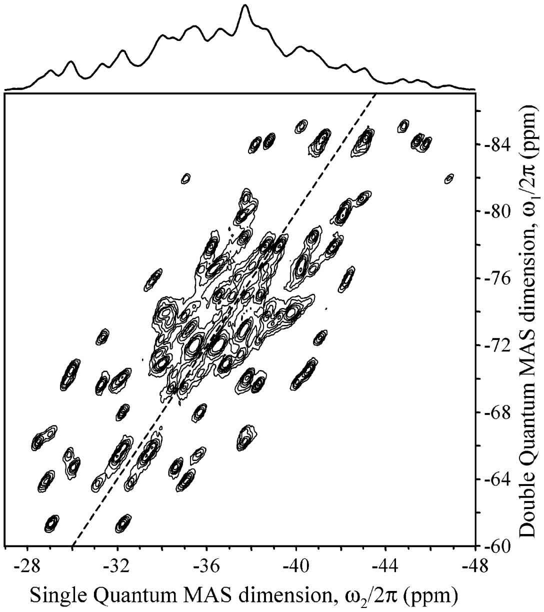

Figure 5. ^{31}P 2D through-bond SQ−DQ MAS correlation spectrum of SnP_2O_7 obtained at 10 kHz spinning frequency using the refocused INADEQUATE[20] experiment. The dashed line indicates the diagonal of the spectrum. The 1D MAS spectrum is shown above the 2D spectrum.

isotropic $^2J(^{31}P-^{31}P)$ coupling (that drives the coherence transfer in the refocused INADEQUATE experiment) is significantly smaller than these line widths and is not resolved as a doublet in the 2D spectrum. Evidence for this coupling can be clearly shown by the 2D *J*-resolved experiment,[21,22] which has been previously used to measure weak ^2J(P−P) couplings in metal phosphine complexes. [29,31] The 2D *J*-resolved MAS spectrum of SnP_2O_7 is shown in Figure 7. In this 2D map, the conventional MAS spectrum is retained along the ω_2 dimension while the homonuclear *J* couplings between two ^{31}P nuclei appear along the ω_1 dimension. In the ω_1 dimension, the line width is about 7 Hz, allowing the clear resolution of the characteristic doublet due to the weak ^2J(P−P) coupling and showing that the line width of the individual resonance in MAS spectra is mainly due to a small distribution of chemical shift. From the observed splittings, the intra-P_2O_7 ^2J(P−P) coupling constants are estimated to range between 16 and 19.5 Hz, similar to the values measured in SiP_2O_7[12] and TiP_2O_7[13] using the TOBSY[32] experiment.

As mentioned above, the refocused INADEQUATE spectrum of SnP_2O_7 reveals the presence of at least 49 P_2O_7 units with two inequivalent P sites in the asymmetric unit, allowing all the space groups with <98 independent P sites to be ruled out. Only four space groups of lower symmetry remain possible: $P2_1$, Pc, $P\bar{1}$, for which 108 crystallographically distinct P sites in general positions are expected, and $P1$, which gives rise to 216 different phosphorus sites in general positions. For $P2_1$, Pc, and $P1$ space groups, no linear P_2O_7 units are required by symmetry, while for $P\bar{1}$, four linear P_2O_7 units with two equivalent P sites (related by a center of inversion) are expected.[2] Such linear P_2O_7 groups with two magnetically equivalent ^{31}P nuclei are not observable in the refocused INADEQUATE spectrum, but they should give rise to diagonal autocorrelation peaks in a through-space dipolar correlation spectrum, as previously observed in the case of ZrP_2O_7.[14] Such autocorrelation peaks were not clearly evidenced in the 2D through-space dipolar correlation spectrum of SnP_2O_7 (Figure 4), making the possibility of space group $P\bar{1}$ unlikely. Before one of the remaining possibilities is adopted, the relative intensities of the 98 distinct resonances should be determined. The quantitative 1D MAS spectrum (10 kHz spinning frequency) was thus fitted with the 49 pairs of coupled resonances determined from the 2D refocused INADEQUATE spectrum. The position and line width of each resonance were fixed and only the intensity was allowed to vary. A reasonable fit of the experimental 1D MAS spectrum (not shown) was obtained with 90 peaks of relative intensities in the range 0.85−1.15, 6 peaks of relative intensities in the range 1.9−2.1, and 2 peaks of relative intensities 3.0. These higher intensity peaks correspond to the strong ones in the 2D refocused INADEQUATE spectrum and

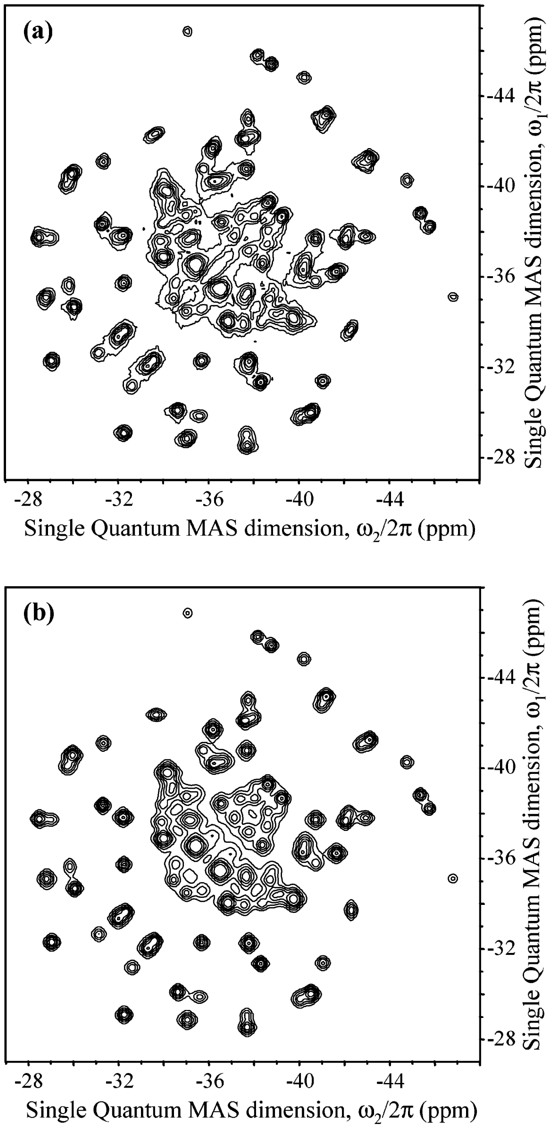

Figure 6. (a) Sheared[21] and symmetrized experimental ^{31}P 2D refocused INADEQUATE spectrum of SnP_2O_7 and (b) its simulation with 98 distinct ^{31}P resonances corresponding to at least 49 P_2O_7 units with two inequivalent P sites.

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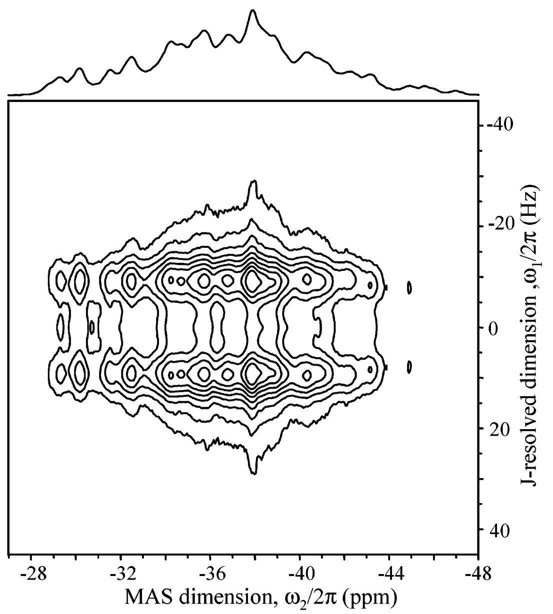

Figure 7. ^{31}P 2D *J*-resolved MAS spectrum of SnP_2O_7 recorded at 15 kHz spinning frequency using a *z*-filtered spin—echo[22] sequence. The 1D MAS spectrum is shown above the 2D spectrum.

are attributed to the presence of several overlapping contributions having very similar frequencies in both the single-quantum and the double-quantum dimensions. Within experimental error, this is consistent with the space groups $P2_1$ and Pc, for which 108 crystallographically inequivalent P sites are expected. These relative intensities would also be in agreement with space group $P1$, but this would correspond to a significantly higher degree of spectral overlap in the refocused INADEQUATE spectrum. These results thus suggest that the room-temperature structure of SnP_2O_7 is monoclinic with $P2_1$ or Pc symmetry. The resolution of the experimental X-ray diffraction powder pattern of SnP_2O_7 does not allow one to distinguish between these two possibilities since the three cell parameters are almost equal and Pawley fits[33] of the X-ray diffraction data using $P2_1$ or Pc space groups give very similar reliability factors (Rwp) of 3.19% and 3.23%, respectively.

Conclusion

In this study, we have examined the room-temperature structure of SnP_2O_7 using various solid-state magic-angle spinning NMR experiments. We show that the use of ^{31}P homonuclear through-bond and through-space correlation NMR spectroscopy allows discrimination between the 12 possible space group symmetries of the structure. In particular, the ^{31}P 2D refocused INADEQUATE experiment provides evidence of an impressive number of distinct ^{31}P resonances and shows that the asymmetric unit contains at least 49 different P_2O_7 groups corresponding to 98 independent P sites, some of which contain accidental degeneracies. These results suggest that the true symmetry of the SnP_2O_7 room-temperature structure is monoclinic with space group $P2_1$ or Pc.

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Supporting Information Available: Table of the ^{31}P isotropic chemical shifts, line widths and relative cross-correlation peak intensities of the 98 distinct resonances obtained from the simulation of the 2D refocused INADEQUATE spectrum of SnP_2O_7 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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