# A solid state <sup>31</sup>P NMR study of the synthesis of phosphorus sulfides from PCI<sub>3</sub> and H<sub>2</sub>S in microporous materials<sup>1</sup>

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**Abstract**: The interaction and reaction of  $PCl_3$  and  $PCl_3$ -H<sub>2</sub>S mixtures with the microporous materials Silicalite, ALPO-5, NaY, NaX, and NaA have been investigated, with the intention of producing phosphorus sulfide clusters in the pores. A rich chemistry was observed and monitored by solid state <sup>31</sup>P NMR. The presence of P<sub>4</sub>S<sub>3</sub>,  $\alpha$ -P<sub>4</sub>S<sub>5</sub>,  $\beta$ -P<sub>4</sub>S<sub>6</sub>, and P<sub>4</sub>S<sub>7</sub> inside the NaY  $\alpha$ -cages was demonstrated, as well as a new species that is possibly a third geometric isomer of P<sub>4</sub>S<sub>4</sub> with C<sub>3v</sub> symmetry. <sup>129</sup>Xe NMR showed the exclusion of Xe from the micropores by the phosphorus sulfides. Sulfides lower than P<sub>4</sub>S<sub>7</sub> are small enough that they undergo rapid pseudo-isotropic reorientation inside the NaY  $\alpha$ -cage.

Key words: phosphorus sulfides, intrazeolitic cluster synthesis.

**Résumé** : On a étudié l'interaction et la réaction du PCl<sub>3</sub> et de mélanges de PCl<sub>3</sub>–H<sub>2</sub>S avec de materiaux microporeux, comme Silicalite, ALPO-5, NaY, NaX et NaA, dans le but de produire des agrégats de sulfures phosphoreux dans les pores. On a observé une chimie intéressante qui a été observée par RMN du <sup>31</sup>P à l'état solide. Dans les cages- $\alpha$  de NaY, on a mis en évidence la présence de P<sub>4</sub>S<sub>3</sub>,  $\alpha$ -P<sub>4</sub>S<sub>5</sub>,  $\beta$ -P<sub>4</sub>S<sub>6</sub> et P<sub>4</sub>S<sub>7</sub> ainsi qu'une nouvelle espèce qui pourrait être un troisième isomère géométrique du P<sub>4</sub>S<sub>4</sub> de symétrie C<sub>3v</sub>. La RMN du <sup>129</sup>Xe montre qu'il y a exclusion du Xe des micropores par les sulfures phosphoreux. Les sulfures de formules inférieures à P<sub>4</sub>S<sub>7</sub> sont suffisamment petits pour subir une réorientation pseudoisotropique à l'intérieur de la cage- $\alpha$  de NaY.

Mots clés : sulfures phosphoreux, synthèse d'agrégat intrazéolitique.

[Traduit par la Rédaction]

# Introduction

The chemistry of the phosphorus–sulfur system is well known, having been extensively studied by crystallographic methods, NMR spectroscopy, and vibrational spectroscopy. A large number of molecules, all based on expansions of the P<sub>4</sub> tetrahedron of elemental white phosphorus, is now established and includes  $P_4S_n$  (n = 3-10) (1, 2). In mixtures of phosphorus and sulfur that contain between 0 and 25 at.% P, glassy materials are formed (3–5). These glasses are particularly attractive to the material sciences due to their optical and electrical properties, particularly their infrared transmitting properties (6).

The renewed interest in the study of phosphorus sulfides is based on the recent developments in solid state NMR allowing increased spectroscopic resolution of both ordered crystalline compounds and disordered systems such as the glasses (7). This permits the identification of chemical environments via chemical shift ranges and provides valuable

Received February 19, 1998.

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information on the short-range order of these potentially useful materials. Currently there is also much interest in nano-clusters with properties much modified from those in the bulk material, and also for nonlinear optical and semiconductor properties. To this end zeolites and other microporous solids are being used as minireactors and templates to grow size-restricted clusters and to produce periodic arrays of clusters or nano-wires (8, 9).

With this in mind and also with a longer term interest in studying clusters and unusual entrapped species, we attempted to synthesize phosphorus–sulfur compounds within the cavities of zeolites and other microporous materials, and used <sup>31</sup>P NMR to characterize the species involved. <sup>31</sup>P NMR is perhaps the most useful tool for studying phosphorus species within zeolites, since many other techniques are hampered to some extent by the nature of the system, e.g., Raman spectroscopy suffers from problems with fluorescence, IR has problems with strong overlapping vibrational modes of the lattice, X-ray diffraction has problems with disorder, EXAFS is not so useful where numerous sites are involved. Here we describe the results of exploratory experiments on PCl<sub>3</sub> in microporous materials and its reactions with H<sub>2</sub>S, focussing particularly on the behaviour with NaY zeolite.

## **Experimental**

Silicalite (UOP), zeolites NaY (LZY-52, Linde), NaX (13X, Linde), NaA (Linde 4A), and aluminophosphate ALPO-5 (a gift of S. Zones, Chevron) were dehydrated

<sup>&</sup>lt;sup>1</sup>Published as NRCC No. 40997.

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Lee et al.

**Fig. 1.** <sup>31</sup>P NMR of PCl<sub>3</sub> in Silicalite. (*a*) Static spectrum showing chemical shift anisotropy powder pattern for PCl<sub>3</sub>. The signal in the vicinity of 3 ppm is probably POCl<sub>3</sub> and other P/O/Cl species. (*b*) MAS spectrum of a sample with twice the loading of PCl<sub>3</sub>,  $v_r = 2.0$  kHz.



under vacuum, at progressively higher temperatures up to 450°C. All the preparative steps were carried out on a vacuum line and great care was taken to exclude all water. Measured quantities of degassed PCl<sub>3</sub> (liquid) were then condensed into these materials from a side arm and sealed in 5 mm o.d. tubes, allowing 4PCl<sub>3</sub> per  $\alpha$ -cage for X, Y, and A. The reactions with H<sub>2</sub>S were carried out "in situ" after first condensing (at liquid nitrogen temperature) a known quantity of the gas onto samples of the microporous materials with PCl<sub>3</sub> already adsorbed (reactant ratio range used:  $PCl_3:H_2S = 4:3-4:10$ ). These samples, in 5 mm o.d. tubes, were then sealed and annealed at various temperatures from 76 to 164°C. One sample was sealed after admitting a small amount of xenon gas. Solid state NMR spectra were recorded on a Bruker MSL 200 spectrometer operating at 80.962 MHz for <sup>31</sup>P and 55.321 MHz for <sup>129</sup>Xe, using a Chemagnetics magic angle spinning (MAS) pencil probe, both static and with spinning rates of 1.9-4.5 kHz. The glass sample tubes were inserted into the zirconia pencil rotors and held in place by Teflon spacer rings. Spectra were acquired using single pulses (90° pulse length 2.8-3.0 µs) with quadrature phase cycling. Positions of isotropic shifts were determined, when necessary, from MAS spectra obtained at different spinning rates. <sup>31</sup>P spectra were referenced to 85%  $H_3PO_4$  and typically required 80 scans with recycle times of up to 100 s. The <sup>129</sup>Xe spectra were referenced to Xe gas at zero pressure.

# **Results and discussion**

With the exception of a short note on <sup>129</sup>Xe, all the following discussion focusses on <sup>31</sup>P NMR results (Figs. 1–6, **Fig. 2.** <sup>31</sup>P NMR MAS spectrum of PCl<sub>3</sub> with NaY,  $v_r = 4.5$  kHz. Residual molecular PCl<sub>3</sub> shows at 220 ppm. Stars indicate spinning side bands of the line tentatively assigned to framework-attached SiOPCl<sub>2</sub>.



8), which show a rich chemistry for phosphorus compounds inside zeolites. Most reactions seem to produce several products and it is a major problem to identify all of the species present. It is convenient to describe results first for the simpler systems with only  $PCl_3$  and then with the addition of  $H_2S$ .

#### (a) PCl<sub>3</sub> with microporous materials

PCl<sub>3</sub> is a liquid (mp –93.6°C) with a <sup>31</sup>P NMR chemical shift of 219 ppm (10). When introduced into Silicalite the spectra, Fig. 1, clearly show that the PCl<sub>3</sub> remains intact. However, the line indicates only a single type of PCl<sub>3</sub>, with a small chemical shift anisotropy:  $\delta_{iso} = 220 \pm 0.4$ ,  $\delta_{11,22} = 227.8 \pm 1.0$ ,  $\delta_{33} = 204.3 \pm 1.0$ , axially symmetric within error, and there is no trace of any sharp liquid line. This anisotropy can only mean that the molecule is adsorbed in the Silicalite channels or on the surface. At the loading levels used there is not enough surface area to accommodate all the PCl<sub>3</sub> and consequently one must conclude that the signal most likely arises from molecules in the channels. Similar behaviour was observed with ALPO-5, which has one-dimensional channels.

With activated NaY and NaX the spectra initially show mainly the PCl<sub>3</sub> resonance, but with time this is very much reduced, Fig. 2, and is replaced by rather broad MAS lines with several spinning side bands that indicate considerable anisotropy. The isotropic shifts, which are at about 180-183 ppm for NaY and 153–156 ppm for NaX, can possibly be assigned to Si-O-PCl<sub>2</sub> and (Si-O-)<sub>2</sub>PCl species (10, 11); the former were recently observed at 184 ppm in studies of PCl<sub>3</sub> reacting with a silica surface (10), and the latter suggested assignment of a line at 156 ppm observed by Bogatyrev et al. (11), though, ideally, further substantiation of these assignments is desirable. The presence of these chemically attached species would imply the production of NaCl (and perhaps a little HCl by reaction with any residual OH groups on the framework). Unfortunately the spectra are not good enough to determine the chemical shift anisotropies.

**Fig. 3.** <sup>31</sup>P NMR spectra of NaY with PCl<sub>3</sub>–H<sub>2</sub>S in a 4:3 ratio after heating to 76°C. (*a*) Static; (*b*) MAS,  $v_r = 3.05$  kHz; (*c*) 10× expansion of (*b*).



**Fig. 4.** <sup>31</sup>P NMR spectra of NaY with PCl<sub>3</sub>–H<sub>2</sub>S in a 4:3 ratio after heating to 100°C. (*a*) MAS,  $v_r = 2.0$  kHz; (*b*) MAS,  $v_r = 2.9$  kHz, 5 days after (*a*). Isotropic peaks of identified species are indicated by  $\bigcirc$ , P<sub>4</sub>S<sub>3</sub>;  $\diamondsuit$ , α-P<sub>4</sub>S<sub>5</sub>;  $\Box$ , β-P<sub>4</sub>S<sub>6</sub>.



These materials also show a line in the 1.8-4.6 ppm range, which is weak in Silicalite (Fig. 1) and stronger in NaY (Fig. 2). One possible source of tis line could be POCl<sub>3</sub>, a

**Fig. 5.** <sup>31</sup>P NMR spectra of NaY with PCl<sub>3</sub>–H<sub>2</sub>S in a 4:5 ratio after heating to 100°C. (*a*) Static; (*b*) MAS,  $v_r = 1.95$  kHz; (*c*) MAS,  $v_r = 3.02$  kHz, 18 days after (*a*, *b*). In (*c*) the spectrum of P<sub>4</sub>S<sub>7</sub> predominates and P<sub>4</sub>S<sub>3</sub> lines are much reduced. Isotropic peaks of identified species are indicated by  $\bigcirc$ , P<sub>4</sub>S<sub>3</sub>;  $\diamondsuit$ ,  $\alpha$ -P<sub>4</sub>S<sub>5</sub>;  $\square$ ,  $\beta$ -P<sub>4</sub>S<sub>6</sub>. The two P<sub>4</sub>S<sub>7</sub> lines are indicated by  $\times = P_3, P_4$ ;  $\blacksquare = P_2, P_1$ . Double symbols indicate the isotropic shift.



common impurity in PCl<sub>3</sub> (less than 1%), which in the liquid state has a shift of 3 ppm (10). However, the intensity of the line in the NaY spectrum cannot be explained by POCl<sub>3</sub> alone, and a more likely alternative with a shift in the same range would be some other P/O/Cl or phosphorus oxy compound produced by reaction of the PCl<sub>3</sub> with any residual - OH groups or defect sites in the framework.

#### (b) PCl<sub>3</sub> and H<sub>2</sub>S within microporous materials

The main phosphorus species observed in the cases of Silicalite (with a  $4PCl_3:3H_2S$  ratio, annealed at  $76^{\circ}C$ ) and ALPO-5 (with a  $4PCl_3:5H_2S$  ratio, annealed at  $80^{\circ}C$ ) was absorbed but unreacted PCl<sub>3</sub>. In the case of Silicalite when annealed at  $170^{\circ}C$ , the main signal was still PCl<sub>3</sub> but several other small signals appeared, at 3.6 and 85 ppm (broad), and 48 and 55 ppm (sharp), which we have not been able to assign with any certainty.

In the reactions combining PCl<sub>3</sub> and H<sub>2</sub>S (in ratios of 4:3, 4:5, and 4:10) with NaY we observe that in samples heated only to 76°C (Fig. 3), PCl<sub>3</sub> remains prominent in the spectra, and there is a trace of the Si-O-PCl<sub>2</sub> species and a strong unidentified broad signal or signals underlying the whole

**Fig. 6.** <sup>31</sup>P NMR spectra of NaY with PCl<sub>3</sub>–H<sub>2</sub>S in a 4:10 ratio after heating to 164°C. (*a*) Static; (*b*) MAS,  $v_r = 2.95$  kHz. Isotropic peaks of identified species are indicated by  $\bigcirc$ , P<sub>4</sub>S<sub>3</sub>;  $\diamondsuit$ ,  $\alpha$ -P<sub>4</sub>S<sub>5</sub>;  $\square$ ,  $\beta$ -P<sub>4</sub>S<sub>6</sub>;  $\blacksquare$ , new species.



spectrum. Heating to 100°C or higher, however, initiates a complex series of reactions, and the spectra show virtually no PCl<sub>3</sub> and numerous new species (Figs. 4-6), which turn out to be phosphorus sulfides, as anticipated, Fig. 7. Assignments were made by comparison with known chemical shift ranges from numerous previous studies of phosphorus sulfides in solution, the melt, and the solid state, summarized in Table 1. In the early stages a major identifiable component is  $P_4S_3$ , with smaller quantities of  $\alpha$ - $P_4S_5$  and  $\beta$ - $P_4S_6$ . Again there are other unidentified species, which in some of the preparations have considerable intensity and large chemical shift anisotropies. The 4PCl<sub>3</sub>:5H<sub>2</sub>S preparation was monitored for some time after heating, and the lines of P<sub>4</sub>S<sub>3</sub> were observed to diminish while those of  $P_4S_7$  grew, Fig. 5c. The structures of the phosphorus sulfides identified are shown in Fig. 7.

A preparation of  $4PCl_3:3H_2S$  with NaX zeolite showed none of the sharp phosphorus sulfide lines observed for the NaY samples. The MAS spectra showed a very broad, intense spectrum centred around 108 ppm with rather broad spinning side bands superimposed, and several sharp lines between 30 and -12 ppm, with the strongest at 2 ppm. The broader features could conceivably be phosphorus sulfides and the sharp features P/O/Cl species. The different behaviour of NaX compared to NaY is noteworthy, but any discussion of this is necessarily speculative due to the lack of any firm assignments in the NaX spectra. The higher cation content of NaX, however, means that there is also a higher Al content in the framework, and as a consequence of this there will likely be more defects where different reactions with PCl<sub>3</sub>-H<sub>2</sub>S and their products could occur.

A reaction with NaA with a  $4PCl_3:7H_2S$  ratio, annealed at  $80^{\circ}C$ , was carried out with the notion that the much smaller

Fig. 7. Molecular structures of  $P_4S_3$ ,  $\alpha$ - $P_4S_5$ ,  $\beta$ - $P_4S_6$ , and  $P_4S_7$  (small atoms represent P).



window into the NaA large cage would prevent access even to  $PCl_3$ . The spectrum showed principally  $P_4S_7$ , again with many spinning side bands, with some  $P_4S_3$ , represented by two single lines, Fig. 8*c*. This was one of the cleanest spectra with only a trace of any other species (a broad line with several spinning side bands).

We now proceed to a detailed discussion of the evidence for the phosphorus sulfide assignments, and whether these molecules are located inside or outside the zeolites:

 $P_4S_3$ 

 $P_4S_3$  is a globular cage molecule (Fig. 7) consisting of a triangle of three basal P<sub>b</sub> atoms each linked via an S atom to a single apical P<sub>a</sub> atom. The two sharp lines, which are seen in many of the current spectra at  $82 \pm 2$  and  $-101 \pm 2$  ppm in a roughly 1:3 intensity ratio, may be assigned confidently to  $P_a$  and  $P_b$ , respectively. The low-frequency resonance is a unique characteristic of  $P_4S_3$  that distinguishes it from the other phosphorus sulfides. There have been numerous previous studies of  $P_4S_3$  in solution (12) and the solid state(13–18). In various solvents the P<sub>a</sub> shift is in the range 62–79 ppm and the  $P_b$  shift is from -100 to -135 ppm (12), whereas the most recent studies of the solid give shifts of 91.0/84.5 and -87.5 ppm for the room temperature  $\beta$ -phase (13). (Note, in the solid, P<sub>a</sub> appears as two lines due to crystallographically inequivalent molecules.) Clearly there is considerable variation depending on the environment, and our results fall well in the middle of the respective shift ranges.

What is most striking about the  $P_4S_3$  resonances seen in the spectra with NaY zeolite is that the lines are isotropic, since they display no spinning side bands under MAS and remain quite sharp and featureless when static. On its own this isotropic behaviour might be taken as evidence for  $P_4S_3$ being inside the  $\alpha$ -cages: Within the Y zeolite  $\alpha$ -cage a single  $P_4S_3$  molecule would have considerable rotational freedom, and since the cage has elements of  $T_d$  symmetry the dynamic averaging of the chemical shift tensor (arising from pseudo-isotropic reorientation of the molecule) would produce an isotropic line. This is in marked contrast to the room temperature crystalline  $\beta$ -phase, which shows rather large chemical shift anisotropies of several hundred ppm (13).

	Equivalent P	Shift ranges	Shifts in NaY	
Compound	atoms <sup>b</sup>	(ppm)	(ppm) <sup>c</sup>	Refs.
$\overline{P_4S_3}$	1	62–91	81.9 ± 1	12–18
	3	(-87)-(-135)	$-101 \pm 2$	
$\alpha - P_4 S_4$	4	201.9		26
$\beta P_4 S_4$	2	205-207.5		2, 26
	1	174.7-185.8		
	1	85.7–97		
$\alpha$ -P <sub>4</sub> S <sub>5</sub>	1	231.7-237.4	$229.6 \pm 1$	2, 13, 22
	1,1	111.4–139.8	$123.8 \pm 6$	
	1	89.6-120.2	98 ± 3	
$\beta P_4 S_5$	2	129.8-142.3		2, 27
	2	80.1-87.2		
$\alpha$ -P <sub>4</sub> S <sub>6</sub>	1	132.3-133.5		2
	1	114.9-115.8		
	1,1	54.9-65.7		
$\beta P_4 S_6$	1	198.9-206.7	$200 \pm 1$	2
	2	178.2–184.8	$178.2 \pm 1$	
	1	55.7-61.0	$59.6 \pm 1$	
$P_4S_7$	2	109.5-113	$110.4 \pm 0.5$	2, 13–15, 22, 23
	2	81.9–98	$97.7 \pm 0.5$	
$P_4S_8$	2	135.4		28
	2	13.4		
$P_4S_9$	1	57.9-67.5		13, 15, 25
	3	57.8-63.6		
$P_4S_{10}$	4	49.7-60.1		13, 15 25

Table 1. Ranges of reported  ${}^{31}$ P NMR isotropic shifts for phosphorus sulfides compared with observed lines for the same in NaY.<sup>*a*</sup>

"Shift ranges from reported values in solution, melt, and solid phases.  $\alpha$ 's and  $\beta$ 's in this instance refer to different molecular structural isomers (not different crystal phases).

<sup>b</sup>Distinct P atoms in isolated molecule.

<sup>c</sup>This work.

Similar anisotropies were also obtained from studies of  $P_4S_3$ dissolved in a nematic phase (19). However, there is a second plausible explanation: Crystalline P<sub>4</sub>S<sub>3</sub> is known to have a plastic phase (16, 18, 20, 21), where the molecule sits on specific lattice sites but reorients rapidly and thus gives rise to an isotropic NMR spectrum. Although the room temperature  $\beta$ -phase transforms to the plastic  $\alpha$ -phase at 313.7 K, the  $\alpha$ -phase can be supercooled to a lower limit of 259 K (20). However, it does not always have to be cooled this far down to transform back to the  $\beta$ -phase; for example in a  $T_1$  study the material supercooled by about 35 degrees (21), though in a MAS study the supercooled state was only observed for a few minutes before it reconverted to the  $\beta$ -phase at ambient temperatures (18). Since the preparation of our zeolite / phosphorus sulfides all involved heating to 100°C or more, it is possible that the isotropic lines are from  $\alpha$ -crystalline P<sub>4</sub>S<sub>3</sub> outside the zeolite. Furthermore, resonances for the  $\alpha$ -phase have been reported at 72 and -113 ppm (16) and, more recently, at 80.1 and -104.0 ppm (18). The latter result is very close to our results for NaY. To distinguish between these two possibilities, two of the NaY reaction samples (4PCl<sub>3</sub>:5H<sub>2</sub>S and 4PCl<sub>3</sub>:10H<sub>2</sub>S) and the NaA reaction sample were cooled to 77 K for 10 min and then allowed to warm back to room temperature; the isotropic lines were unchanged, thus demonstrating unequivocally the presence of  $P_4S_3$  inside these zeolites.

# $\alpha$ -P<sub>4</sub>S<sub>5</sub> and $\beta$ -P<sub>4</sub>S<sub>6</sub>

The static NMR spectra also show series of weak, sharp lines with no chemical shift anisotropy, which we assign to  $\alpha$ -P<sub>4</sub>S<sub>5</sub> and  $\beta$ -P<sub>4</sub>S<sub>6</sub> in the zeolite  $\alpha$ -cage, see Figs. 4–6 and Table 1. The identification of three lines for  $\beta$ -P<sub>4</sub>S<sub>6</sub> is reasonably certain; the lines are in the correct shift regions (Table 1) and in the correct intensity ratio of 1:2:1 (2). The assignment of  $\alpha$ -P<sub>4</sub>S<sub>5</sub> must rely mainly on the unique highfrequency shift at 230 ppm (2, 13, 22), as the other expected resonances are partly obscured by other lines. Plastic (rotator) phases for  $\alpha\text{-}P_4S_5$  and  $\beta\text{-}P_4S_6$  have not been reported and indeed, since both have a pendant S atom that makes these molecules much less globular than  $P_4S_3$  (see Fig. 7), one would not expect them to have plastic phases. Consequently, the argument for these two products being inside the  $\alpha$ -cages and undergoing rapid pseudo-isotropic reorientation is strong.

#### $P_4S_7$

The major product in the preparation of both NaY with  $4PCl_3:5H_2S$ , Fig. 8*a*, and NaA with  $4PCl_3:7H_2S$ , Fig. 8*c*, was  $P_4S_7$ , but this product is in two quite different states. The experiment with NaA produced crystalline  $\alpha$ -P<sub>4</sub>S<sub>7</sub>, which has four resolved peaks at 82, 96, 111.5, and 113 ppm (13, 23), whereas the spectrum of NaY/P<sub>4</sub>S<sub>7</sub> is definitely not that of the crystalline  $\alpha$ -form and the isotropic shifts at 110.4

**Fig. 8.** <sup>31</sup>P NMR MAS spectrum of  $P_4S_7$ . (*a*) NaY/PCl<sub>3</sub>/H<sub>2</sub>S preparation,  $v_r = 3.02$  kHz; (*b*)  $\alpha$ -crystalline preparation (no zeolite),  $v_r = 4.09$  kHz; (*c*) NaA/PCl<sub>3</sub>/H<sub>2</sub>S preparation,  $v_r = 4.03$  kHz. (*a*) and (*c*) both show isotropic  $P_4S_3$  lines and traces of broader underlying resonances. (Note that spectrum (*a*) is the same as in Fig. 5*c*).  $\times = P_3$ ,  $P_4$ ;  $\blacksquare = P_2$ ;  $\blacklozenge = P_1$ . In (*a*)  $P_1$ ,  $P_2$  overlap. Double symbols indicate the isotropic shift.



and 97.7 ppm are very similar to those observed for the amorphous form (measured by Bjorholm at 109.5 and 98 ppm (23)). In both spectra the lines show sizeable anisotropies. The molecular point group symmetry of the free  $P_4S_7$  molecule is  $C_{2v}$ . There are two distinct pairs of equivalent P atoms and hence one expects two <sup>31</sup>P NMR resonances for the  $C_{2v}$  molecule (aside from any *J* couplings). In the solid  $\alpha$ -phase of  $P_4S_7$ , however, the molecule is distorted because of a moderately strong and asymmetric interaction between two P atoms on one molecule and an S

**Table 2.** <sup>31</sup>P NMR isotropic shift and principal components of the apparent <sup>*a*</sup> chemical shift tensors obtained from MAS spectra for  $P_4S_7$  in NaY compared with crystalline  $\alpha$ - $P_4S_7$ .

Atom	$\delta_{iso}$	$\delta_{11}$	δ <sub>22</sub>	δ <sub>33</sub>
$P_{3.4}^{b}$	109.4	254	109	-36
$P_{1,2}^{b}$	97.8	158	92	44
$P_4^c$	113	271	124	-55
$P_3^c$	111.6	275	131	-72
$P_2^c$	96	187	85	20
		170	78	36
$P_1^c$	82	172	84	-6
		163	69	10

<sup>*a*</sup>The reader should note that these are not true chemical shift tensors, since direct and indirect coupling tensors are also involved (see ref. 13). In particular, the dipolar coupling between the directly bonded P atoms will be substantial.

<sup>b</sup>Data for P<sub>4</sub>S<sub>7</sub> in NaY (this work).

<sup>c</sup>Data for crystalline  $\alpha$ -P<sub>4</sub>S<sub>7</sub> (13). The double entries for P<sub>2</sub> and P<sub>1</sub> correspond to *J*-split components.

atom of another molecule, which makes all four P atoms inequivalent. This well-defined intermolecular interaction does not occur in the amorphous solid, which shows only two resonances, at shifts similar to those in the melt and solution. Likewise for a molecule isolated in the  $\alpha$ -cage of NaY, only two resonances would be expected.

Once again we are left with a choice between two equally plausible assignments for the NaY preparation: the amorphous solid outside the zeolite or isolated molecules inside the cages. Moreover, if the  $P_4S_7$  molecule is inside the cages, this time it cannot be undergoing rapid reorientations because the chemical shift anisotropy is not averaged. The principal components of the chemical shift anisotropies for both resonances of NaY– $P_4S_7$  were determined by spinning side-band analysis at various spinning speeds using the Herzfeld–Berger method (24), which is incorporated in the Bruker software, see Table 2. From the table we note that our results, which clearly would not be expected to be the same as for crystalline  $\alpha$ - $P_4S_7$  determined previously (13), nevertheless show anisotropies of similar span and skew. This rules out any question of dynamic averaging.

There are two main arguments that favour the existence of single molecules of  $P_4S_7$  inside the cages of NaY: (*a*) There is the circumstantial evidence of the precursors being inside the cages, and several of the smaller sulfides also being formed there. (*b*) The amorphous form of  $P_4S_7$  has only been formed previously by quenching the melt rapidly to 77 K (23), conditions quite remote from our preparation where the PCl<sub>3</sub> was sublimed into the zeolite and H<sub>2</sub>S gas was added separately before annealing at 100°C.

# P<sub>4</sub>S<sub>9</sub> and P<sub>4</sub>S<sub>10</sub>

Since  $P_4S_7$  appears to be static it is highly unlikely that we would see dynamic  $P_4S_9$  and  $P_4S_{10}$ , which enables us to exclude making any assignment of sharp lines in the 50– 60 ppm region to these species. Although their isotropic shifts fall in this region the static molecules have large chemical shift anisotropies (13, 15, 25).

## A new P<sub>4</sub>S<sub>4</sub> species in NaY ?

The 4PCl<sub>3</sub>:10H<sub>2</sub>S NaY preparation heated to 163°C shows three sharp lines in the static spectrum, at -126.3, 49, and 64 ppm, which do not appear for any of the other samples. Furthermore, when this material was reexamined after considerable aging, the  $P_4S_3$  lines and the 49 ppm line had diminished considerably, and the lines due to  $\alpha$ -P<sub>4</sub>S<sub>5</sub> and  $\beta$ -P<sub>4</sub>S<sub>6</sub> had disappeared completely, leaving a broad background centred around zero shift and more prominent lines at -126.3 and 64 ppm. The latter two lines occur in a roughly 3:1 ratio and appear to be associated with one species. The -126.3 ppm shift is very unusual, and does not appear to have been observed in the solid state before. The unique -101 ppm shift seen for P<sub>4</sub>S<sub>3</sub> arises from its ring of three P atoms, so we suspect that the -126.3 ppm line may also be due to a  $P_3$  ring, perhaps of a  $P_4S_3$  derivative with a pendant S on the unique P atom. In this case the shift of 64 ppm for the unique P is in the region expected for  $S_3P=S$ units. Such a P<sub>4</sub>S<sub>4</sub> molecule would be a new geometric isomer with  $C_{3V}$  symmetry, and it would still have room to undergo pseudo-isotropic reorientation inside the  $\alpha$ -cage. Why this new isomer would form in preference to the  $\alpha$  or  $\beta$ forms is debatable, but it is likely influenced by the zeolite framework. A P<sub>4</sub>S<sub>3</sub> molecule protonated on the unique P,  $P_4S_3H^+$ , is another possibility, though this has not been reported before and the S<sub>3</sub>PH<sup>+</sup> unit would not be expected to have a 64 ppm shift. A chloro derivative seems much less likely since H<sub>2</sub>S is in excess, and in fact it can be excluded, since we have observed the same two resonances in a preparation involving elemental P with H<sub>2</sub>S in NaY annealed at 420°C (work to be reported later). One final possibility is that these resonances are from  $P_4S_3$  in a second distinct kind of environment, though it is difficult to envisage where this might be.

#### <sup>129</sup>Xe NMR results

The characteristic chemical shift of <sup>129</sup>Xe in pure NaY samples arises from exchange of the Xe between the zeolite cavities and the gas phase. The observed shift is a population weighted average of the shifts in the two types of situation (a high-frequency shift inside, and a low-frequency shift outside). The shifts for similar amounts of Xe in pure NaY and in an NaY with  $4PCl_3:3H_2S$  reaction sample were 87.6 and 16.1 ppm, respectively. The much smaller shift of the Xe in the reaction sample indicates that the Xe is effectively excluded from the zeolite, implying that the cages are occupied by the phosphorus compounds. The 16.1 ppm shift, compared to that of the isolated Xe atom, indicates that the Xe is under significant pressure, the shift being caused by collisions with Xe atoms, the HCl reaction product, and any residual H<sub>2</sub>S.

#### **Molecular dimensions**

An important consideration regarding the encapsulation of the phosphorus sulfide molecules is whether they can fit inside the zeolite cage and, if so, whether they have room to rotate. All the dimensions in the following discussion take into account the van der Waals radii of the atoms (O = 1.4, P = 1.9, S = 1.85, and Cl = 1.8 Å (29)). NaY: The diameter of the Y zeolite  $\alpha$ -cage, without taking into account Na<sup>+</sup> cations, is 11.0 Å and the diameter of the 12-ring window is 7.4 Å (30, 31).

NaA: The diameter of the A zeolite  $\alpha$ -cage is 11.4 Å, and the diameter of the 8-ring window is only 4.1 Å (31, 32), excluding the Na<sup>+</sup> ions.

 $P_4S_3$ : The dimensions of  $P_4S_3$  show a maximum diameter of 7.5 Å, and the largest diameter perpendicular to the 3-fold axis is 7.24 Å (calculated from available structural data (20, 33)). Inside the large cages of both NaY and NaA it will have considerable room. This molecule should therefore be able to go easily through the 12-ring window of NaY, but it should not be able to get through the 8-ring window of NaA zeolite.

 $\alpha$ -P<sub>4</sub>S<sub>5</sub>: This is slightly smaller than  $\beta$ -P<sub>4</sub>S<sub>6</sub> with a largest dimension of 9.3 Å (calculated from the crystal structure (34)).

 $\beta$ -P<sub>4</sub>S<sub>6</sub>: This is basically a P<sub>4</sub>S<sub>7</sub> with one pendant S removed, so we have calculated its size based on the structural information for P<sub>4</sub>S<sub>7</sub> (see below). Its largest dimension is 9.4 Å, and from the NMR it would appear that this is still small enough to allow rapid reorientation in the NaY cage.

 $P_4S_7$ : The smallest dimension of  $P_4S_7$  (calculated from the crystal structure information (34–36)) is 7.7 Å and the largest is 10.2 Å.

One molecule of  $P_4S_7$  can therefore fit inside the cage without too much trouble, but it would be difficult to get through the window. This has several implications: (*a*) The particular interactions that distort the molecules in the  $\alpha$ phase should not be present. (*b*) If it is inside the cage the molecule must have formed in situ from smaller precursors. (*c*) Once formed inside, the molecules will remain trapped. When the presence of Na<sup>+</sup> ions is also considered together with the long dimension of the molecule it is highly likely that the  $P_4S_7$  will experience considerable hindrance to rotation, and hence the chemical shift anisotropy will not display the effects of dynamic averaging.

 $P_4S_9$  and  $P_4S_{10}$ : Isolated  $P_4S_{10}$  is a tetrahedral molecule. The largest dimension (between two pendant S atoms) is 10.24 Å, but if the molecule were rotating pseudo-isotropically its effective diameter would be 11.71 Å (calculated from the structural data (34, 35)).  $P_4S_9$  is structurally similar to  $P_4S_{10}$  but with one pendant S removed, hence its largest dimensions are virtually identical.

PCl<sub>3</sub>: PCl<sub>3</sub> is a pyramidal molecule with dimensions (*a*) along a P—Cl bond of 5.74 Å, (*b*) along a Cl—-Cl edge of 6.73 Å, and (*c*) for the pyramid height of 4.65 Å (calculated from microwave structural data (37)). It should therefore have easy access to the NaY  $\alpha$ -cage, and a tetrahedral cluster of four PCl<sub>3</sub> will just fit inside the cage. PCl<sub>3</sub> should not, however, be able to get through the window of the  $\alpha$ -cage of NaA.

#### Other components of the spectra

We will emphasize again that the picture is incomplete as there are signals that we have been unable to assign, in particular, the broad background of signals with large chemical shift anisotropies. The MAS lines of these signals are themselves broad, whereas most crystalline materials would be expected to show sharp MAS lines. The broadening could be due to intermediate rate dynamics but a much more likely explanation is that it is due to a distribution of species and (or) a distribution of environments for the same species.

We may be seeing impure and mixed P–S species outside the zeolite, and any species attached to the framework (inside or on the external surface) would also give broad lines with anisotropies.

#### Chemistry

The chemical complexity of these systems must now be quite apparent, so beyond a few obvious points our comments regarding reactions must necessarily be speculative:

1. A basic assumption is that any -SH will react with P– Cl bonds, provided the two are able to access each other, so if  $PCl_3$  is in excess all the -SH will be depleted and there may be P/S/Cl species present, and, vice versa, in reactions where H<sub>2</sub>S is in excess, any PCl species will disappear and there may be P/S/H species produced. The HCl by-product could itself influence further reactions.

2. We observed  $P_4S_3$  at the early stages after heating to 100°C or more, and that this is depleted as  $P_4S_7$  forms, suggesting a building of S onto the  $P_4S_3$  framework.

3. It was surprising to find  $P_4S_3$  inside NaA (demonstrated by the persistence of isotropic lines after cooling to 77 K). Since  $P_4S_3$  cannot get through the window of NaA it must be constructed inside the cage, and yet  $PCl_3$  is also too large to get through the window. This suggests some smaller precursor must first form at the zeolite surface and migrate into the cages, say, perhaps  $PCl_2^+$ .

4. An interesting feature of these experiments is that the zeolites seem to have a catalytic effect, enhancing the formation of the phosphorus sulfides. The thiosolvolysis reaction of PCl<sub>3</sub> in liquid H<sub>2</sub>S is known to produce some P<sub>4</sub>S<sub>7</sub> as part of a mixture after 60–70 h (38), while PCl<sub>3</sub> and H<sub>2</sub>S in the presence of base react to give P<sub>4</sub>S<sub>3</sub>, among other products (1, 39). We found, however, that a yellowish white solid produced after 4 days of reaction between PCl<sub>3</sub> and H<sub>2</sub>S in the absence of zeolite still showed mainly PCl<sub>3</sub> signals in the <sup>31</sup>P NMR (over 90% of the "observable" phosphorus), and no P<sub>4</sub>S<sub>7</sub> was detected in this solid even after 3 months. The ionic nature of NaY and NaA and their microporosity probably play important roles in orchestrating the chemistry.

## Conclusions

We have clear evidence for the formation of phosphorus sulfides inside the micropores; however, the chemistry is rather complicated. Moreover, with the numerous different products present, the goal of producing a regular array of identical molecules using the zeolite framework has not been realized. However, the results point the way: Perhaps this might be achievable by starting with pure  $P_4S_3$  instead of PCl<sub>3</sub>.

# Acknowledgment

The authors would like to thank J. Bennett for expert technical assistance with the NMR instrumentation, and S. Zones for the kind donation of the ALPO-5.

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