Electronic supplementary information for:

NMR Crystallography of Sodium Diphosphates: Combining Dipolar, Shielding, Quadrupolar, Diffraction, and Computational Information.

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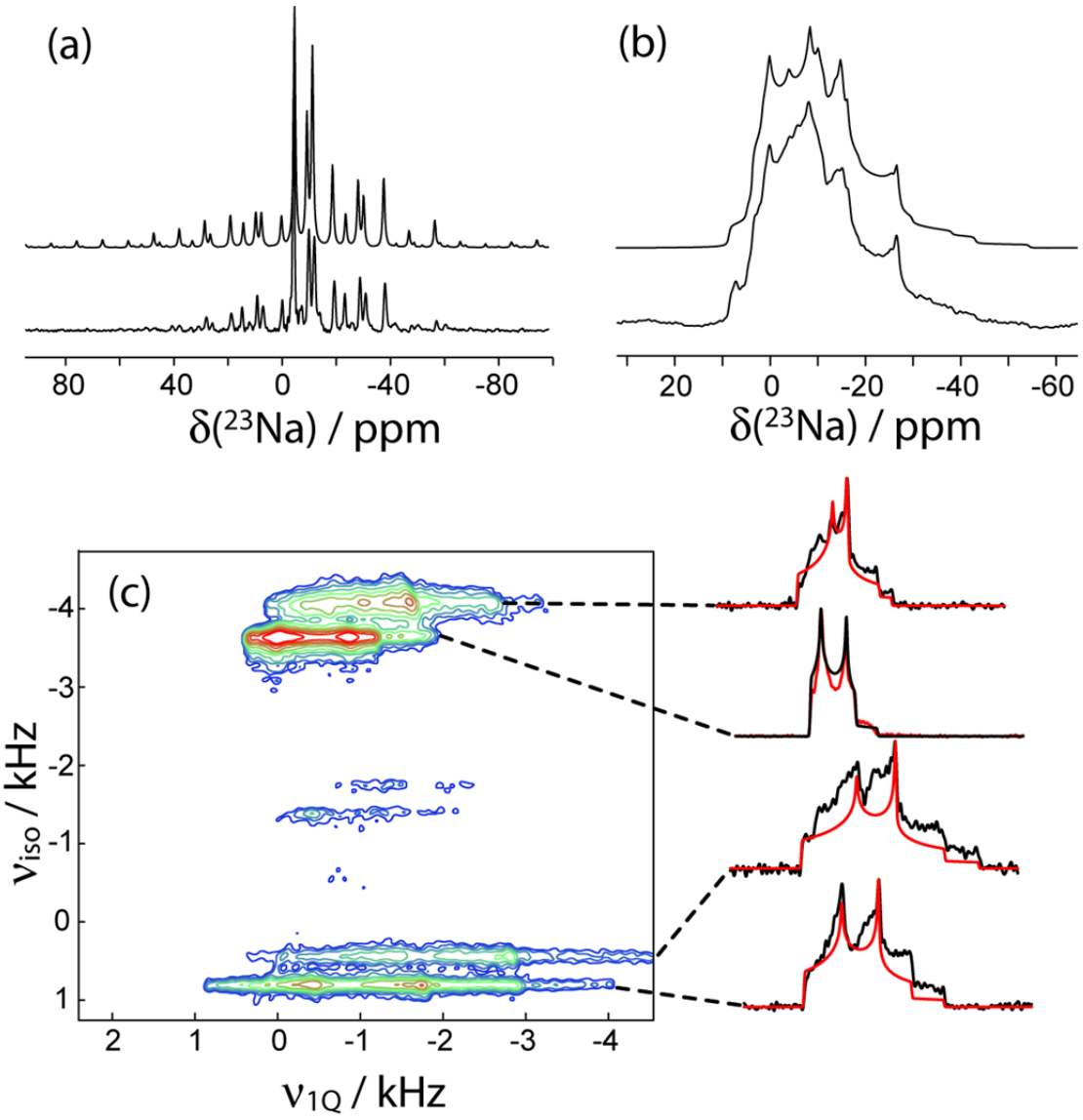

Figure S1. The ^{23}Na NMR spectra of $Na_4P_2O_7$. In (a), the DOR NMR spectrum and its simulation are shown and, similarly, the MAS NMR spectrum is shown in (b). The MQMAS NMR spectrum is shown in (c) where simulations of the anisotropic slices are shown. All spectra were simulated using the known ^{23}Na NMR parameters.[1]

[1] G. Engelhardt, A. P. M. Kentgens, H. Koller and A. Samoson *Solid State Nucl. Magn. Reson.* 1999, **15**, 171.

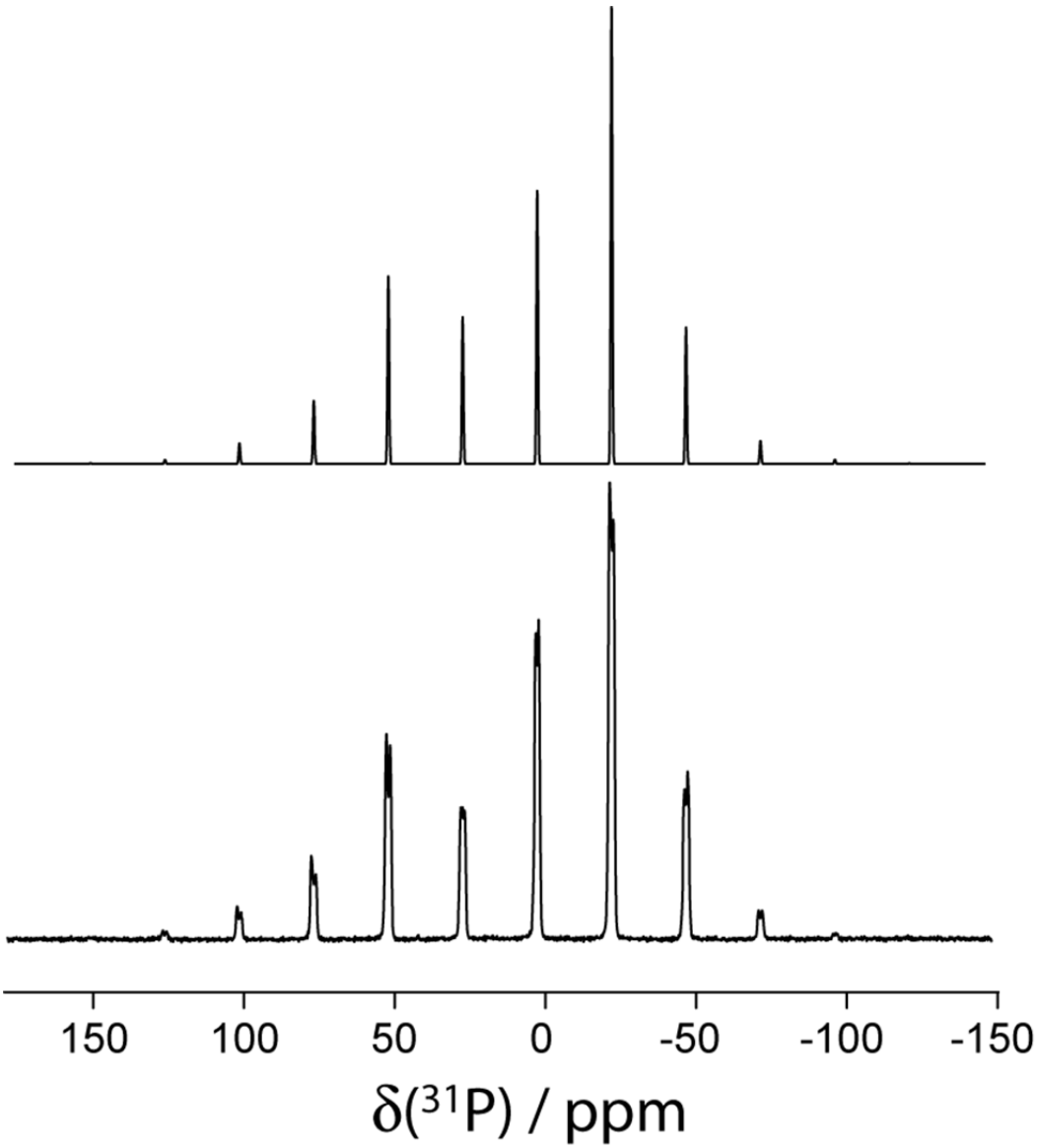

Figure S2. The ^{31}P NMR spectrum of $Na_4P_2O_7$ acquired at 9.4 T (bottom) and its simulation (top). The chemical shifts of the two sites are similar and the spectrum was fit with only one set of parameters.

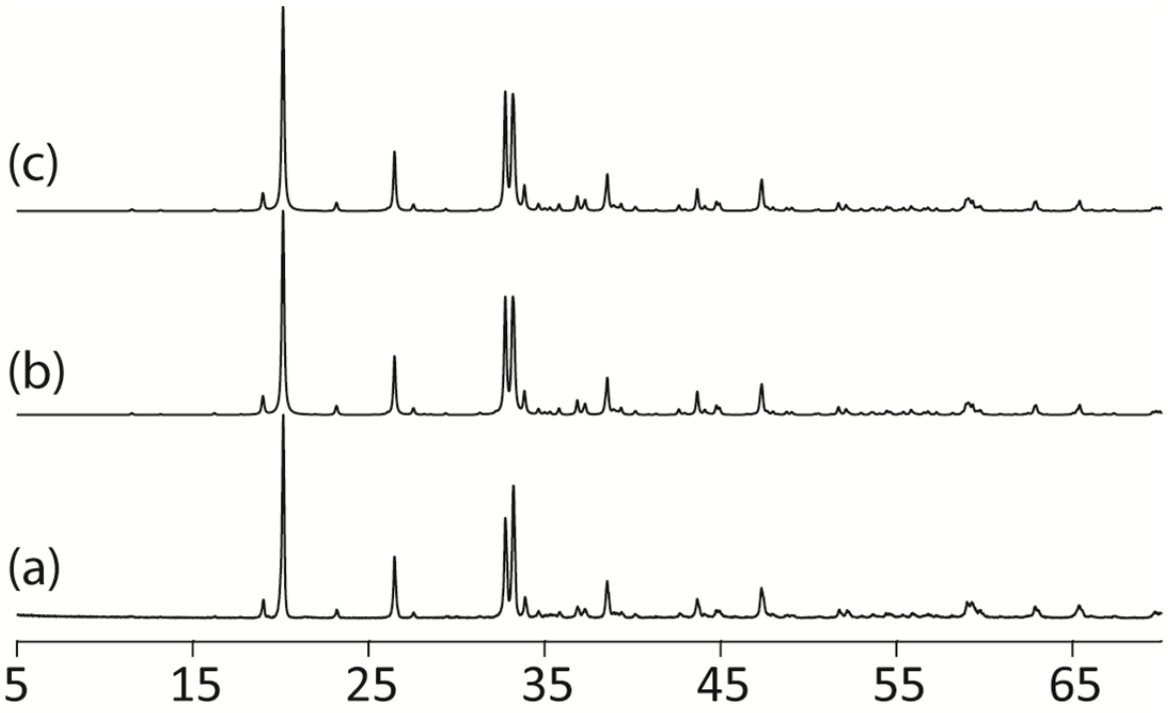

Figure S3. Experimental PXRD pattern (a) for $Na_4P_2O_7$ and those calculated using the SCXRD structure (b) and the NMR/DFT-refined structure (c).

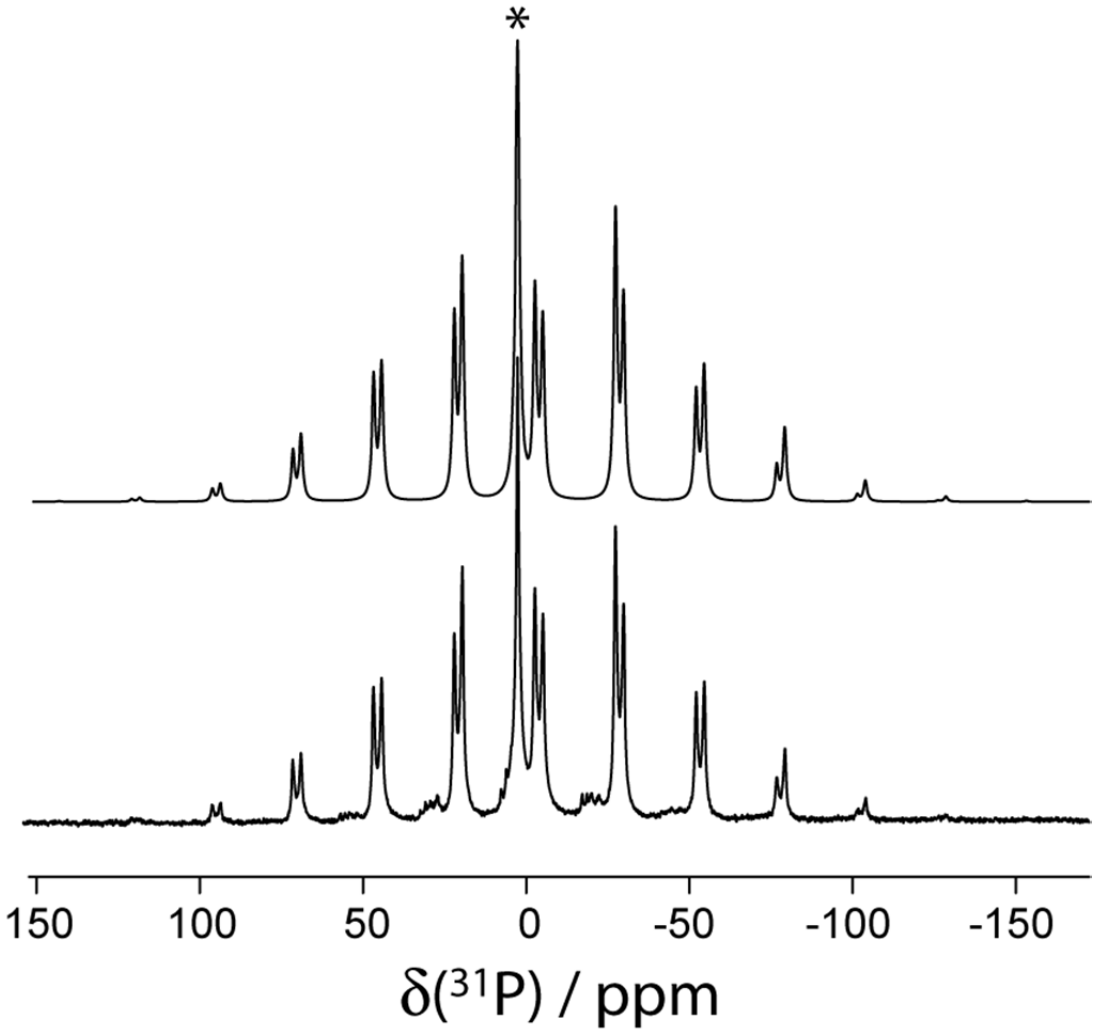

Figure S4. The ^{31}P NMR spectrum of $Na_3HP_2O_7 \cdot H_2O$ acquired at 9.4 T (bottom) and its simulation (top). A star indicates a phosphate impurity.

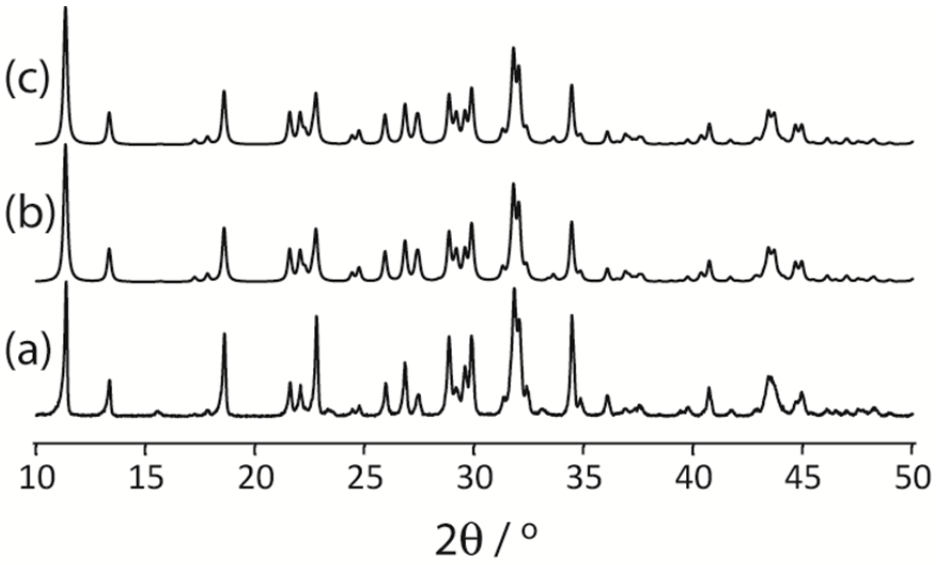

Figure S5. Experimental PXRD pattern (a) for $Na_3HP_2O_7 \cdot H_2O$ and those calculated using the Rietveld-refined structure (b) and the NMR-refined structure (c).

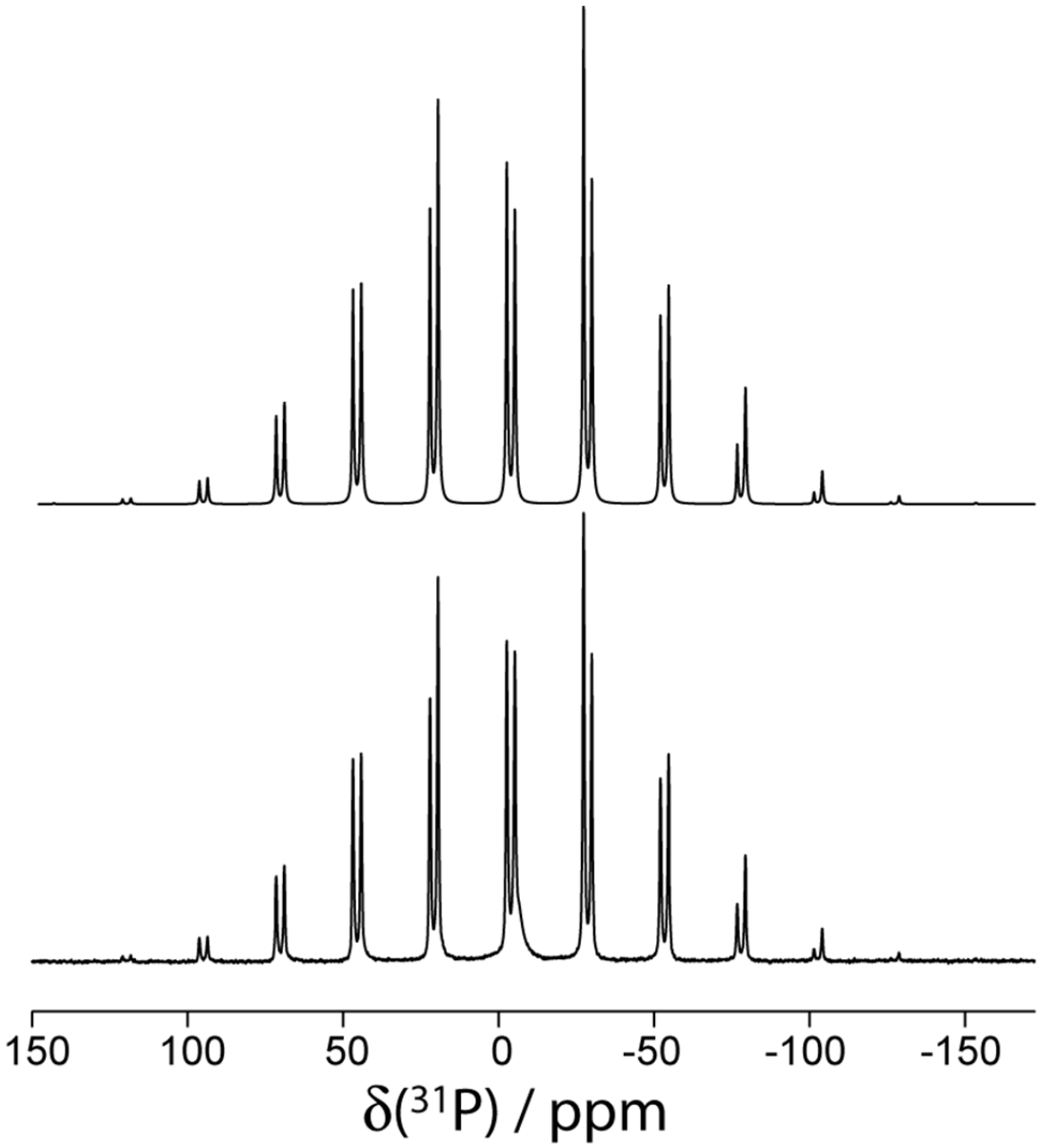

Figure S6. The ^{31}P MAS NMR spectrum of $Na_3HP_2O_7 \cdot 9H_2O$ acquired at 9.4 T (bottom) and its simulation (top).

Table S1. Crystallographic information for $Na_3HP_2O_7 \cdot 9H_2O$

empirical formula	$Na_3P_2O_{16}H_{19}$
formula weight	406.06
crystal size, mm	0.34 x 0.22 x 0.09
crystal system	monoclinic
space group	$\mathbf{P}2_1/n$
Z	4
a / Å	6.0867(2)
b / Å	31.3792(8)
c / Å	8.2848(2)
α / °	90
β / °	108.6180(10)
γ / °	90
volume / Å^3	1499.55(7)
calculated density / Mg/m^3	1.799
absorption coefficient / mm^{-1}	0.453
F(000)	840
Θ range for data collection / °	2.60-28.31
limiting indices	h = ±7, -k = -41 to 39, l = -10 to 11
reflections collected/unique	20041/3636
R(int)	0.0144
completeness to Θ = 28.31 / %	97.5
max and min transmission	0.9603-0.8611
data/restraints/parameters	3636/0/190
goodness-of-fit on F^2	1.010
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0255$, $wR_2 = 0.0739$
R indices (all data)	$R_1 = 0.0265$, $wR_2 = 0.0746$
largest diff peak/hole / e·Å^{-3}	0.360/-0.401

Table S2. ^{31}P NMR parameters for the three compounds studied

sample	site	δ_{iso} / ppm[a]	Ω / ppm[a]	κ[a]
$Na_4P_2O_7$[b]	P1/P2	2.7 ± 0.5	140 ± 10	-0.69 ± 0.05
$Na_3HP_2O_7 \cdot H_2O$	P1	-2.7 ± 0.1	150 ± 10	-0.23 ± 0.05
	P2	-5.1 ± 0.1	180 ± 10	0.08 ± 0.05
$Na_3HP_2O_7 \cdot 9H_2O$	P1	-5.2 ± 0.1	175 ± 10	0.11 ± 0.05
	P2	-2.6 ± 0.1	156 ± 10	-0.27 ± 0.05

[a] The chemical shift tensor parameters, ordered $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, are represented by the isotropic chemical shift, $\delta_{iso} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$, the span ($\Omega \approx \delta_{11} - \delta_{33}$), and the skew ($\kappa \approx 3(\delta_{22} - \delta_{iso})/\Omega$).

[b] These values were also reported in ref. 2.

Table S3. GIPAW DFT calculated ^{31}P NMR parameters for various structures of $Na_4P_2O_7$

site	structure	δ_{11} / ppm[a]	δ_{22} / ppm[a]	δ_{33} / ppm[a]
	Experiment[b]	87.9	-28.0	-51.8
P1	SCXRD	75.7	-34.4	-41.0
	DFT-refined	78.3	-31.9	-38.3
	NMR/DFT-refined	78.4	-32.0	-38.6
P2	SCXRD	80.9	-35.9	-43.9
	DFT-refined	83.9	-34.0	-41.0
	NMR/DFT-refined	83.8	-34.5	-40.3
Average	SCXRD	78.3	-35.1	-42.5
	DFT-refined	81.1	-32.9	-39.6
	NMR/DFT-refined	81.1	-33.3	-39.5

[a] The δ_{ii} values have been scaled for ease of comparison.

[b] The two sites cannot be distinguished experimentally.

[2] L. Griffiths, A. Root, R. K. Harris, K. J. Packer, A. M. Chippendale and F. R. Tromans *J. Chem. Soc. Dalton Trans.* 1986, 2247.

Table S4. (GI)PAW DFT calculated ^{23}Na NMR parameters for various structures of $Na_4P_2O_7$

site	structure	δ_{iso} / ppm[a]	C_Q / MHz[a]	η
Na1	Experiment	5.52	2.08	0.26
	SCXRD	5.70	2.13	0.35
	DFT-refined	5.43	2.07	0.40
	NMR/DFT-refined	5.46	2.07	0.39
Na2	Experiment	1.96	(-)2.3	0.7
	SCXRD	2.22	-2.45	0.68
	DFT-refined	1.89	-2.34	0.68
	NMR/DFT-refined	1.91	-2.33	0.69
Na3	Experiment	10.41	2.9	0.47
	SCXRD	11.03	2.65	0.62
	DFT-refined	10.79	2.67	0.62
	NMR/DFT-refined	10.79	2.70	0.59
Na4	Experiment	6.36	3.22	0.56
	SCXRD	6.04	3.11	0.96
	DFT-refined	6.90	2.82	0.69
	NMR/DFT-refined	6.86	2.85	0.67

[a] The C_Q and δ_{iso} values have been scaled for ease of comparison.

Table S5. GIPAW DFT calculated ^{31}P NMR parameters for various structures of $Na_3HP_2O_7 \cdot H_2O$

site	structure	δ_{11} / ppm[a]	δ_{22} / ppm[a]	δ_{33} / ppm[a]
P1	Experiment	82.8	-0.3	-97.8
	PXRD	75.1	7.7	-86.6
	DFT-refined	71.4	-0.8	-81.8
	NMR-refined	71.0	4.2	-85.3
P2	Experiment	77.6	-14.1	-71.5
	PXRD	69.8	-16.7	-48.4
	DFT-refined	65.1	-6.4	-66.4
	NMR-refined	70.3	-12.8	-57.9

[a] The δ_{ii} values have been scaled for ease of comparison.

Table S6. (GI)PAW DFT calculated ^{23}Na NMR parameters for various structures of $Na_3HP_2O_7 \cdot H_2O$

site	structure	δ_{iso} / ppm[a]	C_Q / MHz[a]	η
Na1	Experiment	4.0	2.55	0.15
	PXRD	4.2	3.34	0.27
	DFT-refined	6.3	1.74	0.48
	NMR-refined	6.1	1.76	0.37
Na2	Experiment	1.0	3.60	0.20
	PXRD	1.3	4.59	0.20
	DFT-refined	0.9	3.44	0.24
	NMR-refined	1.0	3.47	0.26
Na3	Experiment	6.5	3.1	0.10
	PXRD	6.0	4.89	0.38
	DFT-refined	4.3	2.37	0.41
	NMR-refined	4.4	2.44	0.39

[a] The C_Q and δ_{iso} values have been scaled for ease of comparison.

Table S7. Fitted parameters for the rate matrix analysis of the spin diffusion DOR data.

Structure	Parameter	Value
All	A / Å^6 s^{-1}	0.609
$Na_3HP_2O_7 \cdot H_2O$	$B_{1,2}$	1.066
	$B_{1,3}$	0.937
	$B_{2,3}$	1.236
$Na_3HP_2O_7 \cdot 9H_2O$	$B_{1,2}$	0.915
$Na_4P_2O_7$	$B_{1,2}$	0.574
	$B_{1,3}$	1.100
	$B_{1,4}$	0.916
	$B_{2,3}$	1.344
	$B_{2,4}$	0.603
	$B_{3,4}$	1.200

Pseudopotentials

The pseudopotential strings used for all the CASTEP-NMR (GI)PAW DFT calculations are given below.

H 1|0.8|3.675|7.35|11.025|10UU(qc=6.4)[]

O 2|1.3|16.537|18.375|20.212|20UU:21UU(qc=7.5)[]

Na 2|1.3|1.3|1.0|16|19|21|20U:30U:21(qc=7)#[]

P 2|1.8|3.675|5.512|6.982|30UU:31UU:32LGG[]