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Structure and Cation Effects on Phosphorus-31 NMR Chemical Shifts and Chemical-Shift Anisotropies of Orthophosphates*

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We have obtained high-resolution "magic-angle" sample-spinning phosphorus-31 NMR spectra of a variety of orthophosphates, and have derived chemical-shift tensor elements and anisotropies from spinning-sideband patterns. An empirical correlation between isotropic chemical shift and $Z/\sqrt{r}$ is noted, where Z is the cation charge and r the cation radius. The chemical-shift anisotropy varies in an approximately linear fashion with the P–O bond length, and with the deviation of the O–P–O bond angle from the tetrahedral value. These results may be of use in testing models of phosphate bonding in amorphous systems, such as glasses and ceramics.

INTRODUCTION

Orthophosphates (i.e., phosphates in which each oxygen atom is linked to only one phosphorus) are constituents of many important systems, such as teeth and bones (*1*), $AlPO_4$-*n* type materials (*2, 3*), glasses (*4, 5*), and minerals (*6*). Solid-state phosphorus-31 "magic-angle" sample-spinning nuclear magnetic resonance (MASS NMR) spectroscopic studies of orthophosphates have thus far been mostly concerned with mineralized tissue (*7–10*) and model compounds (*11–13*). We report in this note results for a variety of model orthophosphates which provide a basis for interpretation of data obtained on less well characterized, amorphous materials. We show that the isotropic chemical shift can be used to determine the π-bond order around the phosphorus atom and is also sensitive to the cation charge and radius. We show that the chemical-shift anisotropy can be related to the P–O bond length, and to the deviation of the O–P–O bond angle from the tetrahedral value. Such correlations may help determine the nature of the environment around phosphorus in more complex systems that cannot be characterized by diffraction techniques, such as some glasses and ceramics.

EXPERIMENTAL ASPECTS

Proton-decoupled NMR spectra were obtained on an 11.7 T spectrometer (corresponding to a phosphorus-31 NMR frequency of 202.4 MHz) basically as described

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previously (*14, 15*), using a Doty Scientific (Columbia, S.C.) MASS NMR probe. All spectra were recorded using 3–9 μs pulse excitation, where the solution 90° pulse width for 85% H_3PO_4 was 18 μs. Chemical shifts are reported in parts per million (ppm) from an external sample of 85% H_3PO_4, and positive values correspond to low-field, high-frequency, paramagnetic, or deshielded shifts.

Model compounds were of the highest purity commercially available. $NH_4H_2PO_4$, $NaH_2PO_4 \cdot H_2O$, Na_2HPO_4, $NaNH_4HPO_4 \cdot 4H_2O$, $K_2HPO_4 \cdot 3H_2O$, $Ca_3(PO_4)_2$, $CaHPO_4$, and $P_2O_5 \cdot 24WO_3 \cdot nH_2O$ were obtained from Mallinckrodt; $(NH_4)_2HPO_4$ was obtained from Allied Chemical; Li_3PO_4, $Na_3PO_4 \cdot 12H_2O$, $Mg_3(PO_4)_2 \cdot 8H_2O$, BPO_4, $AlPO_4$, and $LaPO_4 \cdot nH_2O$ were obtained from Alfa; KH_2PO_4 was obtained from Baker; and $Be_3(PO_4)_2$ and YPO_4 were obtained from ICN Pharmaceuticals. $GaPO_4$ was prepared by dropwise addition of 85% H_3PO_4 to an aqueous solution of $GaCl_3$, while the pH was maintained in the range of 2.5–7.2 with 0.1 *N* NaOH. The insoluble $GaPO_4 \cdot 2H_2O$ was then collected by filtration, washed, then calcined at 200°C to form anhydrous $GaPO_4$.

The principal values of the chemical shielding tensor (δ_{11}, δ_{22}, δ_{33}) were calculated from the intensities of the spinning sidebands and the isotropic chemical shift, δ_i, using the method of Herzfeld and Berger (*16*). The CSA, $\Delta\delta$, is defined as

$$\Delta\delta = \delta_{33} - \tfrac{1}{2}(\delta_{11} + \delta_{22}) \qquad [1]$$

with

$$|\delta_{33} - \delta_i| \geqslant |\delta_{11} - \delta_i| \geqslant |\delta_{22} - \delta_i|. \qquad [2]$$

RESULTS AND DISCUSSION

We show in Fig. 1 representative phosphorus-31 MASS NMR spectra of the model compounds investigated. Application of proton decoupling was routinely employed for all samples. Many of the compounds studied displayed small or near-zero CSAs, and their spectra are overwhelmingly dominated by the main isotropic peak (see, for example, Figs. 1A, B) while others have large CSAs and show complicated sideband patterns (see, for example, Figs. 1C, D).

The experimentally observed NMR parameters are listed in Table 1, together with the NMR parameters derived from these results, and structure data from the literature (*17–31*). Previous semiempirical studies have indicated that the phosphorus-31 chemical shift is influenced by three main factors: (1) the number and electronegativity of the nearest-neighbor ligands. (2) The bond angles about the phosphorus atom. (3) The occupation of the π-bonding orbitals on the phosphorus atom (*32, 33*). For the orthophosphate ion, (1) and (2) are expected to be constant, or nearly so, and can be ignored, at least to a first approximation. Thus, (3) is the main factor affecting δ_i. Reference (*32*) gives a quantitative expression for δ_i, which, when expressed for the orthophosphate ion (*34*) yields

$$\delta_i = 194 - 156.4\eta_\pi \qquad [3]$$

where η_π is the number of electrons in π orbitals. The value for η_π has been calculated for all of the orthophosphates studied herein, and the results are listed in Table 1, and range from 1.17 to 1.43 π electrons per phosphorus. Van Wazer has calculated that for tetrahedrally coordinated phosphorus there are 1.0 to 1.2 π electrons per phosphorus

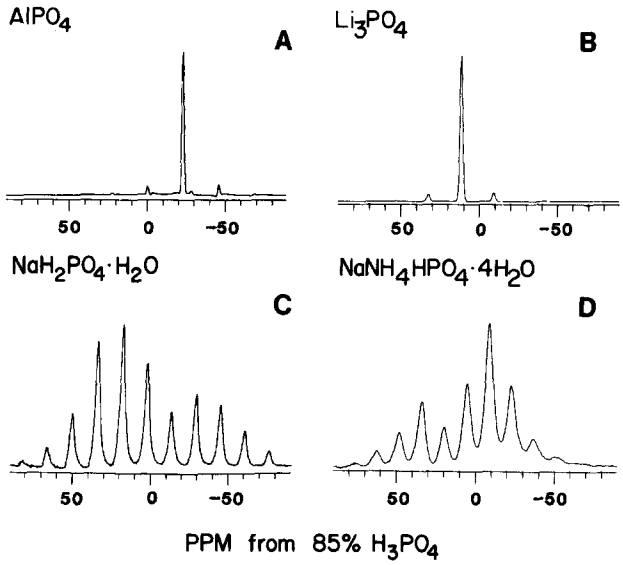

FIG. 1. Representative ^{31}P NMR spectra of several orthophosphates. (A) $AlPO_4$, 4.6 kHz MASS, 20 scans, 4 μs pulse (20° flip angle). (B) Li_3PO_4, 4.2 kHz MASS, 444 scans, 9 μs pulse (45° flip angle). (C) $NaH_2PO_4 \cdot H_2O$, 3.2 kHz MASS, 60 scans, 9 μs pulse (45° flip angle). (D) $NaNH_4HPO_4 \cdot 4H_2O$, 2.8 kHz MASS, 28 scans, 9 μs pulse (45° flip angle). All spectra were recorded using a sweepwidth of 36.4 kHz, a 10 s recycle time, 10 Hz Gaussian line broadening, and ^1H dipolar decoupling was routinely applied for all systems.

(*35*), which is in good agreement with our range of values. From Table 1 it can also be seen that as η_π increases, the average P–O bond length (r_{P-O}) decreases, in agreement with the results of previous workers on other phosphate species (*34*).

In the above discussion, it was assumed that since the nearest neighbor to phosphorus (oxygen) remains constant, the electronegativity of the groups around phosphorus was, to a first approximation, also constant. While this is correct, as has been demonstrated elsewhere, it is the next-nearest-neighbor interactions that are generally of most use in analyzing the structural environment of any MO_4 subunit (e.g., PO_4^{3-}, AlO_4^{5-} or SiO_4^{4-}, (*36–38*). To estimate the importance of next-nearest-neighbors on the ^{31}P chemical shift, we have thus plotted in Fig. 2A the isotropic chemical shift, δ_i, as a function of cation electronegativity (EN) for those orthophosphates which are anhydrous, contain only one cation, and have no other anions present. The results may be expressed in the form:

$$\delta_i(\text{ppm}) = -35.5(\text{EN}) + 41.4 \qquad [4]$$

where EN is the Pauling electronegativity of the cation. The correlation coefficient is 0.92. The results of Fig. 2A demonstrate that a high-field shift occurs as the EN of the cation increases. A similar result was observed for silicon-29 NMR of a variety of silicates (*39*). However, there is clearly a substantial scatter amongst the data points, and the correlation would appear to have little predictive use. We thus investigated the correlation between isotropic chemical shift and the cation potential, Z/r, where Z is the cation charge and r its ionic radius, as shown in Fig. 2B. With the exception

TABLE 1

Phosphorus-31 NMR and Structure Parameters

Compound	δ_i (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	$\lvert\Delta\delta\rvert$ (ppm)	r^a_{P-O} (Å)	$\frac{\sum\lvert 109.5-\theta_{O-P-O}\rvert}{n}$	n_π	Ref.[b]
$NH_4H_2PO_4$	0.9	−15.4	−5.6	23.6	34.1	1.537	1.17	1.23	17
$(NH_4)_2HPO_4$	1.5	−33.6	−9.9	48.0	69.8	1.539	2.38	1.23	18
Li_3PO_4	10.8	NM[c]	NM	NM	NM	1.546	0.68	1.17	19
$Na_3PO_4 \cdot 12H_2O$	7.8	NM	NM	NM	NM	1.526	0.15	1.19	20
$NaH_2PO_4 \cdot H_2O$	2.3	61.1	23.1	−77.3	119.4	1.552	3.87	1.23	21
Na_2HPO_4	6.6	−48.9	−5.7	74.5	101.8	1.550	3.17	1.20	22
$NaNH_4HPO_4 \cdot 4H_2O$	5.1	−36.9	−4.2	56.5	77.0	1.541	2.73	1.21	23
KH_2PO_4	4.3	−15.6	3.9	24.8	30.4	1.538	0.925	1.21	24, 25
$K_2HPO_4 \cdot 3H_2O$	2.1	−45.0	−6.5	57.8	83.6	NA[d]	NA	1.23	—
$Be_3(PO_4)_2$	−9.2	NM	NM	NM	NM	NA	NA		—
$Mg_3(PO_4)_2 \cdot 8H_2O$	4.6	NM	NM	NM	NM	1.538	0.53	1.21	26
$Ca_3(PO_4)_2$	3.0	NM	NM	NM	NM	1.531	2.51	1.22	27
$CaHPO_4$	−0.6	NM	NM	NM	NM	1.541	2.10	1.24	28
$BaHPO_4$ Site 1	−0.5	−40.9	−7.8	47.3	71.7	NA	NA	1.24	—
$BaHPO_4$ Site 2	−2.8	−39.1	−14.9	45.7	72.7	NA	NA	1.26	—
BPO_4	−29.5	NM	NM	NM	NM	NA	NA	1.43	—
$AlPO_4$	−24.5	NM	NM	NM	NM	1.516	0.70	1.40	29
$GaPO_4$	−9.8	NM	NM	NM	NM	1.56	NA	1.30	30
YPO_4	−0.9	NM	NM	NM	NM	1.50	NA	1.25	31
$LaPO_4 \cdot nH_2O$	−3.3	NM	NM	NM	NM	NA	NA	1.26	—
$P_2O_5 \cdot 24WO_3 \cdot nH_2O$	−15.1	NM	NM	NM	NM	NA	NA	1.34	—

[a] Average P–O bond length.
[b] Structure reference.
[c] NM, not measured.
[d] NA, not available.

of the point for BPO_4, the correlation is little different, with a correlation coefficient of 0.88 (boron included) or 0.91 (boron excluded). Finally, we show in Fig. 2C the results of a plot of isotropic chemical shift versus $Z/\sqrt{r}$, which was carried out to improve the fit of the data to a straight-line relationship, as expressed by

$$\delta_i\,(\text{ppm}) = -7.7Z/\sqrt{r} + 18.6. \qquad [5]$$

The correlation coefficient improves to 0.95. Thus, we believe that the results of Fig. 2C suggest that it may be feasible to use phosphorus-31 NMR data to determine which cations are coordinated to an orthophosphate group in complex systems, e.g., to determine if Al or Ca were coordinated in some phosphate glasses (*40*).

In Table 1 the values of δ_{11}, δ_{22}, δ_{33}, and $\Delta\delta$ are listed for those phosphates in which it is possible to determine reasonably accurate values for these parameters (some systems had anisotropies too small to determine, e.g., Li_3PO_4, Fig. 1B). Even with this reduced list of anisotropies, it is still possible to relate them to various structural parameters.

Using various POX_3 compounds having C_{3v} symmetry (X = F, Cl, Br, Me, and O)

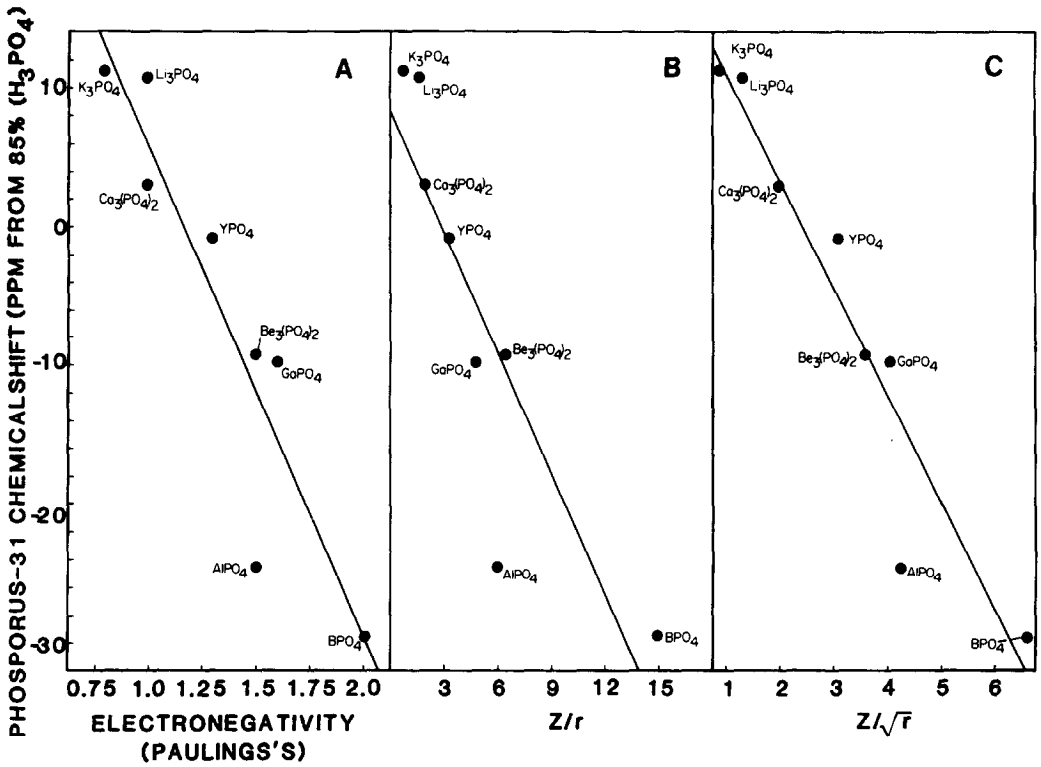

FIG. 2. ^{31}P chemical shift versus (A) cation electronegativity; (B) Z/r and (C) $Z/\sqrt{r}$. The straight lines represent the linear least-squares fits to the data points. The points used in the plot are for K_3PO_4, Li_3PO_4, $Be_3(PO_4)_2$, $Ca_3(PO_4)_2$, BPO_4, $GaPO_4$, $AlPO_4$, and YPO_4. The point for K_3PO_4 at 11.7 ppm comes from Ref. (*38*). Z is the formal cation charge and r its ionic radius.

and two condensed phosphates ($K_2P_2O_7$, P_4O_{10}), Grimmer (*41*) developed a relationship between the chemical-shift anisotropy, $\Delta\delta$, and the P–O bond length, r_{P-O}, as follows:

$$\Delta\delta\ (\text{ppm}) = A(r_{P-O}\ (\text{Å})) + B \qquad [6]$$

where A and B were determined empirically. This relationship has as its basis the idea that a decrease in bond length indicates a higher π-bond order (*35*), and that increased π bonding effects an increase in the chemical-shift anisotropy. Using this approach, we have fitted our orthophosphate data (for $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $NaH_2PO_4 \cdot H_2O$, Na_2HPO_4, $NaNH_4HPO_4 \cdot 4H_2O$, KH_2PO_4) to an equation of the above form as

$$\Delta\delta\ (\text{ppm}) = 5073 r_{P-O}\ (\text{Å}) - 7754 \qquad [7]$$

having a correlation coefficient of 0.93.

A slightly better correlation between $\Delta\delta$ and structure is obtained when the average deviation of the O–P–O bond angle from that of a perfect tetrahedron (109°28′) is employed, as shown in Fig. 3. For the orthophosphates with nonzero $\Delta\delta$ listed above, we have used an equation of the form

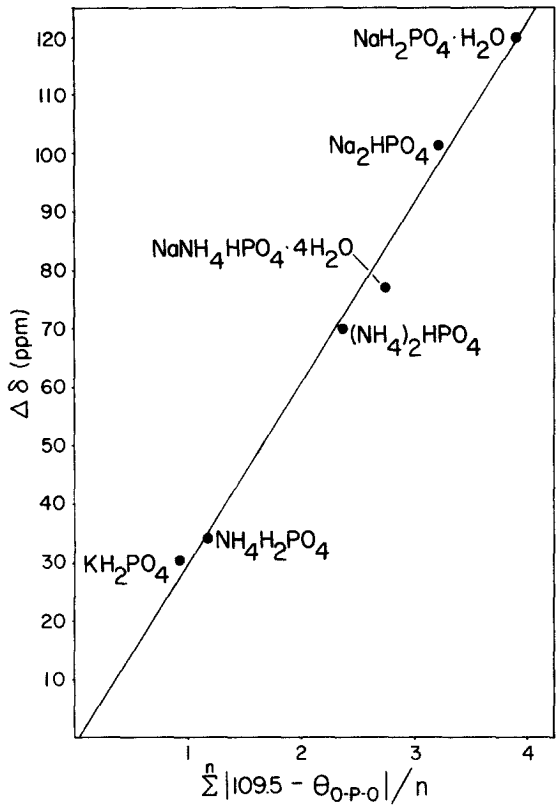

FIG. 3. ^{31}P chemical-shift anisotropy ($\Delta\delta$) versus the average deviation of the O–P–O bond angle from the tetrahedral value. The straight line represents the linear least-squares fit to the points.

$$\Delta\delta\,(\text{ppm}) = 30.90\,(\sum^{n} |109.5 - \theta_{\text{O-P-O}}|/n)\,(\text{Å}) - 1.22 \qquad [8]$$

where 109.5 is the value we use for the tetrahedral angle, $\theta_{\text{O-P-O}}$ is the value for the model compound, and n is the total number of angles involved. We find a correlation coefficient of 0.99 for the six compounds studied, indicating a very good overall fit, as may be seen in Fig. 3. For some of the compounds with nonzero $\Delta\delta$, refined structures were unfortunately not available.

CONCLUSIONS

The results we have presented above indicate that the isotropic phosphorus-31 NMR chemical shift is sensitive to the electronegativity, the charge and the radius of the next-nearest-neighbor cations, and implies that ^{31}P chemical shifts may reveal the details of cation environments in complex, amorphous systems, such as some glasses. Our results also suggest that ^{31}P chemical-shift anisotropies increase linearly with the "average deviation" of the O–P–O bond angle from the tetrahedral value, at least in

the range of chemical-shift anisotropies which can be measured with moderate accuracy, i.e., above about 30 ppm.

Finally, after this work was completed, a paper by Cheetham *et al.* (*42*) appeared which demonstrated a linear relation between the isotropic chemical shift of a variety of inorganic phosphates, and the bond strength sums at the phosphorus oxygens, similar to that observed previously for silicates (*43*). While it is likely that such results may be improved upon by use of a larger data base to obtain group electronegativity sums (*39*), we believe the results of Fig. 2 suggest that alternative direct correlations involving cation charge and radius should also be explored in more depth.

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