Phosphorus-31 and Selenium-77 Nuclear Magnetic Resonance Spectra of Tetraphosphorus Triselenide

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Phosphorus-31 and selenium-77 n.m.r. spectra have been measured for P_4Se_3 containing ^{77}Se in natural abundance, and assigned to give all chemical shifts and coupling constants for the molecules $P_4{}^{o}Se_3$ and $P_4{}^{77}Se^{o}Se_2$, where ^{o}Se represents any natural isotope of Se other than ^{77}Se. Sufficient transitions for the molecule $P_4{}^{77}Se_2{}^{o}Se$ could be observed in its ^{31}P n.m.r. spectrum to allow $^2J_{SeSe}$ to be found.

In ongoing work[1,2] on changes of ^{31}P n.m.r. shifts and couplings with substitution in compounds with a P_4E_3 (E = S or Se) skeleton, we found the need to obtain definitive values for P–P and P–Se coupling constants and chemical shifts for the simple binary compound P_4Se_3 (**1**). These have been reported previously for $P_4{}^{77}Se^{o}Se_2$ (**1b**),* responsible for the 'first' satellite spectrum in the ^{31}P n.m.r. of P_4Se_3, in the pioneering work by Dwek *et al.*,[3] using the nuclear electron Overhauser method of signal enhancement on solutions to which 2,4,6-tri-t-butylphenoxyl radical had been added. It was found that $^2J_{PP}$ for P_4Se_3 was not perturbed by addition of the free radical, so the values of this and the coupling constants found then for the first time were assumed to be those which would have been found for P_4Se_3 in a 'normal' n.m.r. experiment, had that then been possible. Using modern Fourier-transform methods, and operating frequencies of 121.5 and 57.3 MHz for ^{31}P and ^{77}Se respectively, we have now been able to remeasure these parameters under 'normal' conditions. While the ^{31}P n.m.r. spectrum for $P_4{}^{77}Se^{o}Se_2$ simulated from the parameters of Dwek *et al.*[3] [Figure (*d*)] showed a clear resemblance to our experimental spectrum [Figure (*a*)], we were unsuccessful in using it as the starting point for iterative fitting. Starting afresh and using subspectral analysis, we have now arrived at an alternative assignment which does allow a good iterative fit. We therefore conclude that the early assignment by Dwek *et al.*[3] was mistaken, probably because of the relatively poor quality of the spectra then possible, and that the true values of some of the parameters [$^1J_{AX}$ and $^2J_{BX}$ in (**1b**), Scheme] are quite different from those reported. Our assignment was confirmed by inclusion in the fit of transitions from the directly observed ^{77}Se spectrum.

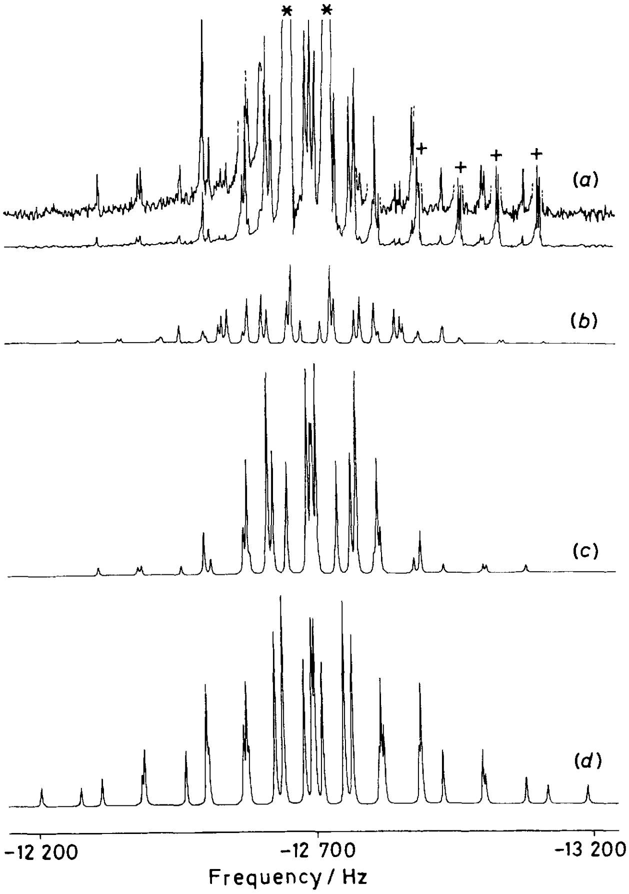

Figure. The basal phosphorus region of the ^{31}P n.m.r. spectrum of P_4Se_3. (*a*) Observed spectrum, with vertically expanded insets; (*b*) computer fitted spectrum for $P_4{}^{77}Se_2{}^{o}Se$ (**1c**); (*c*) fitted spectrum for $P_4{}^{77}Se^{o}Se_2$ (**1b**); (*d*) spectrum simulated for (**1b**) from the parameters of Dwek *et al.*;[3] *, main spectrum [$P_4{}^{o}Se_3$, (**1a**)]; +, impurity peaks due to P_4SeS_2

Results and Discussion

The spin systems for the three molecules which we were able to study in a saturated solution of P_4Se_3 containing ^{77}Se in natural abundance (7.58%), in CS_2, were A_3M for $P_4{}^{o}Se_3$ (**1a**) (main spectrum), AB_2MX for $P_4{}^{77}Se^{o}Se_2$ (**1b**) ('first' satellite spectrum in ^{31}P n.m.r.), and $AA'BMXX'$ for $P_4{}^{77}Se_2{}^{o}Se$ (**1c**) ('second' satellite spectrum in ^{31}P n.m.r.), as shown in the Scheme. The probability of occurrence of $P_4{}^{77}Se_3$ was too low for us to be able to identify any of its transitions.

Spectrum of $P_4{}^{o}Se_3$ (**1a**).—The ^{31}P n.m.r. main spectrum was readily analysed as being almost first order, and an iterative fit using NUMARIT (S.E.R.C. n.m.r. Program Library, Daresbury) converged to an excellent root mean square (r.m.s.) deviation (Table). The value of $^2J_{AM}$, 71.33 Hz, assumed to be positive by analogy with couplings through P–S–P linkages in α-$P_4S_3X_2$ (X = Cl, Br, or CN),[2] was in accord with less precise values published previously,[1,3] although not with the early work of Irgolic *et al.*[4]

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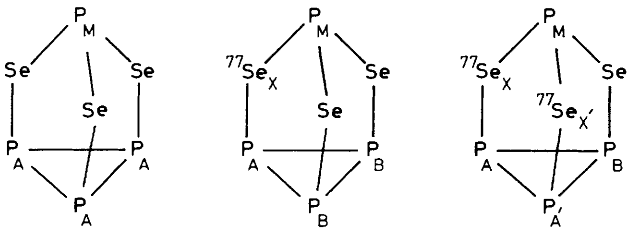
* ^{o}Se represents any natural isotope of Se other than ^{77}Se.



(1a) **(1b)** **(1c)**

Scheme. Labelling of spin systems for isotopic variants of P_4Se_3

Table. N.m.r. parameters for P_4Se_3 (**1**)

Molecule	(**1a**)	(**1b**)	(**1c**)[a]
(*i*) Coupling constants[b] (Hz)			
Apical P–basal P (^2J)	J_{AM} 71.33 (0.06)	J_{AM} 71.4[c] (0.2) J_{BM} 71.2[c] (0.2)	J_{AM} J_{BM} 71.66 (0.08)
Basal P–basal P (^1J)		J_{AB} −149.51 (0.09)	J_{AB} $J_{AA'}$ *d*
Apical P–Se (^1J)		J_{MX} −256.5 (0.2)	J_{MX} −256.2 (0.1)
Basal P–Se (^1J)		J_{AX} −316.4 (0.3)	J_{AX} *d*
Basal P–Se (^2J)		J_{BX} −0.4 (0.2)	J_{BX} $J_{AX'}$ *d*
Se–Se (^2J)			$J_{XX'}$ 64.0 (1.4)
(*ii*) Chemical shifts[e] (p.p.m.)			
Apical P	ν_M 37.4036 (0.0005)	ν_M 37.4091[c] (0.0011)	ν_M 37.4131 (0.0015)
Basal P	ν_A −104.5089 (0.0005)	ν_A −104.5038[c] (0.0013) ν_B −104.5049[c] (0.0011)	ν_A ν_B −104.4995 (0.0006)
Se		ν_X −540.648 (0.002)	ν_X *d*
(*iii*) Iterative fitting			
Number of transitions assigned in P spectrum	14	45	15
Number of transitions assigned in Se spectrum		24	0
R.m.s. deviation (Hz)	0.14	0.50	0.29

[a] Parameters bracketed together were constrained to be equal in the iterative fit. [b] Standard deviations (σ) in parentheses. [c] If the pairs ν_A, ν_B and J_{AM}, J_{BM} were constrained to be equal, respectively, for (**1b**), then $J_{AM} = J_{BM} = 71.40$ (0.11) Hz, $\nu_M = 37.4092$ (0.0011) p.p.m., and $\nu_A = \nu_B = -104.5042$ (0.0006) p.p.m. [d] Parameters fixed at the values obtained for (**1b**). [e] Concurrent measurements on a single solution make small differences significant; molecules (**1a**)—(**1c**) are indistinguishable at levels of precision appropriate to reproducibility, when chemical shifts are: apical P 37.41, basal P −104.50, and Se −540.6 p.p.m.

Spectrum of $P_4{}^{77}Se^oSe_2$ (**1b**).—In subspectral analysis for this molecule, m_X is a good quantum number since it belongs to a different isotopic species (^{77}Se) than the other n.m.r.-active nuclei of the molecule (^{31}P). The approximation was made that m_M is also a good quantum number, since the internal chemical shifts δ_{AM} and δ_{BM} (where $\delta_{AM} = \nu_A - \nu_M$) are large (17 242.3 Hz). The analysis problem then amounted to assigning the four AB_2 subspectra, corresponding to two sign possibilities each for m_M and m_X, in the basal phosphorus region of the ^{31}P n.m.r. spectrum [Figure (*a*)]. Although there are selenium isotope effects on the chemical shifts of neighbouring phosphorus atoms (ν_A) and on transmitted couplings (J_{AM}), these are very small (see below) and could be ignored for the purpose of subspectral analysis, and the approximations made that $\delta_{AB} = 0$ and $J_{AM} = J_{BM}$. The AB_2 subspectra then become two identical pairs: one pair, with effective internal shift $\delta_{AB}{}^* = (J_{AX} - J_{BX})/2$, is the mirror image of the other pair, with $\delta_{AB}{}^* = -(J_{AX} - J_{BX})/2$, and within each pair corresponding transitions are separated by J_{AM}. The constant separation J_{AM} had practically the value already found for the main spectrum, and was readily identified; so, by constructing a spectrum of lines representing the mid-points of each pair of transitions separated by J_{AM}, the problem was simplified to identifying two overlapping AB_2 subspectra which were mirror images of each other, and which had their A parts pointing outwards.

Difficulties arose because almost all of the transitions of the B parts were accidentally overlapped by other transitions, so identification of the subspectra depended on certainty of assignment of the weak outermost A transitions, which stood clear of overlaps, and then maximum use of the various equal separation rules of AB_2 spectra to identify sequentially the B transitions. Long accumulation (25 000 scans) and high sensitivity associated with high operating frequency allowed us to distinguish clearly the weak A transitions from noise [see the vertically expanded inset of Figure (*a*)], and we had the benefit of iterative computer fitting to confirm our assignment, which earlier workers had lacked.[3] The extent of overlap in this system is independent of operating frequency.

Because both m_X and m_M are good quantum numbers, the first-order approximation was used to obtain a value of J_{MX} from the apical phosphorus region of the ^{31}P n.m.r. spectrum, where the 'first' satellite spectrum appeared as an approximate doublet (J_{MX}) of quartets (J_{AM}). Approximations to chemical shifts $\nu_A = \nu_B$, ν_M, and ν_X were obtained by finding the centres of approximate symmetry of the basal phosphorus, apical phosphorus, and selenium multiplets respectively.

The signs of the coupling constants were guessed from those in analogous compounds and confirmed by computer fitting. Thus $^1J_{AB}$ was assumed to be negative and $^2J_{AM}$ and $^2J_{BM}$ were assumed to be positive, by analogy with phosphorus–sulphur compounds (see above), while $^1J_{AX}$ and $^1J_{MX}$ were taken to be negative, as found previously for ^1J phosphorus–selenium couplings.[5] The value of $^2J_{BX}$ found by subspectral analysis was zero, so no sign needed to be arbitrarily decided; the negative sign of the low value finally found came directly from the iterative fitting process.

The approximate parameters thus obtained enabled easily-recognised simulated ^{31}P and ^{77}Se spectra to be generated using NUMARIT, which were then used as starting points for a successful iterative fit (Table). It may be noted that the ^{77}Se spectrum resembled a doublet of doublets of triplets, with the doublet splittings approximating to J_{AX} and J_{MX} respectively. However, the triplet splitting was *ca.* 113.5 Hz, whereas J_{BX}, for which it might have been mistaken, was found to be −0.4 Hz. This is an extreme case of an 'X splitting' being different from an 'X coupling'.[6]

The good agreement between observed and simulated spectra is illustrated for the basal phosphorus region in Figure (*a*) and (*c*). The most noticeable remaining discrepancy is the incomplete overlap of the two centre transitions of the simulated spectrum. Experiment has shown that this discrepancy is not reduced in computer fits starting with the other possible combinations of relative signs of J_{AB}, J_{AM}, and J_{AX}, and it remains unexplained.

Our values of ${}^1J_{AB}$ (-149.51 Hz) and ${}^1J_{MX}$ (-256.5 Hz) are as expected and are compatible with those of Dwek *et al.*[3] (157 ± 10 and 263 ± 10 Hz respectively). However, their value of 536 ± 20 Hz for ${}^1J_{AX}$ was surprising, since it is not clear why this coupling through an approximately single bond to selenium should be numerically so much larger than the other directly-bonded phosphorus–selenium coupling, ${}^1J_{MX}$. We have now found that although ${}^1J_{AX}$ is numerically larger than ${}^1J_{MX}$, its value is only -316.4 Hz, so the two ${}^1J$ couplings to selenium are not unusually different. The previously reported[3] value of ${}^2J_{BX}$ of 57 Hz (changing the sign to accord with present knowledge of signs of the other couplings) seemed, in contrast, a reasonable value for a ${}^2J$ coupling from phosphorus through phosphorus to selenium, since ${}^2J$ phosphorus–phosphorus couplings through sulphur are often of this order. We were surprised, therefore, to find our value of only -0.4 Hz for ${}^2J_{BX}$.

Spectrum of $P_4{}^{77}Se_2{}^{o}Se$ (**1c**).—While even after an accumulation of 17 600 scans, the ${}^{77}Se$ n.m.r. spectrum was too noisy for certain identification of peaks due to this molecule, the greater sensitivity of ${}^{31}P$ n.m.r. allowed three peaks in the apical phosphorus region, and six peaks in the basal phosphorus region, to be used in iterative fitting.

Ignoring isotope effects on shifts and transmitted couplings, the parameters already found for $P_4{}^{77}Se{}^{o}Se_2$ (**1b**) were taken, together with a trial value of zero for the remaining selenium–selenium coupling ${}^2J_{XX'}$, and a simulated spectrum produced, using NUMARIT. Transitions were then assigned to the observed peaks in the basal phosphorus region, by trial and error, until an iterative fit was found to converge. By including the apical phosphorus peaks, sufficient information was available from the spectrum for $J_{AM} = J_{BM}$, J_{MX}, $J_{XX'}$, $\nu_A = \nu_B$, and ν_M to be determined, if the remaining parameters were fixed at the values found for (**1b**) (Table). The contribution of (**1c**) to the basal phosphorus region of the spectrum is shown in Figure (*b*), the intensity of which is of the right order for comparison with the inset spectrum of Figure (*a*).

The most interesting result is the rare observation of a selenium–selenium coupling, ${}^2J_{XX'}$, here found indirectly from the phosphorus spectrum by virtue of the symmetry of the spin system. Its value was 64 ($\sigma = 1.4$) Hz.

Selenium Isotope Effects.—Discussion of differences in phosphorus chemical shifts due to a neighbouring selenium atom being the ${}^{77}Se$ isotope or not is difficult because one is comparing the properties of ${}^{77}Se$ with a weighted average of the properties of ${}^{74}Se$ (0.87), ${}^{76}Se$ (9.02), ${}^{78}Se$ (23.52), ${}^{80}Se$ (49.82), and ${}^{82}Se$ (9.19%), all of which have $I = 0$ and hence have no n.m.r. coupling effects to distinguish them. However, if, to maintain comparability, an average chemical shift for basal phosphorus in $P_4{}^{77}Se{}^{o}Se_2$ (**1b**) were computed by constraining ν_A and ν_B to be refined together in an iterative fit, clear trends in both apical and basal chemical shifts could be observed for the series of molecules (**1a**), (**1b**), and (**1c**) (Table). An increase of *ca.* 0.005 p.p.m. in both apical and average basal shifts was produced by each substitution of ${}^{77}Se$ for non-active selenium. The transmitted coupling J_{AM} also increased with ${}^{77}Se$ substitution, but the increment was comparable with the standard deviation of the measurements.

Experimental

P_4Se_3 was prepared from the elements as described previously,[1] and a saturated solution made under nitrogen by stirring the solid for 1 h at 20 °C with AnalaR CS_2, dried by distillation from P_4O_{10}.

N.m.r. spectra were measured using a Bruker WM300WB spectrometer, operating at 121.5 MHz for ${}^{31}P$ and 57.3 MHz for ${}^{77}Se$. A capillary containing $(CD_3)_2CO$ was used as a lock. ${}^{31}P$ Chemical shifts were calculated relative to D_3PO_4–D_2O. The spectral reference value used for calculating ${}^{77}Se$ shifts was such that a saturated solution of H_2SeO_3 in water had a shift of zero when the same $(CD_3)_2CO$ capillary was used as a lock.

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