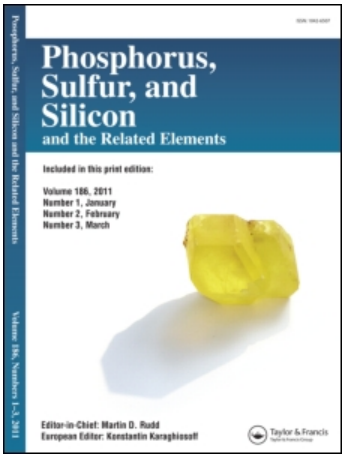

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CRYSTAL AND MOLECULAR STRUCTURE AND SOLID STATE NMR STUDIES OF BIS(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINAN-2-YL) SELENIDE

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CRYSTAL AND MOLECULAR STRUCTURE AND SOLID STATE NMR STUDIES OF BIS(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINAN-2-YL) SELENIDE

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The structural investigation of the phosphoroorganic selenium-containing title compound $C_{10}H_{20}O_6P_2Se$ (**1**) was carried out. The structure of **1** has been determined by X-ray analysis and correlated with the solid state NMR studies, its purity and identity was confirmed by elemental analysis. The following crystal data were found: triclinic, $P\bar{1}$, a = 5.6557(6) Å, b = 10.2717(8) Å, c = 13.761(1) Å, α = 105.580(7)°, β = 90.992(7)°, γ = 101.745(8)°, and Z = 2. Two six-membered rings in the molecule of **1** are in the chair conformation. The selenium atom which bridges the rings is situated axially with respect to both rings. The exocyclic oxygens are, consequently, in equatorial positions.

Key words: Dioxaphosphorinane rings, NMR, X-ray diffraction.

INTRODUCTION

Organic phosphates and pyrophosphates play an important role in biology.[1,2] A number of modified phosphates as well as pyrophosphates have been synthesized and applied in mechanistic and enzymatic studies.[3] Recently, Veres *et al.* have founded that selenophosphates have been implicated in biosynthesis of seleno tRNA.[4] A few years ago we reported the first general synthesis of seleno analogues of pyrophosphates containing a selenium bridge between two phosphoryl centers.[5] Our preliminary studies have shown that symmetrical tetra-alkyl monoselenopyrophosphates are very reactive towards such nucleophiles as water, alcohols, and undergo thermal and catalysed izomerization.[6,7] In contrast, neither traces of hydrolysis nor methanolysis of bicyclic anhydride bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide **1** have been observed in solvolytic conditions during 2 days.[6,7] This compound (Figure 1) may be stored for weeks at room temperature without any traces of isomerization or decomposition. It is supposed that this unique

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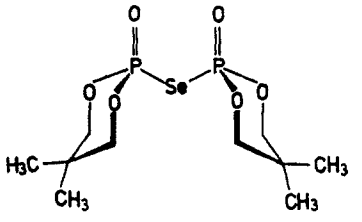

FIGURE 1 The investigated compound **1**.

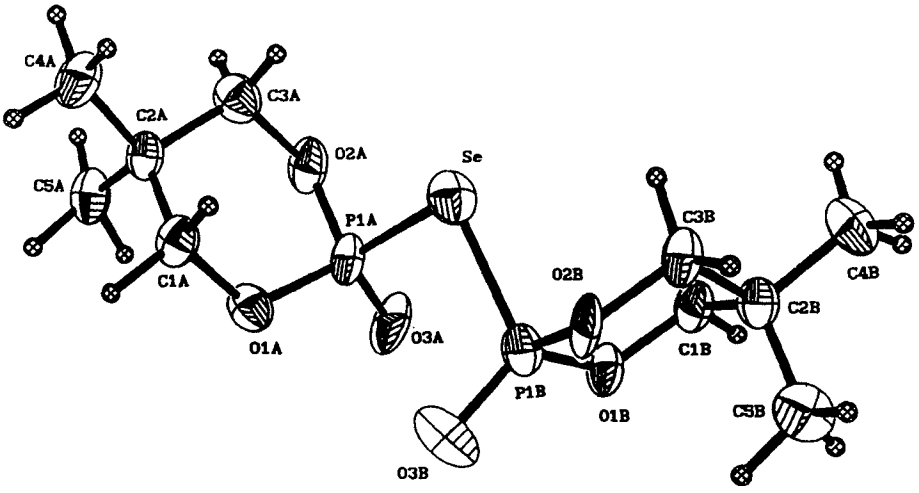

FIGURE 2 Thermal ellipsoidal view (ORTEP) of compound **1** with atom numbering scheme.

properties are connected with the presence of 5,5-disubstituted 1,3,2-dioxaphosphorinane rings.

Because of the importance of modified pyrophosphates systems in biochemistry we decided to undertake this study in order to examine the effect of linking to 1,3,2-dioxaphosphorinane rings by selenium atom on the conformations of the rings, on the symmetry of molecule, as well as on the bond lengths and bond angles.

We have been able to synthesize the solid compound **1** in high yield and to obtain suitable crystals for X-ray analysis. We have also undertaken the solid state NMR studies to determinate the structure of the compound **1** and correlate it with X-ray results.

It is interesting to compare our results with the crystal and molecular structures of analogues of **1**[8–15] published in literature.[16]

RESULTS AND DISCUSSION

The thermal ellipsoidal view of the molecule of investigated compound **1** with the atom numbering scheme is shown in Figure 2. Positional parameters together with estimated standard deviations are given in Table I. Bond lengths and bond angles involving nonhydrogen atoms are listed in Table II.

TABLE I

Atomic coordinates and equivalent isotropic displacement coefficients (Å²)

Atom	x	y	z	B(eq)
Se	0.1129(1)	0.48984(6)	0.24023(4)	3.28(1)
P1A	0.3152(3)	0.3273(1)	0.25092(9)	2.93(3)
O1A	0.4181(7)	0.3636(3)	0.3651(2)	2.95(7)
O2A	0.1045(8)	0.1965(3)	0.2347(2)	3.42(8)
O3A	0.5035(8)	0.3063(4)	0.1805(3)	4.77(9)
C1A	0.242(1)	0.3585(5)	0.4427(3)	2.9(1)
C2A	0.066(1)	0.2195(5)	0.4177(3)	2.6(1)
C3A	-0.070(1)	0.1915(6)	0.3138(4)	3.3(1)
C4A	-0.124(1)	0.2274(6)	0.4968(4)	3.8(1)
C5A	0.197(1)	0.1039(5)	0.4194(4)	3.6(1)
P1B	0.4429(3)	0.6549(1)	0.24329(9)	2.94(3)
O1B	0.5205(7)	0.6310(3)	0.1310(2)	3.07(7)
O2B	0.3340(8)	0.7883(3)	0.2661(2)	3.44(8)
O3B	0.6435(9)	0.6656(4)	0.3154(3)	4.7(1)
C1B	0.358(1)	0.6510(5)	0.0542(3)	3.0(1)
C2B	0.297(1)	0.7935(5)	0.0882(3)	2.7(1)
C3B	0.174(1)	0.8067(5)	0.1876(4)	3.3(1)
C4B	0.113(1)	0.8032(6)	0.0083(4)	4.0(1)
C5B	0.523(1)	0.9078(5)	0.1006(4)	3.8(1)

The equivalent isotropic displacement parameter of anisotropically refined atoms takes the form:

$$(4/3)\ (a^2B_{11}+b^2B_{22}+c^2B_{33}+abB_{12}\cos\gamma+acB_{13}\cos\beta+bcB_{23}\cos\alpha)$$

TABLE II

Bond lengths (Å) and valence angles (°)

			A	B
Se	P1		2.241(2)	2.243(1)
P1	O1		1.585(3)	1.582(3)
P1	O2		1.566(4)	1.573(4)
P1	O3		1.462(5)	1.461(5)
O1	C1		1.478(6)	1.471(7)
O2	C3		1.486(7)	1.474(7)
C1	C2		1.514(6)	1.524(7)
C2	C3		1.539(8)	1.531(8)
C2	C4		1.542(8)	1.535(8)
C2	C5		1.526(8)	1.521(7)
P1A	Se	P1B	95.74(6)	
Se	P1	O1	107.1(2)	107.0(1)
Se	P1	O2	101.8(2)	101.7(2)
Se	P1	O3	116.1(3)	115.9(2)
O1	P1	O2	105.7(2)	105.7(3)
O1	P1	O3	112.0(2)	112.4(2)
O2	P1	O3	113.2(2)	113.3(2)
P1	O1	C1	117.8(3)	118.6(3)
P1	O2	C3	118.9(3)	119.2(3)
O1	C1	C2	111.4(3)	111.0(3)
C1	C2	C3	109.6(4)	108.9(4)
C1	C2	C4	108.0(4)	108.1(4)
C1	C2	C5	111.1(5)	111.1(5)
C3	C2	C4	107.1(5)	107.5(5)
C3	C2	C5	110.9(4)	111.0(4)
C4	C2	C5	110.1(5)	110.1(5)
O2	C3	C2	110.4(5)	110.4(5)

The angle P1A-Se-P1B of the selenium bridge between 1,3,2-dioxaphosphorinane rings in **1** adopts the value 95.74(6)° and corresponds well with the decreasing value of that angle depending on atom bridging two 1,3,2-dioxaphosphorinane rings (O→S→Se). The "bridge" angles found in literature[16] for structures containing oxygen as bridging atom are in the range 129.2–146.1°.[8–13] In two structures containing sulfur as bridging atom those angles are 102.2° and 103.3°.[14,15]

The bond lengths P1A-Se and P1B-Se, describing the selenium bridge in the molecule of **1**, are practically identical (2.241(2) Å and 2.243(1) Å, respectively, see Table II). The analysis of torsion angles and asymmetry parameters, describing the conformation of two independent dioxaphosphorinane rings A and B in the molecule **1** (Tables III and IV) indicates the chair conformation of both rings, with all atoms O1,O2,C1,C3 building the basic plane lying almost ideally in that plane. The average values (modules) of endocyclic torsion angles are 51.8° and 51.5°, respectively for rings A and B.

The selenium atom in **1** is situated axially with respect to both six-membered rings (Figure 2). That phenomenon can be explained by calculated distances of the selenium atom from the least-squares planes passing through four endocyclic atoms O1,O2,C1,C3, which are equal to 2.757(1) Å and −2.749(1) Å, respectively for

TABLE III

Selected torsional angles (°)

				A	B
P1B	Se	P1A	O1A	76.7(2)	
P1B	Se	P1A	O2A	-172.6(1)	
P1B	Se	P1A	O3A	-49.2(2)	
P1A	Se	P1B	O1B	84.2(2)	
P1A	Se	P1B	O2B	-165.2(1)	
P1A	Se	P1B	O3B	-42.0(2)	
Se	P1	O1	C1	64.3(3)	66.2(3)
O2	P1	O1	C1	-43.6(4)	-41.6(4)
O3	P1	O1	C1	-167.3(3)	-165.7(4)
Se	P1	O2	C3	-68.1(4)	-69.8(4)
O1	P1	O2	C3	43.6(4)	41.7(4)
O3	P1	O2	C3	166.6(4)	165.3(4)
P1	O1	C1	C2	54.5(5)	53.7(5)
P1	O2	C3	C2	-53.2(5)	-53.5(5)
O1	C1	C2	C3	-58.6(6)	-59.5(6)
O1	C1	C2	C4	-175.0(4)	-176.1(4)
O1	C1	C2	C5	64.3(5)	63.0(5)
C1	C2	C3	O2	57.4(6)	59.0(5)
C4	C2	C3	O2	174.3(4)	176.0(4)
C5	C2	C3	O2	-65.6(6)	-63.5(6)

TABLE IV

Asymmetry parameters of a 1,3,2-dioxaphosphorinane rings in **1**

	Ring A	Ring B		Ring A	Ring B
ΔC_s(P1)	1.0(2)	0.3(2)	ΔC_2(O1–C1)	14.4(2)	17.7(2)
ΔC_s(O1)	11.0(2)	12.8(2)	ΔC_2(P1–O1)	8.6(2)	9.5(2)
ΔC_s(O2)	10.0(2)	12.6(2)	ΔC_2(P1–O2)	7.1(1)	9.2(2)

rings A and B (sign " − " indicates the opposite direction). The distances of equatorially situated exocyclic oxygen atoms O3A and O3B are 0.246(4) Å and −0.192(5) Å, respectively. The conformations about the bridge bonds in the pyrophosphate groups are approximately staggered what is described by the respective torsion angles P1B-Se-P1A-O3A = −49.2(2)° and P1A-Se-P1B-O3B = −42.0(2)°.

The geometry and self-arrangement of six-membered heterorings in the molecule of **1** are described by dihedral angles between respective least-squares planes, shown in Table V. The flattening of the chair conformation of 1,3,2-dioxaphosphorinane rings at the phosphoryl centres (P1A and P1B) in molecule **1** equals 15.0(4)° for ring A and 17.9(4)° for ring B (Table V) and is similar as described in literature[16]

TABLE V

Interesting least-squares planes in the molecule of **1**

Plane and atoms building plane	Distance of atom (Å) from plane 1A	Distance of atom (Å) from plane 1B
1A: O1A, O2A, C1A, C3A	P1A: 0.577(1)	P1B: -0.554(1)
2A: P1A, O1A, O2A	C2A: -0.697(5)	C2B: 0.714(5)
3A: C1A, C2A, C3A	O3A: 0.246(4)	O3B: -0.192(5)
1B: O1B, O2B, C1B, C3B	Se: 2.757(1)	Se: -2.749(1)
2B: P1B, O1B, O2B	C4A: -0.535(6)	C4B: 0.588(6)
3B: C1B, C2B, C3B	C5A: -2.178(6)	C5B: 2.181(6)
4: P1A, Se, P1B		

Dihedral angles (deg) between planes		
1A/2A: 37.4(3)	1B/2B: 35.6(3)	1A/1B: 62.0(2)
1A/3A: 52.4(4)	1B/3B: 53.5(4)	1A/4: 82.4(2)
2A/3A: 15.1(9)	2B/3B: 17.9(8)	1B/4: 59.8(3)

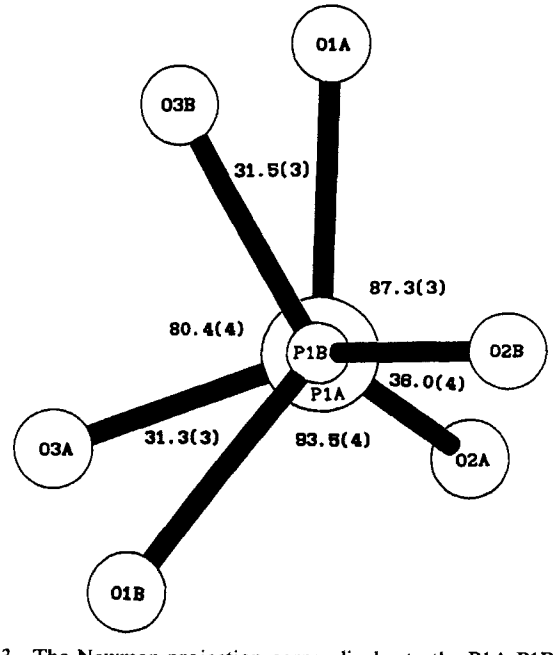

FIGURE 3 The Newman projection perpendicular to the P1A-P1B direction.

for compounds containing two 1,3,2-dioxaphosphorinane rings with phosphoryl centres bridged by oxygen or sulfur atoms.[8–15] The dihedral angle between basic planes O1,O2,C1,C3 of rings A and B in molecule **1** is equal to 62.0(2)°. The self-arrangement of rings A and B of molecule **1** is presented also in the Newman projection perpendicular to the P1A-P1B direction (Figure 3).

The results obtained from multinuclear, high resolution solid state NMR studies are in excellent agreement with the X-ray single-crystal data. Figure 4 displays ^{13}C (4a), ^{31}P (4b) and ^{77}Se (4c) spectra recorded at room temperature employing the cross-polarization magic angle spinning (CPMAS) technique. The ^{13}C spectrum

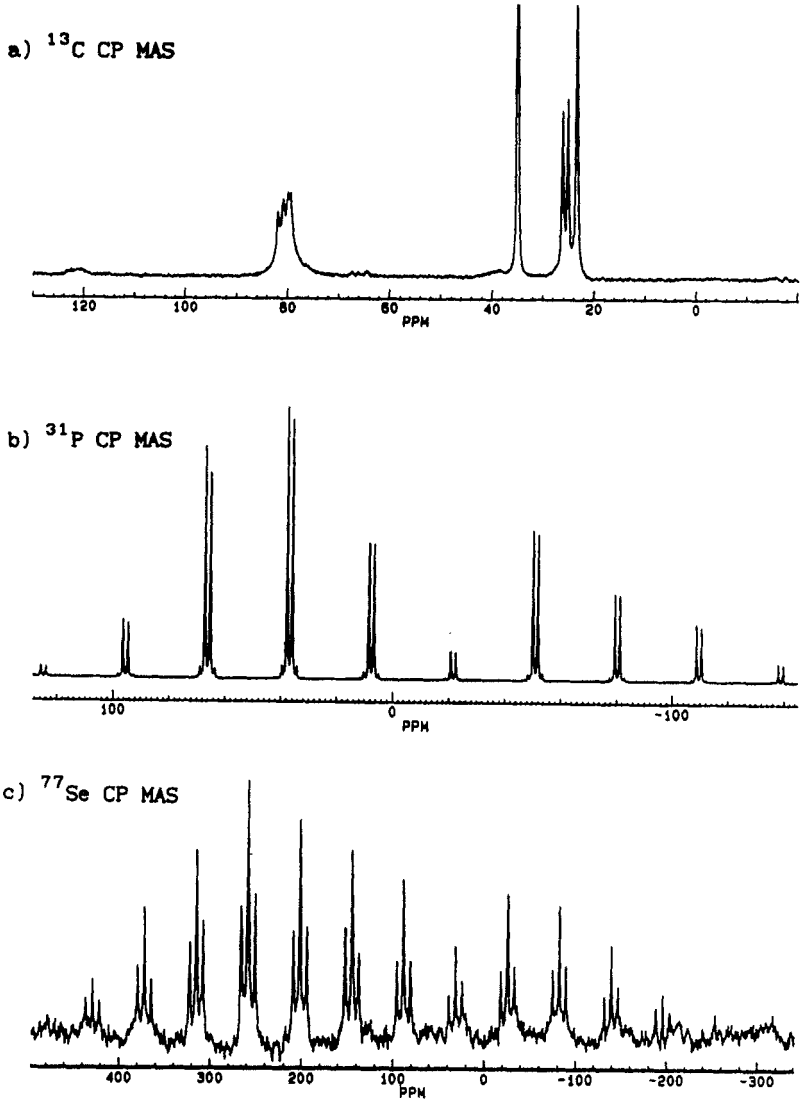

FIGURE 4 The solid state ^{13}C CP MAS (a), ^{31}P CP MAS (b) and ^{77}Se CP MAS (c) NMR spectra of compound **1**.

(Figure 4a) shows well resolved resonances which can be unambiguously assigned to each carbon atom. The assignment of quaternary carbons was obtained from the dipolar dephasing experiment by changing the dephasing time in range from 40 μs to 120 μs.[17] The two signals at δ = 34.94 ppm and δ = 34.70 ppm of quaternary carbon atom suggest that the whole molecule is an asymmetric part of the unit cell. This conclusion is further supported by analysis of the methylene signals at ca δ = 80 ppm. The four resonances of CH_2 carbons are due to crystallographic and magnetic inequivalence of methylene groups in the unit cell. The analysis of the methyl resonances can be slightly misleading owing to the presence of the three instead of the expected four resonances. This discrepancy can be explained by the overlapping effect, the two to one ratio of intensities of the most upfield (δ = 23.21 ppm) methyl signals compared to the others (δ = 24.99 ppm and δ = 26.05 ppm) is apparent.

Figure 4b shows the ^{31}P CP MAS spectrum of the bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide (**1**). Due to large shielding anisotropy the sample shows a number of spinning sidebands. The dipolar coupling from the protons was eliminated through proton decoupling during data acquisition. Non-zero spin isotope of the oxygen constituted only minute coupling with the phosphorus and was below the detectable limit. The scalar *J*-coupling between phosphorus and adjacent selenium is very evident from the spectrum. The satellites are partially overlapped by main signals, hence only two out of four lines are seen. The calculated scalar $J_{^{31}P\text{-}^{77}Se}$ coupling was found to be 427 Hz (value typical for single P—Se bond). As the scalar coupling is first order interaction and should not disturb the spinning sideband pattern and further the experimental procedure ensured that the phosphorus resonances were governed by the chemical shift interactions, it was possible by using MAS line-shape analysis to obtain the shielding anisotropy ($\Delta\delta$), the asymmetry parameter (η) and the isotropic values (δ_{iso}). The calculated values of the principal elements of the chemical shift tensors and shielding parameters obtained from graphical methods of Berger and Herzfeld[18] are collected in Table VI.

Two phosphorus resonances seen in Figure 4b, separated by δ = 1.68 ppm further confirmed that the whole molecule is an asymmetric part of the unit cell. Moreover, very similar shielding parameters (anisotropy ($\Delta\delta$) and asymmetry parameter (η)), for P1A and P1B sites suggest that their local environment is almost identical. It is commonly known that ^{31}P shielding parameters can be considered as a source of unique information about molecular structure of the phosphorus moieties. General conclusion given by Herzfeld *et al.* which combined chemical shift anisotropy with degree of departure from cubic symmetry is consistent with a recent paper of Turner and coworkers who confirmed that ^{31}P CSA increase linearly with deviation of the O—P—O angle from the tetrahedral value.[19,20] Furthermore, very recently the relationship between the ^{31}P shielding parameters obtained from high resolution solid state NMR studies and molecular structure of dithiophosphates has been reported.[21]

The calculated value of anisotropy parameter ($\Delta\delta$) ca 214 ppm for bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide **1** is rather large compared to other phosphoroorganic compounds and reflects the distortion of phosphorus geometry from tetrahedral value owing to both presence of six-membered ring and adjacent selenium.

TABLE VI

Principal elements of the chemical shift tensor and shielding parameters for ^{31}P and ^{77}Se nuclei[a]

Nucleus	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	η
^{31}P	8.34	86.9	72.6	-134.5	214.5	0.10
	6.66	86.9	67.0	-134.0	211.0	0.14
^{77}Se[b]	201.88	402.5	241.6	38.4	360.5	0.67

a) Errors in the experimental principal components of the chemical shift tensor are ± 2 ppm.

b) Calculated for central line of the triplet.

TABLE VII

Crystal data and experimental details

Molecular formula	$C_{10}H_{20}O_6P_2Se$
Space group	$P\bar{1}$
a (Å)	5.6557(6)
b (Å)	10.2717(8)
c (Å)	13.761(1)
α (°)	105.580(7)
β (°)	90.992(7)
γ (°)	101.745(8)
V (Å^3)	752(2)
Z	2
μ (cm^{-1})	57.0
Dc (g/cm^3)	1.666(2)
Crystal dimensions (mm)	0.20,0.25,0.40
Maximum 2θ (°)	150
Radiation, λ (Å)	CuKα, 1.54178
Scan mode	$\omega/2\theta$
Scan width (°)	0.76+0.14tanθ
hkl ranges	h= 0 7 k= -12 12 l= -17 17
No. of refl. collected:	
unique	3411
with I≥3σ(I)	3112
EAC correction factors:	
min.	0.9441
max.	1.0000
aver.	0.9741
No. of parameters refined	252
Weighting scheme	unit weight
Largest diff. peak (eÅ^{-3})	0.650
Largest shift/error	0.02
R	0.048

The selenium high resolution solid state NMR investigations of the powder pattern are not commonly used in structural studies. However, as shown by Collins *et al.* for series of the model compounds such measurements can provide useful information about the effect of crystallographic inequivalence and the range of ^{77}Se anisotropic chemical shielding.[22]

The ^{77}Se CP MAS NMR spectrum of powdered sample is shown in Figure 4c. From the spectrum analysis the triplet with phosphorus-selenium scalar coupling equal to 427 Hz can be unambiguously assigned. The splitting of ^{77}Se resonance line by ^{31}P nuclei to triplet suggests that local environment of the selenium is very similar. In fact, the P—Se bond lengths in P1A-Se-P1B unit of **1** were found to be 2.241(2) Å and 2.243(1) Å, respectively for atoms A and B. As in case of the phosphorus nucleus, due to large shielding anisotropy of the selenium, the isotropic resonance is symmetrically flanked by the spinning sidebands. The principal elements of the chemical shift tensor of the central line and averaged values of the shielding parameters are shown in Table VI.

EXPERIMENTAL

X-ray Diffraction

Crystal and molecular structure of **1** was determined by using of data collected at room temperature on a CAD4 diffractometer with graphite monochromatized radiation. Compound **1** crystallizes in triclinic system, space group $P\bar{1}$. The unit-cell parameters, other crystal data and experimental details are collected in Table VII.

Lattice constants were refined by least-squares fit of 25 reflections in the θ range 18.6–29.1°. The decline in intensities of three control reflections (1,3,−5; 1,−4,−3; 2,−3,−5) was 3.1% during 43.0 hours of exposure. Absorption correction was applied by using of the EAC program[23,24] (Table VII). A total of 3112 observed reflections with $I \geq 3\sigma(I)$ were used to solve the structure by direct methods[25,26] and to refine it by full-matrix least-squares using F's.[23,27] All hydrogen atoms were found in a difference Fourier map and refined isotropically. Anisotropic thermal parameters were applied for all nonhydrogen atoms. Final refinement converged to R = 0.048 with unit weight for 252 refined parameters (see Table VII). Values of F_{obs}/F_{calc} and the full crystallographic data are deposited at the Cambridge Crystallographic Data Centre.[28]

NMR Spectroscopy

Cross-polarization magic angle spinning solid-state ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 300 MSL instrument with high-power decoupling at 75.468 MHz for ^{13}C, at 121.49 MHz for ^{31}P and 57.22 MHz for ^{77}Se. Powder sample was placed in cylindrical rotor and spun at 3.0–4.2 kHz. For ^{13}C experiments the field strength for ^{1}H decoupling was 1.05 mT; contact time 5 ms, repetition time of 6 s and spectral width of 20 kHz were used, and the FID was represented by 8 K data points. Spectra were accumulated 100–500 times to achieve a reasonable signal to noise ratio. The ^{13}C chemical shifts were calibrated indirectly through the glycine carbonyl peak observed at 176.34 ppm relative to tetramethylsilane.

For the ^{31}P experiments, the field strength for ^{1}H decoupling was 1.05 mT; a contact time of 5 ms, a repetition time of 6 s and a spectral width of 20 kHz were used, and 8 K data points represented the FID. Spectra were accumulated 12–500 times which gave a reasonable signal to noise ratio. The ^{31}P chemical shifts were calibrated indirectly through the 85% phosphoric acid peak set at 0 ppm.

For the ^{77}Se experiment, the field strength for ^{1}H decoupling was 1.05 mT; contact time of 5 ms, repetition time of 10 s and spectral width of 100 kHz were used, and 8 K data points represented the FID. Spectrum was accumulated 10 K, which gave reasonable signal to noise ratio. Ammonium selenate was used as convenient material for setting up CP experiment and also as a secondary chemical shift reference standard set at 1040 ppm (dimethyl selenide is usually taken as primary reference standard).

The principal elements of the chemical shift tensor of the ^{31}P resonance for powdered samples were calculated from spinning sidebands intensities using the method of Berger and Herzfeld.[18] Employing the commonly used notation, the isotropic chemical shift is given by the expression

$$\delta_{iso} = (1/3)(\delta_{11} + \delta_{22} + \delta_{33}).$$

Asymmetry parameter, η, is given by the equation

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso}).$$

The anisotropy parameter, $\Delta\delta$, is defined as

$$\Delta\delta = \delta_{33} - (1/2)(\delta_{11} + \delta_{22})$$

with principal elements δ_{ii} defined by the relationship

$$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|.$$

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