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Two-dimensional and variable temperature ^{31}P solid-state NMR studies of single crystals containing symmetrical/unsymmetrical bis[6-*O*,6-*O′*-(1,2:3,4-diisopropylidene-α-D-galactopyranosyl)thiophosphoryl] dichalcogenides†

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The organisation and phase transition of single crystals containing three isostructural bis[6-*O*,6-*O′*-(1,2:3,4-diisopropylidene-α-D-galactopyranosyl)thiophosphoryl] dichalcogenide derivatives: disulfide 1, diselenide 2 and mixed seleno-sulfide 3, was deduced upon 1D, 2D and variable temperature ^{31}P NMR experiments.

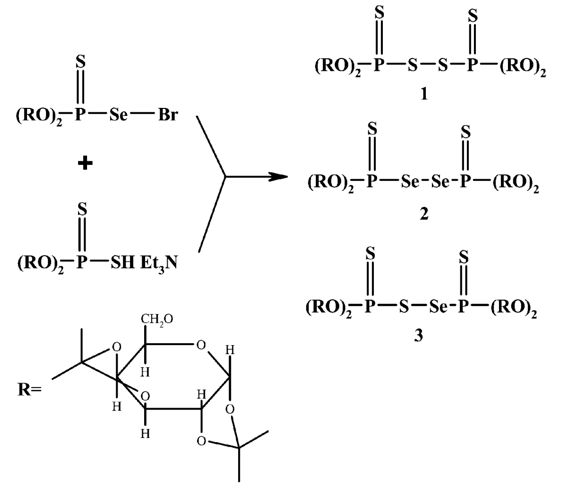
Our continuing interests in understanding the nature of C–H···X=P (X = chalcogenide) intermolecular contacts as well as developing of spectroscopic techniques, which aid characterisation,[1] prompted us to extend our project to new models permitting the observation of such interactions directly. From the point of view of NMR the best candidate for this purpose is selenium, which possesses attractive spectroscopic parameters. The natural abundance of the magnetically active ^{77}Se isotope is 7.58%, $I = \frac{1}{2}$ (*i.e.* no quadrupolar moment) and its receptivity is *ca.* three times larger than ^{13}C.[2]

In a previous paper we revealed that bis[6-*O*,6-*O′*-(1,2:3,4-diisopropylidene-α-D-galactopyranosyl)thiophosphoryl] disulfide **1**, which forms inclusion complexes with distinguishable NMR parameters, is a very useful 'host' molecule to search for C–H···S interactions in the solid state.[3] In this context, the seleno-analogs of **1** seemed to be promising models to observe C–H···Se contacts. As we found, among different modifications, products obtained in the synthesis of the mixed seleno–sulfide derivative of **1** have the most intriguing features.

The preparation of mixed seleno–sulfides with high yield is still a challenge for synthetic chemistry.[4] Hence, we were not surprised that in reaction of selenyl bromide and triethylamine dithiophosphoryl salt[5] we obtained single crystals comprising of a mixture of three products; disulfide **1**, diselenide **2** and mixed seleno–sulfide **3** (Scheme 1).

Their assignment in the liquid phase was based upon ^{31}P NMR spectral characteristics (Fig. 1(a)), values of direct phosphorus 31–selenium 77 spin–spin coupling constants and HRMS.‡

The fact that this complex mixture forms regular crystals containing a 1 : 1 : 1 ratio of the individual components **1**, **2** and **3** was rather unexpected and motivated us to carry out more advanced solid-state studies. A selected single crystal was placed in a 4 mm zirconium rotor filled with silica gel and spun at 10 kHz. The ^{31}P CP/MAS spectrum recorded with RAMP cross-polarization[6] and TPPM decoupling[7] is shown in Fig. 1(b). It is apparent that the solid-state NMR spectrum is much more complex compared to that obtained in solution. According to our previous observation published elsewhere,[8] for this class of compounds, the number of signals in the isotropic region depends on the symmetry of the unit cell. When the whole molecule is an independent part of the asymmetric unit two signals for crystallographically and magnetically nonequivalent phosphorus sites are seen. When the half molecule is an asymmetric unit only one signal is observed. The assignment of a ^{31}P CP/MAS spectrum showing eight signals in the isotropic part is a challenging problem. Useful information was obtained from a 2D spin-exchange experiment, which allowed establishing of the connectivity between phosphorus sites. From inspection of spectrum recorded with a mixing time of 1 s (Fig. 2(a)) it is clear that site A is connected with C, B with F, D with E and G with H. Relatively long mixing times correspond to large P···P separations, which for **1** is *ca.* 4.4, for **2** is 4.8 and for **3** should be in between. By analogy to assignments in solution,



Scheme 1

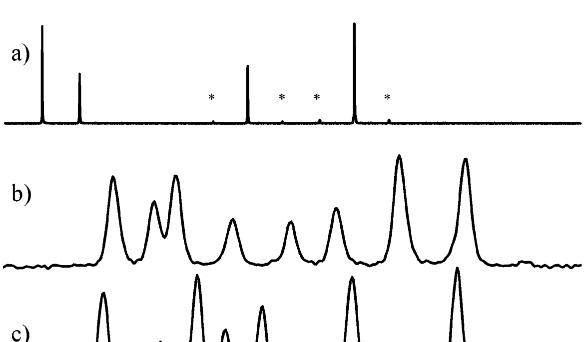


Fig. 1 (a) 202.40 MHz ^{31}P spectrum of a crystal dissolved in CDCl$_3$. Asterisks denote the satellites corresponding to ^{31}P–^{77}Se *J* coupling. (b) 121.49 MHz ^{31}P CP/MAS spectrum of a single crystal held in silica gel and spun at 10 kHz. (c) 121.49 MHz ^{31}P CP/MAS spectrum of a single crystal heated to 390 K. Other conditions of measurement as in (b).

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† Electonic supplementary information (ESI) available: ^{77}Se CP/MAS spectra of untreated and heated crystals, and DSC profile. See http://www.rsc.org/suppdata/cc/b2/b204627j/

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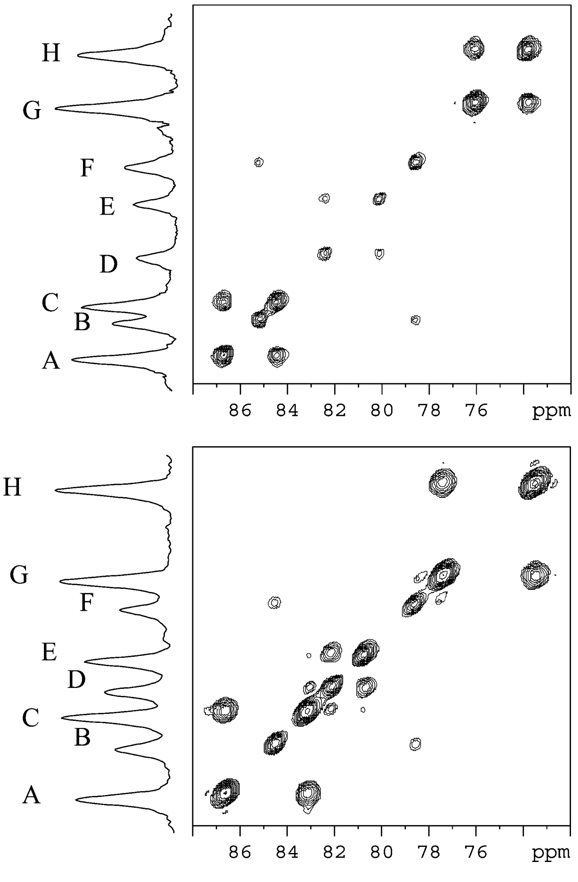

Fig. 2 ^{31}P 2D spin-exchange MAS spectrum obtained with a mixing time of 1 s at 10 kHz spinning rate: (a) crystal at ambient temperature (upper) and (b) crystal heated to 390 K (bottom).

we assume that A, C resonances arise from disulfide **1**, B, F from **3** and G, H from diselenide **2**.

The question arises as to the origin of D and E signals, for which the ^{31}P chemical shift is not diagnostic and assignment is ambiguous. The ^{77}Se CP/MAS experiment provides an additional probe and establish that these peaks arise from seleno–sulfide **3** (ESI†). Two types of molecules of **3** in the crystal may be due to the presence of solvents inside the lattice and different types of solute–solvent interactions and/or specific architecture of domains. ^{13}C CP/MAS experiments and DSC studies confirmed the presence of solvent in the crystal (ESI†). The variable temperature (VT) ^{31}P measurements revealed the change of phase organisation. Fig. 1(c) shows the ^{31}P CP/MAS spectrum at 390 K, which corresponds to the DSC region after the release of solvent but below the melting point. As seen, values of ^{31}P chemical shifts are different from the sample before heating but the gross structure of the crystal is retained. A 2D spin exchange experiment for the heated material (Fig. 2(b)) shows more connections between phosphorus sites, *i.e.* new cross-peaks between C and D, C and E as well as F and G. The long-range connectivity is even better seen at a longer mixing time of 7 s (Fig. 3).

The weak-intensity cross-peaks prove that without the solvent in the crystal lattice there are a number of P···P contacts below 10 Å, which are not seen for crystal at ambient temperature. In Fig. 3 it is interesting to note the lack of the correlation peaks for B and F resonances. This is due to significant differences of ^{31}P T_1 relaxation times for components of the crystal. At long mixing times the intensity for both signals is greatly reduced. We predict that the T_1 parameter can be important and a very diagnostic probe in investigation of inclusion phenomena. Finally, melting completely destroys the crystal architecture and the recorded spectrum is very broad and featureless.

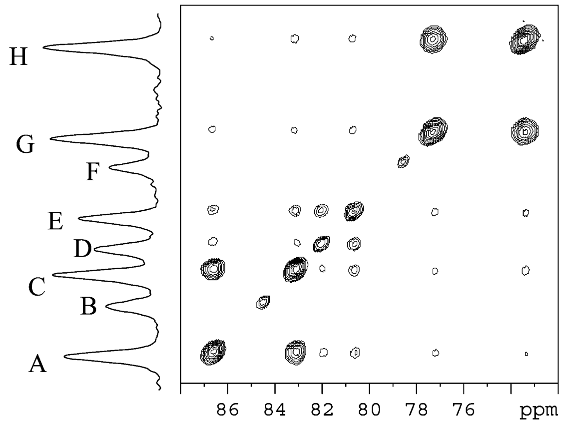

Fig. 3 ^{31}P 2D spin-exchange MAS spectrum obtained with mixing time of 7 s at 10 kHz spinning rate of a crystal heated to 390 K.

In conclusion, we present the unique solid-state features of isostructural molecules, which belong to 'axes-wheels' host models. The formation of three component crystals with occluded guest molecules is rather unusual. Our preliminary studies show that this system possesses great ability to include other solvents. Hence it can be used to investigate of mechanism of inclusion as well as the relationship between intermolecular contacts and NMR spectral parameters. The current project covers the assignment of X-ray structure for this material. The solid-state NMR data can be considered as an important director in choosing the best refinement.

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Notes and references

‡ Unit cell determination showed that the crystals are trigonal, space group $P3_2$, with a = 11.87, b = 11.87, c = 44.77 Å; the full crystal structure has not yet been determined. ^{31}P chemical shifts in CDCl$_3$: for **1**, δ 88.8; for **2**, δ 77.3; for **3**, δ 87.4 and 81.2. $^{1}J_{^{31}\mathrm{P}-^{77}\mathrm{Se}}$ for **2** and **3** = 515 Hz. ^{77}Se chemical shifts in CDCl$_3$: for **2**, δ 397.5; for **3**, δ 451.2. HRMS (*m*/*z*): for **1**, 1249.47 (M + Na); for **2**, 1297.39 (M + Na); for **3**, 1265.44 (M + Na).

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