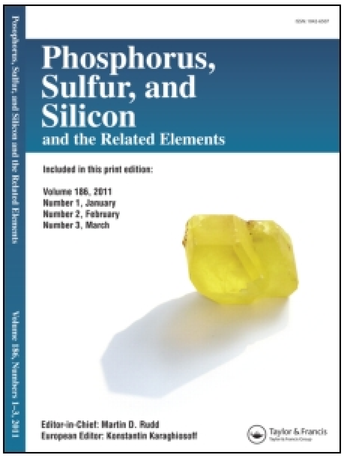

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HIGH RESOLUTION SELENIUM SOLID STATE NMR SPECTROSCOPY AS A TOOL FOR STRUCTURAL STUDIES OF ORGANOSELENIUM COMPOUNDS.

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ABSTRACT; This communication shows several applications of ^{1}H-^{77}Se CP/MAS NMR; i) X-ray crystallography and ^{77}Se solid state NMR spectroscopy as complementary tools for studies of polymorphs, ii) sensitivity of ^{77}Se to molecular packing effect, iii) recent progress in studies of phosphoroorganic diselenides and relationship between the molecular structures and ^{77}Se effective dipolar/chemical shift parameters T_{ii}.

Keywords; Organoselenium compounds, solid state NMR, ^{77}Se CP/MAS.

INTRODUCTION

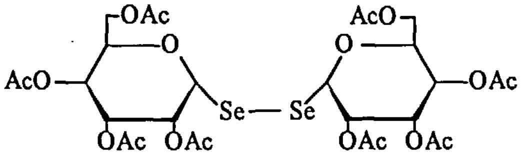
Solid state NMR spectroscopy has become one of the most powerful methods for structural studies of all kinds of solids including single crystals, crystalline powders, amorphous powders and glasses. Due to recent progress in NMR technique the number of nuclei can be studied now by means of the NMR spectroscopy, however selenium-77 is one of the most attractive.[1] Its natural abundance is 7.58%, nuclear quantum number I is 1/2 (*i. e.* it has no quadrupolar moment) and its receptivity is ca 3 times larger compared to ^{13}C. ^{77}Se chemical shift which covers range ca. 3000 ppm is sensitive probe to very subtle structural effects both in liquid and solid phase. In this communication a few applications of high resolution ^{77}Se solid state NMR spectroscopy (Cross-Polarization Magic Angle Spinning experiment, CP/MAS) in structural studies of organoselenium compounds are reported.

X-RAY CRYSTALLOGRAPHY AND ^{77}Se SOLID STATE NMR SPECTROSCOPY AS COMPLEMENTARY TOOLS.

Solid state NMR provides the link between NMR data obtained in solution or liquid phase and results from single-crystal X-ray or neutron diffraction studies. Comparing the isotropic chemical shifts and further the structural results characterizing the geometry of molecules in the crystal lattice it is possible to draw conclusions regarding the changes of conformation, configuration, the nature of the intermolecular contacts in both phases as well as formation of different polymorphs. Since the solid state NMR use a powder specimen not only one selected single-crystal this method can provide immediate indication of the presence of polymorphs, solvates, inclusion complexes *etc.* that may exist in the crystalline state.

The investigation of bis(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl) diselenide **1** (Scheme 1) shows that by the little change the crystallization conditions using the same solvent it is possible to obtain polymorphs with different molecular structure.[2]

Scheme 1



The diselenide **1** crystallized from methanol forms three polymorphs. Crystal and molecular structure of two of them were assigned by X-ray crystallography; crystals **1a** are orthorhombic, with space group $P2_12_12_1$ whereas crystals **1b** are orthorhombic with space group $P2_12_12$. Polymorphs **1a** and **1b** have molecular structures with *anti-syn* and *anti-anti* arrangements of the C-C-Se-Se-C-C backbone. The **1a** modification crystallize with one molecule as asymmetric part of the unit cell while **1b** with half molecule as asymmetric unit. The high resolution solid state ^{77}Se NMR employed to investigation of **1a** and **1b** immediately shows the differences in molecular symmetry and molecular packing (Fig.(1)).

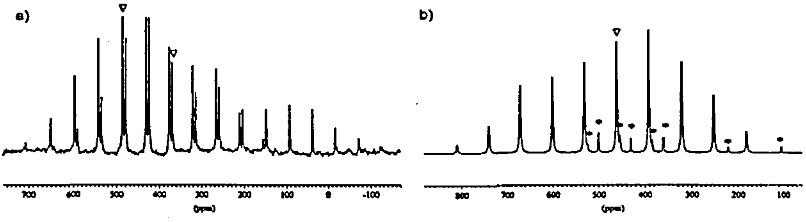


Fig.1.^{1}H-^{77}Se CP/MAS spectra of bis(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl) diselenide **1a** (a) and **1b** (b). Both spectra have 8K data points, 50 Hz line broadening, 1 ms contact time. Asterisks denote peaks from the **1c** polymorph. The isotropic lines are marked by triangles.

The principal elements (δ_{ii}) of the ^{77}Se chemical shift tensors for polymorphs **1a** and **1b**, determined from spinning sideband intensities and further the anisotropy and asymmetry parameters very well correlate to changes of the local geometry around of selenium centers. The structure of modification **1c**, which gave crystals of insufficient quality for XRD measurements, was deduced from solid state NMR and molecular mechanics calculations.

SENSITIVITY OF ^{77}Se NMR TO CHANGES OF MOLECULAR PACKING IN THE CRYSTAL LATTICE.

The excellent example showing the sensitivity of ^{77}Se CP/MAS NMR spectroscopy to molecular packing effect is investigation of triphenylphosphine selenide **2**.[3] The compound **2** crystallizes in $P2_1/c$ space group with two molecules in the asymmetric part of the unit cell. Although the presence of two molecules of phosphine selenide in the unit cell is apparent the ^{31}P CP/MAS experiment is not sensitive enough to distinguish them (Figure 2a). Figure 2b shows the ^{77}Se CP/MAS spectra of sample **2** enriched with 70% ^{77}Se. Two spinning sideband systems corresponding to A and B molecules in the asymmetric unit are observed. This result is in excellent agreement with X-ray data and shows that in this case selenium NMR is much more sensitive probe to search the molecular packing effect compared to phosphorus.

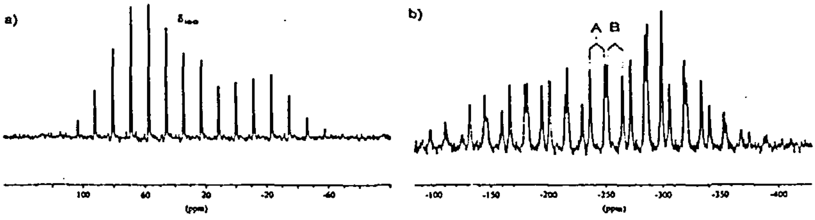


Fig. 2 a) 121.49 MHz ^{1}H-^{31}P CP/MAS experimental spectra of triphenylphosphine selenide **2**. Spectrum has 8K data points, a contact time 5 ms and 100 scans. b) 57.26 MHz ^{1}H-^{77}Se CP/MAS experimental spectrum of enriched sample (70% ^{77}Se) **2**. Spectrum has 8K data points with 10 Hz line broadening, a contact time of 1 ms and 2K scans.

RECENT PROGRESS IN STUDIES OF PHOSPHOROORGANIC DISELENIDES. THE RELATIONSHIP BETWEEN THE MOLECULAR STRUCTURE AND ^{77}Se CHEMICAL SHIFT PARAMETERS.

As shown in our previous papers, phosphoroorganic dichacolgenides are useful models for investigation of structure and dynamics of phosphoroorganic compounds in the solid state. Comparing the molecular structure of bis(organothiophosphoryl) diselenides it was found that Se-Se bond length depends on P-Se-Se-P torsion angle. The values of asymmetry parameters η and κ obtained for series of diselenides indicate that Se shielding is not localized to a particular bond but is averaged out over the entire tetrahedral.[4,5] The comparison of Ω values show that anisotropy parameters for diselenides differ *ca.* 160 ppm and there is linear relationship between Se-Se distance and span Ω. Analysis of the effective dipolar/chemical shift tensor parameters T_{ii} revealed linear correlation between T_{33} and phosphorus-selenium distance.

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