High-Resolution Solid-State NMR Studies of Inclusion Complexes

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Abstract  New applications of 1D and 2D solid state (SS) NMR spectroscopy in structural studies of inclusion complexes (ICs) formed by organic host lattices (cyclodextrins, calixarenes, cyclophosphazenes, and fullerenes) are described. Each section of the review gives short characteristics of host molecules and recent applications of SS NMR. Less common systems, which are interesting as models for SS NMR studies, (bis[6-O,6-O’-(1,2;3,4-diisopropylidene-α-D-galactopyranosyl) thiophosphoryl] disulfide (DGTD) and 1,2-dichloroethane/tris(5-acetyl-3-thienyl) methane (TATM)), are also discussed.

Keywords  CP/MAS · Host-guest chemistry · Molecular motion · Calixarenes · Cyclodextrins · Cyclophosphazenes · Fullerenes · Solid-state NMR
1 Introduction

One of the most important challenges before modern chemistry is to understand the nature of processes responsible for the formation of complex multi-component structures. Such assemblies are synthesized with the intention of obtaining products with desired properties and potentially being used as “molecular machines” [1]. There are several classes of compounds which can form multi-component structures [2], and inclusion complexes (ICs) are one of the most important. Synthetic procedures and structural studies of inclusion compounds have been exhaustively discussed and described in several textbooks [3]. The nature of host-guest interactions, the spatial arrangement of components, and the character of inter-molecular contacts have been analyzed different techniques in the liquid and solid phase [4].

Solid State (SS) NMR is a spectroscopic technique which can answer most of these questions for any solids; crystalline, polycrystalline, amorphous phases, glasses, etc. Thus the growing popularity of NMR spectroscopy as a tool for structural elucidation of different solid supramolecular assemblies is fully understandable. Ripmeester and Ratcliffe reviewed the literature on applications of solid state NMR in supramolecular chemistry up to 1996 [5] where a short introduction to the theoretical background, experimental NMR techniques, and examples of problems which can be resolved by NMR, are presented.

In this chapter, we would like to present recent achievements of high-resolution solid-state NMR in the field of structural studies of inclusion complexes. A similar subject was recently covered by Ripmeester and colleagues in a review published in the Encyclopedia of Nuclear Magnetic Resonance Spectroscopy [6]. However, as the authors stated “a great variety of both organic and inorganic hosts and guests are amenable to study by NMR spectroscopic techniques, but it is not possible to cover the field in a comprehensive manner as it has now so widely diversified”. Although only two years have passed from the publication of Ripmeester et al., a similar problem occurred during the preparation of this article. This fact clearly proves how SS NMR has become a common and important diagnostic tool in structural studies of ICs.

The inclusion complexes are two-component assemblies consisting of host and guest molecules. Although NMR spectroscopy is a technique which permits the monitoring of both components in one experiment, in more advanced structural studies different methodological approaches are usually implemented. The most powerful method of exploring the structure and dynamics of guest molecules in a host lattice is $^2$H NMR broad-line shape analysis. The current literature describing $^2$H SS NMR of ICs is very extensive, and as it seems to us that low resolution $^2$H NMR forms a separate topic, it will not be discussed here.

Narrowing the field of discussion further, we will only present here NMR studies of ICs formed by organic host molecules. Readers interested in inor-