SOLID-STATE ^{39}K NMR SPECTROSCOPY FOR ORGANIC SALTS AT 19.6 T

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Introduction

Although K^+ ions are crucially important in biological systems, it is generally difficult to directly probe K^+ ion binding by NMR spectroscopy. This is because ^{39}K (spin = 3/2) is a quadrupolar nucleus and has a very low Larmor frequency. In addition, the ^{39}K chemical shift range for K^+ ions is small. For these reasons, it is difficult obtain ^{39}K NMR spectra containing resolved signals. One obvious way for overcoming these difficulties is to perform solid-state ^{39}K NMR experiments at the highest magnetic field possible. Here we report 2D MQMAS ^{39}K NMR spectra for organic compounds at 19.6 T.

Experimental

All solid-state ^{39}K NMR experiments were performed at NHMFL.

Results and Discussion

Fig. 1 shows solid-state ^{39}K NMR spectra for hydrated dipotassium glucose-1-phosphate. The crystal structure of this compound suggests that the two K^+ ions are crystallographically distinct. One K^+ ion is coordinated with eight ligand atoms and the other is penta-coordinated. The two K^+ ions thus exhibit very different NMR parameters. The spectral features from the two K^+ sites are overlapped. To obtain better resolution, we used the 2D MQMAS method. Fig. 2 shows the self-assembly process and solid-state ^{39}K NMR results for 5'-tert-butyl-dimethylsilyl-2',3'-O-isopropylidene guanosine (**G1**). This guanosine nucleoside is known to form a G-quadruplex structure containing three K^+ ions. As seen from Fig. 2, the self-assembled structure is reminiscent of an ion channel. In this case, the three K^+ ions are very similar, each coordinating to eight carbonyl oxygen atoms. Even at 19.6 T, it is not possible to resolve these sites in the ^{39}K MAS spectrum. In the 2D MQMAS spectrum, on the other hand, two groups of signals are clearly seen. The tentative assignment is indicated in Fig. 2.

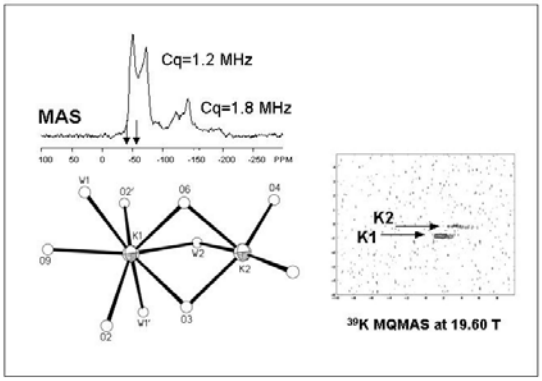

Figure 1

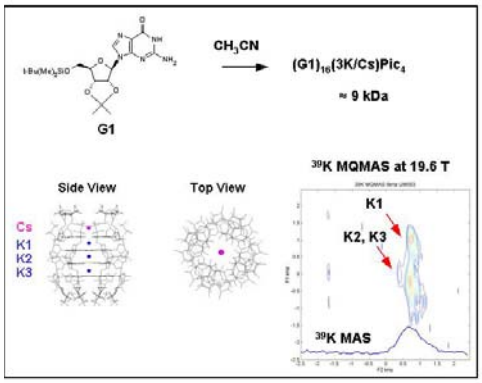

Figure 2

Conclusions

Our preliminary results demonstrate that, with the 19.6-T magnet, it is possible to detect a single K^+ ion in a 9-kDa molecular system. We anticipate that the sensitivity for solid-state ^{39}K NMR will be further improved with the new installation of the 21-T magnet at NHMFL.

Acknowledgement

This research was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.