

Analysis of chloride ion binding environments in organic and inorganic systems using chlorine-35/37 solid-state NMR spectroscopy

David L. Bryce, Becky P. Chapman, Gregory D. Sward and Elijah B. Bultz

Department of Chemistry, University of Ottawa, Ottawa, Ontario

dbryce@uottawa.ca

In the past year we have made significant progress using chlorine solid-state nuclear magnetic resonance as a probe of the chlorine binding environments in both inorganic and organic systems. Due to the NMR properties of both chlorine-35 ($I = 3/2$; $\Xi = 9.809$ MHz; N.A. = 75.53 %; $Q = -8.165$ fm²) and chlorine-37 ($I = 3/2$; $\Xi = 8.165$ MHz; N.A. = 24.47 %; $Q = -6.5$ fm²), high magnetic fields such as the 21.1 T instrument at the National Ultrahigh-Field NMR Facility for Solids are desirable for these studies. The advantage of the high field for these studies is two-fold: (i) the second-order quadrupole interaction scales inversely with magnetic field, leading to narrower lines and (ii) the effects of chemical shift anisotropy (CSA) increase with field, often allowing for the extraction of both sets of parameters.

Much work has been done in the past year in the area of ionic inorganic solids, with a study of the chloride binding environments in the anhydrous Group 13 chlorides having been completed. These studies benefited greatly from access to the 21.1 T system, as the large chlorine-35/37 quadrupolar coupling constants (C_Q) rendered experiments at 11.7 T unsuccessful. A total of four materials were studied using variable-offset QCPMG ^{35/37}Cl solid-state NMR: AlCl₃, InCl₃, GaCl₂ and GaCl₃. The observed magnitudes of $C_Q(^{35}\text{Cl})$ ranged from 22.5 to 40.44 MHz, corresponding to central transition spectra ranging from 1.0 to 2.5 MHz in breadth. The experimental and simulated ³⁷Cl NMR spectra of solid GaCl₃ are shown in Figure 1.

This material crystallizes in a dimeric structure in which there are two terminal chloride sites and one bridging site. In addition, the high field instrument allowed for CSA parameters to be extracted for three of the materials, despite the large amount of second order quadrupolar broadening. The chemical shift spans observed ranged from 200-500 ppm, much greater than those observed in organic hydrochlorides. In addition to the chlorine studies, indium-113/115 and gallium-69/71 solid-state NMR experiments were also carried out on the 21.1 T instrument. The results from this study are summarized in a recent *Physical Chemistry Chemical Physics* article [1]. Studies into the NMR properties of these and related materials are ongoing; specifically, we are analyzing the influence of structure on the chlorine NMR properties of bridging and terminal chlorine sites using computational methods.

Work has also continued on the study of the chlorine binding environment in organic systems, particularly the study of polymorphism and pseudo-polymorphism using chlorine solid-state NMR.

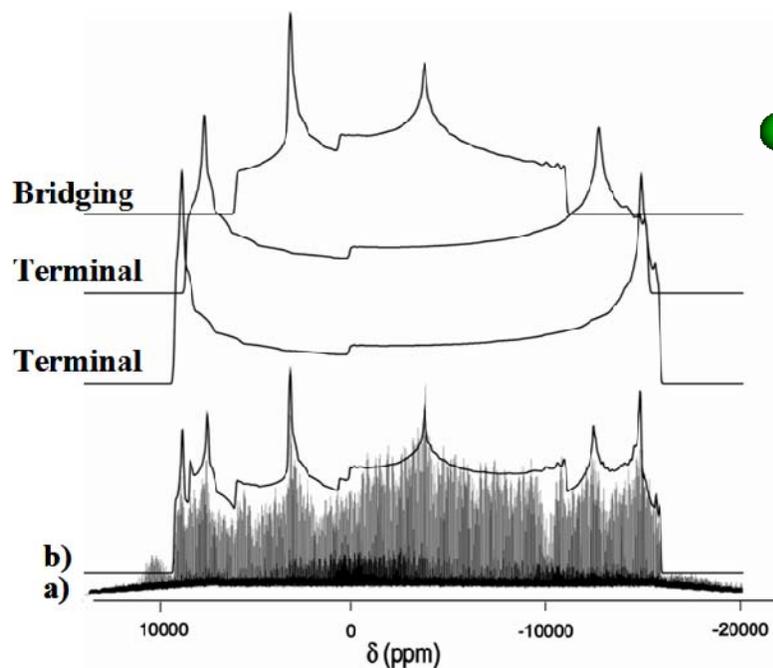
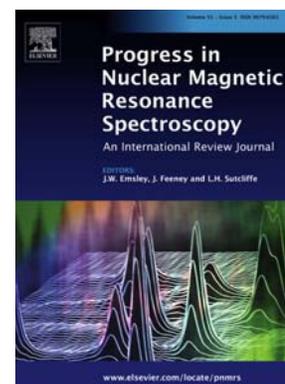


Figure 1: Local structure, and experimental (a) and simulated solid-state chlorine-37 NMR spectra of gallium trichloride at 21.1 T. The best-fit simulation appears in (b). Simulations of the three individual sites appear above. Taken from reference [1].

Lysine hydrochloride dihydrate, a material which was included in an earlier study of amino acid hydrochlorides, is known to have two different polymorphs in the anhydrous phase: α , formed through heating at a temperature above 115 °C and β , formed by heating below 90 °C. We have initiated a study of these two polymorphs, for which there are no known crystal structures, by carbon ^{13}C and $^{35/37}\text{Cl}$ solid-state NMR. Preliminary results have been carried out on the α form at 9.4 and 11.7 T. The use of the 21.1 T instrument will be crucial for the completion of the study, as it will allow for the collection of $^{35/37}\text{Cl}$ fast MAS NMR spectra and provide improved resolution in the possible case of multiple crystallographic sites.

In the past year we have also written two review articles on chlorine, bromine, and iodine solid-state NMR for *Annual Reports on Nuclear Magnetic Resonance Spectroscopy* and *Progress in Nuclear Magnetic Resonance Spectroscopy*, both of which are now available [4, 5].



References

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