High Resolution ^{113}Cd Nuclear Magnetic Resonance by Pulse Fourier Transform

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Summary High resolution ^{113}Cd n.m.r. signals have been obtained in the pulse Fourier transform mode for a few representative species; typical relaxation times and the high sensitivity of the chemical shift parameter make ^{113}Cd a promising nuclide for detailed studies of complexation in solution.

The ^{113}Cd nuclide (natural abundance 12·3%, $1{\cdot}09 \times 10^{-2}$ as sensitive as ^{1}H for equal number of nuclei, $I = \frac{1}{2}$) is one of the nuclides that has been largely neglected from the point of view of nuclear magnetic resonance. Although there have been wide-line n.m.r. studies,[1] no results on high resolution ^{113}Cd work have been published. We report the results of preliminary pulse Fourier transform experiments on this nuclide in liquid samples, using nearly the same techniques which are common in ^{13}C n.m.r. work. Spectra were obtained on natural abundance samples in 10 mm tubes at 19·97 MHz, using a Brüker HFX-90 spectrometer with a Digilab FTS/NMR-3 Data System and 400-2 Pulser.

Spin-lattice relaxation times were obtained by a 180°-τ-90° sequence on a Bu_2Cd sample (synthesized by the method of Sanders and Ashby)[2] and on a saturated aqueous solution of $CdCl_2$; values of about 0·2 s and 16 s, respectively, were obtained. These values appear to be typical of the samples studied so far and indicate that common high-resolution ^{13}C n.m.r. approaches will generally be suitable for ^{113}Cd studies. Although a quantitative nuclear Overhauser effect was not determined for Bu_2Cd in this study, there was clearly not a signal inversion; strong negative N.O.E.'s have been reported for some ^{29}Si spectra,[3] another case in which the magnetic moment has the opposite sign from that of ^{1}H.

The Table, which gives the chemical shifts of a few species, displays the wide range of shieldings one expects of heavy metal nuclides.[4] The aqueous $Cd(ClO_4)_2$ results at 0·1 M and 4·2 M are nearly the same (only 8·11 p.p.m. difference), whereas the analogous $Cd(NO_3)_2$ results differ by 45·69 p.p.m., and the $CdCl_2$ chemical shifts differ by 67·72 p.p.m. These results, together with the fact that the chemical shifts of 0·1 M-aqueous solutions of $Cd(NO_3)_2$ and $Cd(ClO_4)_2$ and a 4·2 M-solution of $Cd(ClO_4)_2$ are within 8 p.p.m. of each other, whereas the shift of 0·1 M-$CdCl_2$ differs from these by about 57 p.p.m., are consistent with the view that the cadmium exists primarily as hydrated Cd^{2+} in the former three solutions and is more strongly involved in complexation with chloride in the 0·1 M-$CdCl_2$ solution.

Table

Sample	Chemical shift[a]	Line width (Hz)
Bu_2Cd[b]	489·11	15
3·8 M-Aqueous $CdCl_2$ . .	124·75	4
0·1 M-Aqueous $CdCl_2$ . .	57·03	5
0·1 M-Aqueous $Cd(ClO_4)_2$ . .	0	3
0·1 M-Aqueous $Cd(NO_3)_2$	−3·72	4
4·2 M-Aqueous $Cd(ClO_4)_2$[c] . .	−8·11	5
4·5 M-Aqueous $Cd(NO_3)_2$ . .	−49·41	4

[a] P.p.m. with respect to 0·1 M aqueous solution of $Cd(ClO_4)_2$, increasing values correspond to decreasing shielding. All spectra recorded at 298 K unless otherwise indicated. [b] Spectrum obtained at 228 K in 100 s of elapsed time during data accumulation, using 1000 repetitive pulses (0·1 s between pulses). The line width was not changed by an increase in the data acquisition time following each pulse. Signal-to-noise ratio, taken as the simple ratio of peak height to r.m.s. noise level, was 47·0. Peak position was 19,970,900 Hz in a field locked to the ^{19}F signal of a capillary of C_6F_6 at 84·67088 MHz. Proton decoupling centre band at 89.991025 MHz [c] Spectrum obtained in 500 s of elapsed time during data acquisition, using 25 repetitive pulses of approximately 90°. Resolution of the data system was 2·5 Hz. Signal-to-noise ratio was 40·5. Peak position was 19,960,986 Hz in a field locked to the ^{19}F signal of a capillary of C_6F_6 at 84·67088 Hz.

The high sensitivity of ^{113}Cd chemical shifts of cadmium salts in solution to changes in the concentration and/or identity of the salt provides a means of studying the equilibrium and dynamics of complexation in such systems. With large sample tubes and long-term averaging, experiments on 0·001 M to 0·01 M samples are practicable.

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[1] For examples, see J. Winter, 'Magnetic Resonance in Metals,' Oxford University Press, Oxford, 1971, pp. 89—90; W. G. Proctor and F. C. Yu, *Phys. Rev.*, 1949, **76**, 1728; D. C. Look and D. L. Moore, *Phys. Rev. B.*, 1972, 3506.

[2] J. R. Sanders and E. C. Ashby, *J. Organometallic Chem.*, 1970, **25**, 277.

[3] R. L. Scholl, G. E. Maciel, and W. K. Musker, *J. Amer. Chem. Soc.*, 1972, **94**, 6376; G. C. Levy, *ibid.*, p. 4793.

[4] P. R. Wells in 'Determination of Organic Structures by Physical Methods,' vol. 4, eds. F. S. Nachod and J. J. Zuckerman, Academic Press, New York, 1971.