MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 222–226 (1997)

A Lithium-6 CP/MAS Standard

Glenn H. Penner* and Jennifer Hutzal
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

The ^{6}Li cross polarization magic angle spinning (CP/MAS) spectra of several commercially available lithium-containing solids were obtained. Lithium acetate hydrate is evidently the sample of choice for setting up the ^{6}Li{^{1}H} CP/MAS experiment. A ^{6}Li spectrum of the sample without spinning yields a Pake doublet that can be best simulated with a ^{6}Li quadrupolar coupling constant, $\chi(^6\mathrm{Li})$, of 2.5 ± 0.2 kHz and an asymmetry parameter, η, of less than 0.2. A noticeable asymmetry in the intensities of the two halves of the powder line shape, enhanced by increasing the static magnetic field by a factor of 2.5, is probably due to the effects of chemical shift anisotropy. © 1997 by John Wiley & Sons, Ltd.

Magn. Reson. Chem. **35**, 222–226 (1997) No. of Figures: 4 No. of Tables: 1 No of References: 9

Keywords: lithium-6 CP/MAS standard; quadrupolar coupling constant; chemical shift anisotropy

Received 19 August 1996; revised 22 October 1996; accepted 29 October 1996

INTRODUCTION

Lithium-7 has been a much exploited nuclear isotope for both solution[1] and solid-state[2] NMR studies. In recent years, ^{6}Li NMR spectroscopy has become increasingly popular in solution-state studies.[1,3] In contrast, reports of solid-state ^{6}Li NMR spectroscopy are relatively rare.[4] Although the receptivity of ^{6}Li is only 0.23% that of ^{7}Li, it is 3.6 times higher than that of ^{13}C. A much more serious problem is that of long ^{6}Li relaxation times. If the T_1 is dominated by the quadrupolar mechanism ^{6}Li T_1 values will be 638 times longer than those for ^{7}Li. This implies that long relaxation delays would be required in the implementation of single-pulse experiments. As demonstrated recently by Harris and Minoja,[4a] the use of a cross polarization (CP) experiment is an attractive alternative. The main advantage of CP is that the experimental relaxation delay depends on the much shorter proton relaxation time. Another advantage is the signal enhancement provided by transfer of polarization from ^{1}H to ^{6}Li: a maximum enhancement factor, $\gamma(^1\mathrm{H})/\gamma(^6\mathrm{Li})$, of 6.8 is expected.

In the past, ^{7}Li has been the nucleus of choice over ^{6}Li for studying lithium-containing solids. One disadvantage that ^{7}Li and other odd half-integer spin nuclei have is that the strong central $1/2 \leftrightarrow -1/2$ transition is broadened by the second-order quadrupolar interaction. This is not the case for ^{6}Li, which has a spin $I = 1$. Similarly, the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions for ^{7}Li are not broadened by this interaction, but obtaining high-resolution spectral information from the spinning sidebands of these satellite transitions depends critically on the ability to adjust the magic angle accurately and on the stability of sample spinning.[5] In addition, since the quadrupole moment for ^{6}Li is a factor of 49 times smaller than that for ^{7}Li, it is usually possible to concentrate all of the ^{6}Li spectral intensity into the centerband with typical sample spinning rates. Lithium-6 and several ^{6}Li salts are commercially available, enriched at about the 95% level, at affordable prices. Lithium-6 enrichment at the 95% level should increase the signal-to-noise ratio by a factor of about 13 and ^{6}Li–^{6}Li interactions will replace ^{6}Li–^{7}Li dipolar interactions, resulting in a reduction in the line broadening by a factor of approximately 2. Despite these advantages, the use of ^{6}Li or CP with magic angle spinning (MAS) has been reported only three times.[4a–c]

This paper reports a brief ^{6}Li CP/MAS investigation of several lithium-containing solids with emphasis on lithium acetate dihydrate (**1**), which has proven to be the best standard to date. The non-spinning CP spectrum of **1** is also discussed in terms of the relative contributions of the quadrupolar and chemical shift interactions to the ^{6}Li static lineshape. All the spectra obtained in this study were from samples with natural abundance (7.42%) ^{6}Li.

EXPERIMENTAL

All samples were of commercial origin (Aldrich or Strem).

^{6}Li spectra were obtained using a Bruker ASX-200 NMR spectrometer operating at ^{6}Li and ^{1}H frequencies of 29.447 and 200.111 MHz, respectively. Samples were packed into 7.0 mm o.d. rotors and spun at 5.0 kHz. A standard CP pulse sequence was used with 90° pulses of 3.7 μs and relaxation delays ranging from 10 to 120 s. Contact times of 10 ms were used, unless stated otherwise. A commercial sample (Aldrich) of lithium acetate dihydrate was used to set up the Hartmann–Hahn match (see below).

Air-sensitive or extremely hygroscopic samples were packed in a dry-box. Rotor caps, without holes, were

---

* *Correspondence to*: G. H. Penner.

Contract grant sponsor: National Science and Engineering Research Council of Canada.

CCC 0749–1581/97/040222–05 $17.50

chosen and 'painted' with a permanent marker pen. These were the only precautions taken and it should be pointed out that a number of very air-sensitive samples have been kept for days in these rotors without significant decomposition. In some cases inserts, based on the design of Merwin *et al.*,[6] were used.

Spectral simulations were performed using the program MXQET.[7] Fitting of the contact time-dependent signal intensity was effected with the software supplied by Bruker.

RESULTS AND DISCUSSION

There are several commercially available lithium- and hydrogen-containing compounds that may be considered for setting up the ^{6}Li CP/MAS experiment. Some are moderately air sensitive ($LiBH_4$, $LiNH_2$ and $LiOCH_3$) or highly air sensitive [most organolithium derivatives and $LiN(CH_3)_2$]. There are a number of hydrogen-containing lithium salts that are indefinitely stable and not highly hygroscopic. Hydrated salts such as $LiBr \cdot H_2O$, $LiOH \cdot H_2O$, $LiBO_2 \cdot 2H_2O$, $Li_2SO_4 \cdot H_2O$, $Li_2B_4O_7 \cdot 5H_2O$, $LiO_2CCH_3 \cdot 2H_2O$ and $LiCH_3COCHCOCH_3$ are potential candidates; the last two also have methyl hydrogens. In two previous studies, Harris and Minoja[4a] used hydrated lithium metaborate pentahydrate ($Li_2B_4O_7 \cdot 5H_2O$). The other two ^{6}Li investigations[4b,c] did not state what sample was used to set up the CP/MAS experiment. Our first choice was $LiO_2CCH_3 \cdot 2H_2O$ (lithium acetate dihydrate, **1**), which is available from non-specialist chemical companies and may often be found in one or more laboratories within a chemistry department. Initial single-pulse experiments, with high-power proton decoupling, indicated that the ^{6}Li T_1 in **1** is of the order of many minutes. The Hartmann–Hahn match condition was not difficult to achieve and a ^{6}Li CP/MAS spectrum of **1**, under optimized conditions (contact time 10 ms and relaxation delay 90 s), is shown in Fig. 1. The signal-to-noise ratio is about 276, which is comparable to that for the ^{13}C CP/MAS signals of adamantane on the same spectrometer! The linewidth at half-height is 12 Hz. The curve for signal intensity, $I(t_{CP})$, as a function of contact time, t_{CP}, is shown in Fig. 2. A well defined maximum is located at $t_{CP} \approx 10$ ms. If it is assumed that a perfect Hartmann–Hahn match is obtained and the ^{6}Li $T_{1\rho}$ is neglected, the CP curve can be described by the following function:[8]

$$I(t_{cp}) = I_0\left(\frac{T_{1\rho}}{T_{1\rho} - T_{CP}}\right)\left[\exp\left(-\frac{t_{CP}}{T_{1\rho}}\right) - \exp\left(-\frac{t_{CP}}{T_{CP}}\right)\right] \qquad (1)$$

where $T_{1\rho}$ is the relaxation time of the protons in the rotating frame and T_{CP} is the cross polarization time for the transfer of magnetization from protons to lithium-6. A non-linear least-squares fit of 14 points to Eqn (1) yields values of $T_{CP} = 3.4$ ms and $T_{1\rho} = 89.5$ ms. The maximum intensity value of $I(t_{CP})$ corresponding to $t_{CP} = 10$ ms is equal to $0.87I_0$. By comparison, the signal-to-noise ratio for $Li_2B_4O_7 \cdot 5H_2O$, under optimum conditions (contact time 2 ms and relaxation delay 60 s), is only 16. The ^{6}Li signal for this sample is reported to be at 6.0 ppm with respect to aqueous LiCl at infinite dilution.[4f] The ^{6}Li signal for **1** is at -0.2 ppm with respect to $Li_2B_4O_7 \cdot 5H_2O$, giving it a chemical shift of 5.8 ppm with respect to LiCl at infinite dilution. Table 1 gives the ^{6}Li chemical shifts for a number of commercially available lithium compounds. Compound **1** is one of the most readily available lithium salts, it is indefinitely stable, is not hygroscopic and yields a very strong ^{6}Li CP/MAS signal in one transient, and at present it is clearly the best choice of commercially available compounds for setting up the ^{6}Li CP/MAS experiment. It is often convenient to have standards that are pre-packed into inserts which may be easily inserted and removed from the rotors. We currently use the inserts designed by Merwin *et al.*[6] This eliminates the need to repack a standard every time it is required. We have also found that there is much less difficulty spinning the samples when they are packed into inserts. A disadvantage of these inserts is that they take about one fifth of the volume of a standard 7 mm o.d. rotor. Therefore, it is necessary to use standard samples that give significant signal-to-noise ratios. In the case of **1**, a typical 7 mm rotor holds about 280 mg whereas an

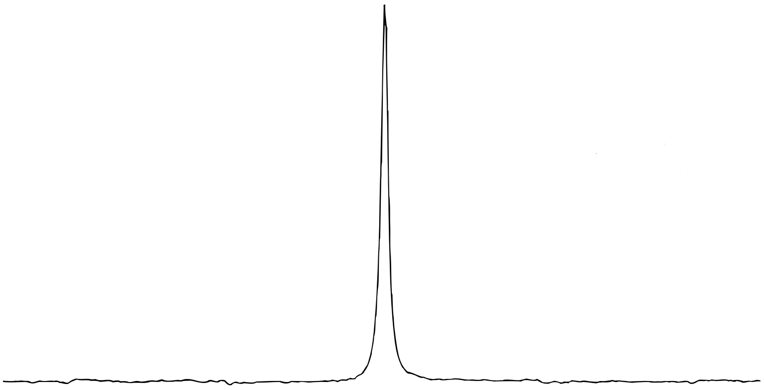

Figure 1. Natural abundance ^{6}Li CP/MAS spectrum of lithium acetate dihydrate (**1**) obtained with a single transient and a sample spinning rate of 3 kHz.

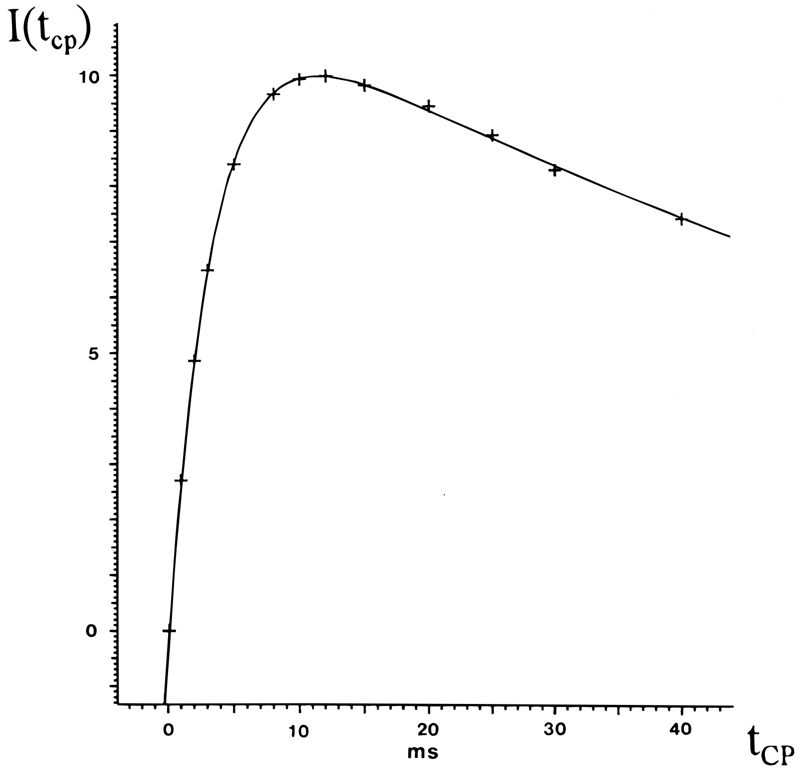

Figure 2. Relative intensity of the ^{6}Li CP/MAS resonance of **1** as a function of contact time.

insert holds only about 70 mg, a factor of four less (the factor is 1/4 instead of 1/5 because an insert can be packed much more tightly than a rotor). When an insert is used the ^{6}Li signal for **1** is easily sufficient to set up the Hartmann–Hahn match and determine the 90° pulse.

The CP spectrum of a non-spinning powder sample of **1** is shown in Fig. 3(C). The detailed features of a typical spin-1 powder lineshape are not apparent, mainly owing to large ^{6}Li–^{7}Li dipolar interactions. The lineshape can be approximately simulated with a ^{6}Li quadrupolar coupling constant, χ, of 2.5 ± 0.2 kHz, an asymmetry parameter, η, of less than 0.2 and a line broadening factor of 450 ± 50 Hz [see Fig. 3(B)]. A simulation of the spectrum with only 50 Hz of line broadening, showing clearly the peaks and shoulders of a typical $I = 1$ Pake powder lineshape, is depicted in Fig. 3(A). An interesting feature of this powder spectrum is the difference in the intensities of the two subspectra that make up the total lineshape, i.e. the $1 \leftrightarrow 0$ and $0 \leftrightarrow -1$ transitions. This is probably due to the additional effects of a small but detectable chemical shift anisotropy (CSA), $\Delta\delta$. One test of this would be to obtain the spectrum at a higher and/or lower magnetic field. A spectrum obtained at a field of 11.74 T (AMX-500) can be seen in Fig. 4. It is evident that an increase in field (by a factor of 2.5) has enhanced the effect. Unfortunately, the spectra in Figs 3(C) and 4 are not detailed enough to lend themselves to complete or accurate analysis. In addition, a proper analysis would require a knowledge of the relative orientations of the chemical shift and electric field gradient tensors (in general, three Euler angles α, β and γ are required) as well as the values of the tensor components. In principle, it should be possible to improve the lineshape by performing a triple resonance experiment involving ^{6}Li{^{1}H} CP plus simultaneous decoupling of ^{1}H and ^{7}Li. The ^{6}Li nuclei could then be considered as a dilute spin system. Work is in progress in this direction. It is also possible that one of the ^{6}Li subspectra is being

Table 1. Lithium-6 chemical shifts[a] of various lithium-containing solids

Compound	No.	δ (ppm)	Compound	No.	δ (ppm)
$LiO_2CCH_3 \cdot 2H_2O$	**1**	5.8	$LiBr \cdot H_2O$	**8**	4.9
$LiOCH_3$	**2**	5.8	$LiNH_2$	**9**	7.3
$LiOH \cdot H_2O$	**3**	6.5	$LiN(CH_3)_2$	**10**	6·0
Li acetylacetonate	**4**	7.6, 7.3, 6.8	$LiBH_4$	**11**	4.3
$LiBO_2 \cdot 2H_2O$	**5**	5.9	Li C_5H_5 (LiCp)	**12**	−8.0
$Li_2B_4O_7.5H_2O$	**6**	6.0	Li $C_5(CH_3)_5$ (LiCp*)	**13**	−7.5
$Li_2SO_4 \cdot H_2O$	**7**	5.4, 4.8	Li(2,4,6-triisopropylphenyl)	**14**	0.7

[a] In ppm with respect to aqueous LiCl at infinite dilution.

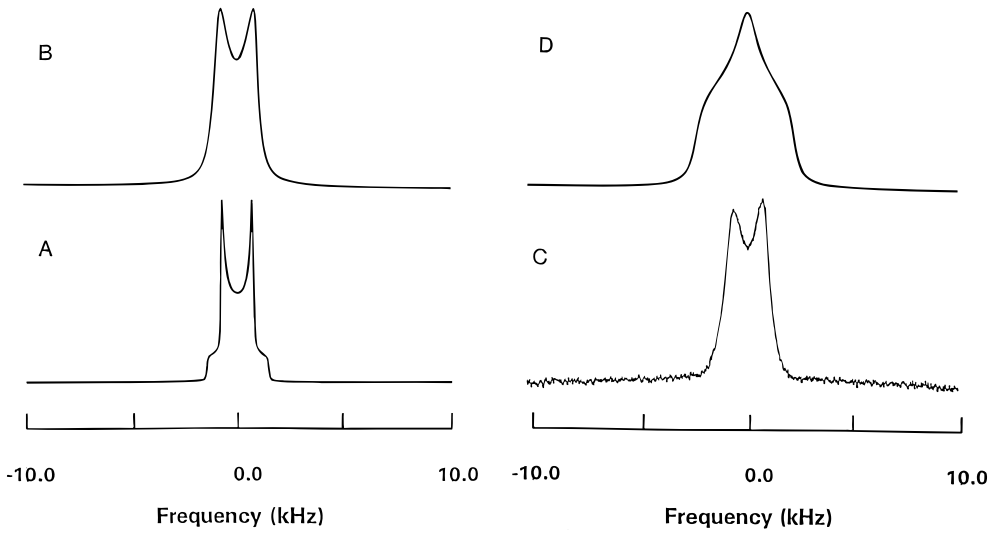

Figure 3. (A) Simulation of the powder spectrum of an $I = 1$ nucleus with a ^{6}Li quadrupolar coupling constant, χ, of 2.5 kHz, an asymmetry parameter, η, of 0.0 and only 50 Hz of line broadening. (B) The simulation with a line broadening of 0.45 kHz. (C) The experimental lineshape for a powder sample of **1**; 400 transients were obtained. (D) The lineshape simulated with the parameters of Bhat *et al.*[9] ($\chi = 3.16$ kHz and $\eta = 0.9$).

enhanced more than the other during the CP process. This could be checked by performing a single-pulse experiment (with high-power proton decoupling). Unfortunately, the ^{6}Li relaxation time is so long that an (unsuccessful) attempt indicated that such an experiment would require many days of spectrometer time (at least at natural abundance).

The χ value for ^{6}Li can be scaled by a factor of 48.9 to give a ^{7}Li quadrupolar coupling constant of 122 ± 10 kHz, which is lower than the value of 154.6 kHz obtained for a single crystal of **1**.[9] There is a significant discrepancy in the value of the asymmetry parameter, η. The single-crystal value of Bhat *et al.*[9] is reported to be 0.9, much larger than the estimated value reported here. It is possible that the difference is due to a different degree of hydration. A ^{6}Li spectrum simulated with the parameters of Bhat *et al.* is shown in Fig. 3(D). The simulated spectrum is significantly different than the observed powder spectrum [Fig. 3(C)]. Three different commercial sources of **1** gave spectra identical with that in Fig. 3(C) (Aldrich). Elemental analysis of a commercial sample of **1** was consistent with the formula $LiO_2CCH_3 \cdot 2H_2O$.

CONCLUSIONS

The potential of several commercially available lithium-containing compounds as ^{6}Li CP/MAS standards has been investigated. No one sample has proven to be ideal but lithium acetate dihydrate appears to be the best. It

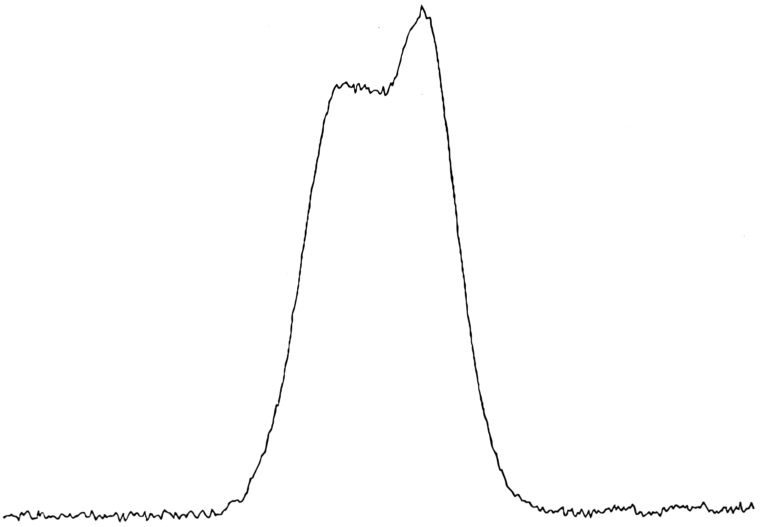

Figure 4. ^{6}Li powder spectrum of **1** obtained at 11.7 T (AMX-500); 500 transients were obtained.

is stable, not hygroscopic, it is one of the lithium salts most readily found in a typical chemistry department and the spectrum consists of a single, narrow resonance with a signal-to-noise ratio that is comparable to the CP/MAS ^{13}C resonances of adamantane. A disadvantage is that the ^{1}H T_1 is long, but this is largely compensated by the high signal-to-noise ratio.

The non-spinning CP spectra of **1** at 4.7 T (ASX-200) and 11.7 T (AMX-500) show an obvious asymmetry in the lineshape which increases with increase in field. This may be due to a small contribution of chemical shift anisotropy.

Acknowledgements

Professor Bill Power of the University of Waterloo is thanked for the 11.7 T spectrum of lithium acetate dihydrate. This work was supported by a grant from the Natural Science and Engineering Research Council of Canada.

REFERENCES

1. See, for example (a) W. Bauer and P. v. R. Schleyer, *Adv. Carbanion Chem.* **1**, 89 (1992): (b) D. Mota DeFreita, *Methods Enzymol.* **227**, 78 (1992).
2. See, for example, (a) D. Johnals, *J. Organomet. Chem.* **445**, 1 (1993); (b) L. M. Jackman, D. Çizmeciyan, P. G. Williard and M. A. Nichols, *J. Am. Chem. Soc.* **115**, 6262 (1993); (c) E. A. C. Lucken, *J. Organomet. Chem.* **4**, 25 (1965); (d) R. K. Harris, P. Jackson, L. H. Merwin and B. J. Say, *J. Chem. Soc., Faraday Trans. 1* **84**, 3649 (1988); (e) T. Pietrass and P. K. Burkert, *Z. Naturforsch., Teil B* **48**, 1555 (1993).
3. See, for example, (a) D. B. Collum, *Acc. Chem. Res.* **26**, 227 (1993); (b) S. Berger and F. Müller, *Chem. Ber.* **128**, 799 (1995).
4. See, for example, (a) R. K. Harris and A. P. Minoja, *Magn. Reson. Chem.* **33**, 152 (1995); (b) H. Gornitzka and D. Stalke, *Angew. Chem., Int. Ed. Engl.* **33**, 693 (1994); (c) J. F. O'Gara, G. Nazri and D. M. MacArthur, *Solid State Ionics* **47**, 187 (1991); (d) S. P. Bond, A. Gelder, J. Homer, W. R. McWhinnie and M. C. Perry, *J. Mater. Chem.* **1**, 327 (1991); (e) J. F. Stebbins, Z. Xu and D. Vollath, *Solid State Ionics* **78**, L1 (1995); (f) J. E. Espidel, R. K. Harris and K. Wade, *Magn. Reson. Chem.* **31**, 166 (1994).
5. W. P. Power, *Magn. Reson. Chem.* **33**, 220 (1995), and references 1–12 cited therein.
6. L. H. Merwin, A. Sebald, J. E. Espidel and R. K. Harris, *J. Magn. Reson.* **84**, 367 (1989).
7. M. S. Greenfield, A. D. Ronemus, R. L. Vold, R. R. Vold, P. D. Ellis and T. R. Raidy, *J. Magn. Reson.* **72**, 89 (1987).
8. (a) M. Mehring, *Principles of High Resolution Magnetic Resonance in Solids*, pp. 151*ff*. Springer, Berlin (1988); (b) E. O. Stejskal and J. D. Memory, *High Resolution NMR in the Solid State*, pp. 69*ff*. Oxford University Press, New York (1994).
9. V. S. Bhat, A. C. Padmanabhan and S. Srinivasan, *Acta Crystallogr., Sect. B* **30**, 846 (1975).