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High-field 19.6 T ^{27}Al solid-state MAS NMR of in vitro aluminated brain tissue

Pamela L. Bryant,[a,*] Walter J. Lukiw,[b] Zhehong Gan,[c] Randall W. Hall,[d] and Leslie G. Butler[e,1]

[a] *Department of Physical Sciences, Howard Payne University, Brownwood, TX 76801-2794, USA*
[b] *Neuroscience Center and Department of Ophthalmology, Louisiana State University Health Sciences Center, New Orleans, LA USA*
[c] *National High Magnetic Field Laboratory, NHMFL, Tallahasse, FL USA*
[d] *Department of Chemistry, Louisiana State University, Baton Rouge, LA USA*
[e] *Department of Chemistry, Louisiana State University, Baton Rouge, LA USA*

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Abstract

The combination of ^{27}Al high-field solid-state NMR (19.6 T) with rapid spinning speeds (17.8 kHz) is used to acquire ^{27}Al NMR spectra of total RNA human brain temporal lobe tissues exposed to 0.10 mM Al^{3+} (as $AlCl_3$) and of human retinal pigment epithelial cells (ARPE-19), grown in 0.10 mM $AlCl_3$. The spectra of these model systems show multiple Al^{3+} binding sites, good signal/noise ratios and apparent chemical shift dispersions. A single broad peak (−3 to 11 ppm) is seen for the aluminated ARPE-19 cells, consistent with reported solution-state NMR chemical shifts of Al-transferrin. The aluminated brain tissue has a considerably different ^{27}Al MAS NMR spectrum. In addition to the transferrin-type resonance, additional peaks are seen. Tentative assignments include: −9 to −3 ppm, octahedral AlO_6 (phosphate and water); 9 ppm, condensed AlO_6 units (Al–O–Al bridges); 24 ppm, tetrahedral AlO_3N and/or octahedral Al–carbonate; and 35 ppm, more N-substituted aluminum and /or tetrahedral AlO_4. Thus, brain tissue is susceptible to a broad range of coordination by aluminum. Furthermore, the moderate ^{27}Al C_Q values (all less than 10 MHz) suggest future NMR studies may be performed at 9.4 T and a spin rate of 20 kHz.

Keywords: ^{27}Al solid-state NMR; Human brain; RNA; Aluminum coordination; Alzheimer's disease

1. Introduction

Human exposure to aluminum is unavoidable; drinking water, buffered aspirin, food, food additives, utensils, food packaging, dust, vitamins, cosmetics, and anti-perspirant deodorants all contain variable amounts of aluminum [1]. Additionally, dust, combustion of fossil fuels, talcum powder, cat-box litter, and cigarette smoke all contribute to elevation of the aluminum concentrations in air [2]. Aluminum as Al^{3+} is a potential though controversial neurotoxin. Laser ablation microprobe mass analysis (LAMMA) has been used to quantify the amount of aluminum in brain tissue. Detection limits in the parts-per million range are obtained without using stained and treated tissues, thus avoiding contamination problems associated with tissue preparations [1,3–5]. However, measurement of aluminum concentrations is not sufficient to fully assess the role of aluminum in Alzheimer's and Parkinson's diseases. Aluminum liganding, absorption, transport, and accumulation as it passes from one area of the body to another is complex and varied. According to Martin [6], Al^{3+} can bind transferrin, di-, and triphosphate nucleosides and citrates in biological fluids. He states that Al^{3+} can displace other cations such as Mg^{2+} from nucleotides. If nucleotides are in low concentrations, catecholamines and double-helical deoxyribonucleic acid (DNA) will bind to aluminum

* Corresponding author. Fax: 1-325-649-8948.
E-mail addresses: pbryant@hputx.edu (P.L. Bryant), lbutler@lsu.edu (L.G. Butler).
[1] Fax: 1-225-578-3463.

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and in the cell nucleus Al^{3+} probably binds to nucleotide phosphates or phosphoproteins. Aluminum has been shown by several independent laboratories to be detrimental to the normal function of nucleic acids and appears to specifically alter the DNA transcription. This may be particularly important in the neuronal and glial cells of the brain which intrinsically show higher rates of transcription [7]. The determination of aluminum coordination may be necessary to understand the role aluminum plays in brain disease.

In our efforts to study aluminum coordination in diseased brains and in experimental cell models, we sought to determine if ^{27}Al NMR is a viable probe of the Al^{3+} coordination sites in representative biological tissues. Aluminum-27, 100% abundant, has a relatively small quadrupole moment [8], $Q = 146.6 \times 10^{-31}$ m^2 with a nuclear spin of 5/2 and good receptivity (gyromagnetic ratio $= 6.9704 \times 10^7$ rad/T s; [9]). However, a literature search of ^{27}Al NMR of biological tissues yielded few examples. The solution-state spectra are often broad, due to slow molecular motion, asymmetric ligand fields, multiple equilibria, and/or complexation. Very short relaxation times, shorter than the instrument dead time, make some aluminum sites undetectable. Solution-state ^{27}Al NMR [10] including low-field solution-state ^{27}Al NMR [11] and multi-field solution-state ^{27}Al NMR [12–18] have been used to study aluminated biological proteins and peptides. The ^{27}Al line width was used to index the quadrupolar coupling constant, C_Q, for alumichrome [19] but, unfortunately the value reported lies well above the known range for 6-coordinate sites.

^{27}Al solid-state NMR should be more compatible than solution-state NMR with biological tissues. ^{27}Al solid-state NMR requires no pretreatment, retains the quadrupolar information, and has no interfering solution matrix. There is only one previous report of solid-state ^{27}Al NMR of biomolecules. About 9.4 T MAS NMR spectra were acquired from the isolated senile plaques of two patients with senile dementia of the Alzheimer type [20]. Though both 4- and 6-coordinate aluminum sites were observed, the spectrum showed low signal/noise (250,000 scans) and broad line widths ($\sim$20 kHz).

Currently, innovative NMR techniques such as multiple quantum NMR [21], rotor assisted polarization transfer (RAPT; [22]), high-field, high-spin speed MAS NMR [23], 2D satellite transition NMR (STNMR[23]), and frequency-stepped NMR [24] have been introduced as methods to reduce or refocus the second order broadening and provide greater signal-to-noise ratios, increased spectral resolution, and/or improved quadrupolar information. Recently, we have used high-field (19.6 T; 833 MHz ^{1}H), high-spin speed (15–35 kHz) ^{27}Al NMR, and field-swept or frequency-stepped ^{27}Al NMR to determine the quadrupolar information for aminato and propanolato aluminum clusters [25] which have resonances indistinguishable from the background under normal NMR conditions. Hence, the application of solid-state ^{27}Al NMR to the determination of the local structure around the metal binding sites for non-crystalline biological samples is well justified.

To test this hypothesis, we acquired the spectra of aluminated total ribonucleic acid (RNA) brain tissue and aluminated human retinal pigment epithelial cells (ARPE-19) using high-field/high-spin speed solid-state ^{27}Al NMR. Multiple sites are found and chemical shift assignments are made for the coordination sites of these aluminated biological tissue models.

2. Experimental

2.1. Brain

Total RNA was extracted using Trizol reagent (phenol/guanidine isothiocyanate; Invitrogen) from one half of a whole human temporal lobe (total dissected wet weight $\sim$5.7 g) and was incubated in vitro with 0.10 mM Al^{3+} as aluminum chloride and then washed in neutral sterile saline (0.15 M NaCl, pH 7.0), solution. RNA was first precipitated with ultrapure isopropyl alcohol, washed in 80% ultrapure ethanol, and then lyophilized from 100% ultrapure ethanol. The lyophilized sample weight of total RNA recovered was 3–6 mg, representing a yield of approximately 1 mg total RNA from 1 g of tissue wet weight. Aluminum has an exceedingly high affinity for both RNA and cultured retinal cells [7]; washing of both total brain RNA and ARPE-19 cells with sterile physiological saline after incubation with aluminum chloride was utilized to remove any non-bound or peripheral aluminum. Due the preliminary nature of this work, aluminum analysis of progressive washings was not done.

2.2. Retinal

Spectra were also acquired for the whole nuclear extracts obtained from ARPE-19 cells grown in culture in 84 3.5-cm diameter wells until 80–100% confluent. The growth medium F12/DMEM (4 ml in each well) is normally changed every 72 h. The last F12/DMEM media contained 0.10 mM $AlCl_3$ and cells were incubated for 72 h. Cells were scraped out of the dishes, collected, and centrifuged; the pellet was washed twice in sterile physiological saline (0.15 M NaCl, pH 7.0), washed and precipitated from acetone, then lyophilized. The lyophilized sample weight was approximately 30–60 mg.

2.3. NMR

Solid-state ^{27}Al NMR spectra were obtained with an 833 MHz (19.6 T) ultra-narrow bore (31 mm bore size)

superconducting magnet at the National High Magnetic Field Laboratory (NHMFL) with a 40 kHz MAS probe. The chemical shift was set with α-alumina, Al_2O_3, to 18.8 ppm [26]. Samples were loaded in a 2 mm zirconia rotor, about 15 mg capacity, and spun with air at a rate of 17.8 kHz. Each spectrum was acquired using 512

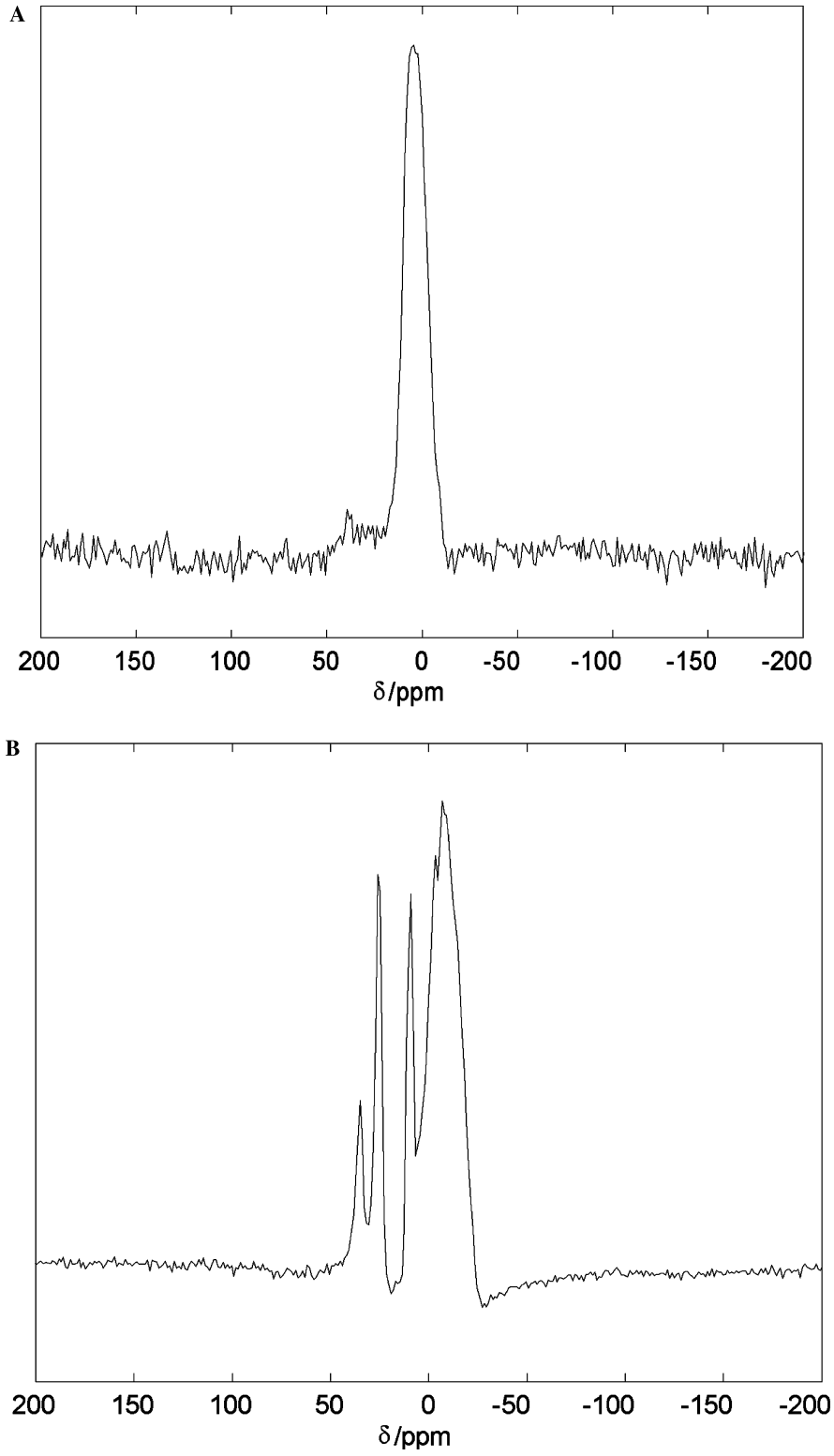

Fig. 1. 19.6 T ^{27}Al solid-state NMR ($\nu_r = 17.8$ kHz) for (A) whole nuclear extracts obtained from human retinal pigment epithelial (ARPE) cells grown in media containing 0.10 mM Al^{3+} and (B) total RNA isolated human brain superior temporal lobe tissues exposed to 0.10 mM Al^{3+} then washed in neutral saline and lyophilized.

transients, a recycle delay of 5 s, and a spectral width of 1 MHz. The broad, ca. 1000 ppm, aluminum probe background was digitally subtracted from the spectra.

3. Results and discussion

These ^{27}Al NMR spectra show (Fig. 1) multiple Al^{3+} binding sites, sufficient signal-to-noise ratio, and good chemical shift dispersion. For the lyophilized RNA brain tissue, no spinning sidebands are evident and at least three different biologically relevant sites are apparent with a fourth site that may be an inorganic precipitate or a fourth biological site. Since no spinning sidebands exist in either spectrum at 833 MHz with a 17.8 kHz spin rate (Fig. 1), the C_Q value must be less than 15 MHz for all the Al^{3+} sites in both spectra (vida infra).

Simulations of the 9, 24, and 35 ppm resonances for the total RNA isolated brain sample show the quadrupolar coupling constants (C_Q) for each of the three sites to be less than 5 MHz due to the narrow resonances. A literature search of chemical shift values were used to determine possible representative coordinations at each site (Table 1) with representative C_Q values as shown in Table 2.

These preliminary results are striking and highly encouraging. The results show that brain tissue is susceptible to a broad range of coordination with aluminum. The aluminum chemical shifts can be correlated with (a) aluminum sites coordinated to oxygen and/or nitrogen in the first coordination sphere and (b) the site symmetry of aluminum-octahedral, distorted octahedral or tetrahedral. The ^{27}Al NMR spectrum could have been a broad, featureless absorption composed of many unresolved resonances. Instead, a useful, informative spectrum is found, as shown here for in vitro aluminated total RNA isolated from a human brain sample. In contrast, a single, broad resonance indicative of transferrin (−3 to 11 ppm) is seen for the in vitro aluminated retinal (ARPE-19) cells.

A significant problem with solid-state ^{27}Al MAS NMR is an insufficiently large magnetic field, B_0, and/or insufficiently fast magic angle spin rate, v_r. Then, ^{27}Al NMR resonances may be undetectable or grossly distorted. For the instrument conditions of B_0 and v_r, Fig. 2 shows the maximum C_Q value ($\eta = 0$ and 1) for which spectra can be acquired [25,27]. For 6-coordinate aluminum sites, one of the largest reported C_Q values is 15.26 MHz (see Table 2). Spectra for this site are easily acquired at 19.6 T and $v_r = 20$ kHz. However, in an aqueous environment, 6-coordinate aluminum sites should dominate, with very

Table 1
^{27}Al tentative chemical shift assignments

Chemical shift (ppm)	Geometry	Tentative assignment	Reference
Brain			
−9	Octahedral	AlO_6 (phosphate)	[28,29]
−7	Octahedral	$AlO_x(OH_2)_{(6-x)}$(phosphate and water)	[30,31]
−3	Octahedral	AlO_5N; (N substitution upfield shift)	[12–18]
9	Octahedral	Oligomers of AlO_6(Al–O–Al bridges)	[29,31,32]
24	Octahedral	AlO_6 carbonates	[33,34]
	Tetrahedral	AlO_3N	[35]
35	Octahedral	AlO_4N_2	[36,37]
	Tetrahedral	AlO_4	[29,31,32,38]
Retinal			
−3 to 11	Octahedral	AlO_6(phosphates, hydrates, oxy bridges)	[28–31]
35	Octahedral	AlO_4N_2	[36,37]
	Tetrahedral	AlO_4	[29,31,32,38]

Table 2
Examples of experimental ^{27}Al NMR C_Q values and coordination sites

Compound	Site	C_Q/MHz	η	Reference
$Al[(\mu\text{-}O^iPr)_2Al(O^iPr)_2]_3$	6-coordination AlO_6	<2	ND*	[25]
$Al[(\mu\text{-}O^iPr)_2Al(O^iPr)_2]_3$	4-coordination AlO_4	12.31	0.14	[25]
Al_2SiO_5(Andalusite)	5-coordination AlO_5	5.96	0.7	[39]
	6-coordination AlO_6	15.26	0.08	[39]
$[(Me_2N)_2Al)(NMe_2)]_2$	4-coordination AlN_4(4-member ring)	12.2	0.8	[25]
$[(Me_2Al)(NMe_2)]_2$	4-coordination AlC_2N_2(4-member ring)	15.8	1	[25]
$[(MeAl)(NC_6H_5)]_6$	4-coordination $AlCN_3$ (cage)	17.51	0.52	[25]
$[(MeAl)(N(2,6\text{-}^iPrC_6H_3))]_3$	3-coordination $AlCN_2$ (6-member ring)	37	0	[25]
Al^{3+}/Transferrins, CO_3^{2-}(aq)		3–4.1	ND*	[12–18]

* ND, not determined.

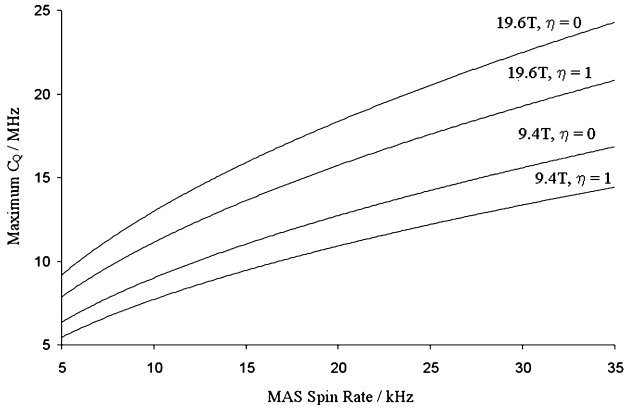

Fig. 2. The calculated maximum C_Q ($\eta = 0$ and 1) values for which a line-narrowed ^{27}Al spectrum can be obtained as a function of MAS spin rate and magnetic fields of 9.4 and 19.6 T (^1H frequencies of 400 and 833 MHz, respectively). Line-narrowed spectra can be acquired for C_Q values lying below the traces.

few, if any, of the more difficult to observe high C_Q (Table 2) distorted 3- and 4-coordinate sites. Based on these preliminary results, productive NMR studies of Al^{3+} coordinating with RNA and DNA in aqueous environments should be possible with a 9.4 T, 400 (^1H) MHz NMR spectrometer fitted with an MAS probe having a spin rate of 16.8 kHz or higher (see Fig. 2).

4. Conclusion

From this study it seems reasonable to conclude that ^{27}Al NMR spectroscopy can be used to compare the coordination of aluminum in Alzheimer's diseased brain tissue vs. normal brain tissue. Further studies will involve the use of ^{27}Al solid-state NMR to study if and how Al^{3+} coordinates with β-amyloid plaque or if dissolution of β-amyloid plaque is inhibited by Al^{3+} coordination.

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References

[1] C. Bouras, P. Giannakopoulos, P.F. Good, A. Hsu, P.R. Hof, D.P. Perl, A laser microprobe mass analysis of drain aluminum and iron in dementia pugilistica: comparison with Alzheimer's disease, Eur. Neurol. 38 (1997) 53–58.
[2] H.R. Casdorph, M. Walker, Toxic Metal Syndrome, Avery Publishing Group, Garden City Park, 1995.
[3] P.F. Good, D.P. Perl, L.M. Bierer, J. Schmeidler, Selective accumulation of aluminum and iron in the neurofibrillary tangles of Alzheimers-disease—a laser microprobe (lamma) study, Ann. Neurol. 31 (1992) 286–292.
[4] H.M. Wisniewski, G.Y. Wen, Aluminum and Alzheimer's disease, Ciba F. Symp. 169 (1992) 142–164.
[5] J.H.S. Stekhoven, K. Renkawek, I. Otte-Holler, A. Stols, Exogenous aluminum accumulates in the lysosomes of cultured rat cortical neurons, Neurosci. Lett. 119 (1990) 71–74.
[6] R.B. Martin, Aluminium speciation in biology, in: D.J. Chadwick, J. Whelan (Eds.), Aluminium in Biology and Medicine, Wiley, New York, 1992, pp. 5–25.
[7] W.J. Lukiw, Aluminum and gene transcription in the mammalian central nervous system, in: C. Exley (Ed.), Aluminum and Alzheimer's Disease, The Science That Describes the Link, Elsevier, New York, 2001, pp. 147–168.
[8] P. Pyykko, Spectroscopic nuclear quadrupole moments, Mol. Phys. 99 (2001) 1617.
[9] R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 63 ed., CRC Press, Boca Raton, FL, 1987, pp. E-78–E-82.
[10] S. Jemil, A. Fatemi, D.J. Williamson, G.R. Moore, A Al-27 NMR investigation of Al^{3+} binding to small carboxylic acids and the proteins albumin and transferrin, J. Inorg. Biochem. 46 (1992) 35–40.
[11] S.B. Vyas, L.K. Duffy, Stabilization of secondary structure of Alzheimer β-protein by aluminum (III) ions and D-Asp substitutions, Biochem. Biophys. Res. Commun. 206 (1995) 718–723.
[12] J.M. Aramini, M.W. Germann, H.J. Vogel, Field-dependent ^{27}Al NMR studies of the transferrins: an approach for the study of metal ion binding sites in larger proteins, J. Am. Chem. Soc. 115 (1993) 9750–9753.
[13] J.M. Aramini, H.J. Vogel, ^{27}Al and ^{13}C NMR studies of Al^{3+} binding to ovotransferrin and its half-molecules, J. Am. Chem. Soc. 115 (1993) 245–252.
[14] J.M. Aramini, J.A. Saponja, H.J. Vogel, Spectroscopic studies of the interaction of aluminum(III) with transferrins, Coordin. Chem. Rev. 149 (1996) 193–229.
[15] J.M. Aramini, H.J. Vogel, The effects of temperature, viscosity, and molecular size on the aluminum-27 QCT NMR of transferrins, J. Magn. Reson. B 110 (1996) 182–187.
[16] J.M. Aramini, M.W. Germann, H.J. Vogel, Soft-pulsed aluminum-27 quadrupolar central transition NMR studies of ovotransferrin, J. Magn. Reson. 129 (1997) 111–114.
[17] J.M. Aramini, H.J. Vogel, Quadrupolar metal ion NMR studies of metalloproteins, Biochem. Cell Biol. 76 (1998) 210–222.
[18] M.W. Germann, J.M. Aramini, H.J. Vogel, Quadrupolar metal-ion NMR-study of ovotransferrin at 17.6 T, J. Am. Chem. Soc. 116 (1994) 6971–6972.
[19] M. Llinas, A. De Marco, ^{27}Al NMR, a quadrupolar probe for the entatic state and stability of metallochromophores. A study of ferrichrome peptides at 65.1 MHz, J. Am. Chem. Soc. 102 (1980) 2226–2230.
[20] J.M. Candy, J. Klinowski, R.H. Perry, E.K. Perry, A. Fairbairn, A.E. Oakley, T.A. Carpenter, J.R. Atack, G. Blessed, J.A. Edwardson, Aluminosilicates and senile plaque formation in Alzheimer's disease, Lancet 15 (1986) 354.
[21] L. Frydman, J.S. Harwood, Isotropic spectra of half-integer quadrupolar spins from bi-dimensional magic-angle spinning NMR, J. Am. Chem. Soc. 117 (1995) 5367–5368.
[22] S. Prasad, H.-T. Kwak, T. Clark, P.J. Grandinetti, A simple technique for determining nuclear quadrupole coupling constants with RAPT solid-state NMR spectroscopy, J. Am. Chem. Soc. 124 (2002) 4964–4965.

[23] Z. Gan, P. Gor'kov, T.A. Cross, A. Samoson, D. Massiot, Seeking higher resolution and sensitivity for NMR of quadrupolar nuclei at ultrahigh magnetic fields, J. Am. Chem. Soc. 124 (2002) 5634–5635.
[24] P.L. Bryant, L.G. Butler, A.P. Reyes, P. Kuhns, ^{27}Al field-swept and frequency-stepped NMR for sites with large quadrupole coupling constants, Solid State Nucl. Magn. Reson. 16 (2000) 63–67.
[25] P.L. Bryant, C.R. Harwell, A.A. Mrse, E.F. Emery, Z. Gan, T. Caldwell, A.P. Reyes, P. Kuhns, D.W. Hoyt, L.S. Simeral, R.W. Hall, L.G. Butler, Structural characterization of MAO and related aluminum complexes. 1. Solid-state ^{27}Al NMR with comparison to EFG tensors from ab initio molecular orbital calculations, J. Am. Chem. Soc. 123 (2001) 12009–12017.
[26] T. Vosegaard, H.J. Jakobsen, ^{27}Al chemical shielding anisotropy, J. Magn. Reson. 128 (1997) 135–137.
[27] J. Skibsted, H. Bildsøe, H.J.P. Jakobsen, High-speed spinning versus high magnetic field in MAS NMR of quadrupolar nuclei, J. Magn. Reson. 92 (1991) 669–676.
[28] D. Champmartin, P. Rubini, A. Lakatos, T. Kiss, Complexes of aluminium(III) with glucose-6-phosphate in aqueous solutions, J. Inorg. Biochem. 84 (2001) 13–21.
[29] J. Klein, M. Ushio, L.S. Burrell, B. Wenslow, S.L. Hem, Analysis of aluminum hydroxyphosphate vaccine adjuvants by ^{27}Al MAS NMR, J. Pharm. Sci. 89 (2000) 311–321.
[30] R.F. Mortlock, A.T. Bell, C.J. Radke, ^{31}P and ^{27}Al NMR investigations of the effects of pH on aqueous solutions containing aluminum and phosphorus, J. Phys. Chem. 97 (1993) 775–782.
[31] D. Muller, I. Grunze, E. Hallas, G. Ladwig, High-field ^{27}Al NMR investigations on the aluminum coordination in crystalline aluminum phosphates, Z. Anorg. Allg. Chem. 500 (1983) 80–88.
[32] C.S. Blackwell, R.L. Patton, ^{27}Al and ^{31}P nuclear magnetic resonance studies of aluminophosphate molecular-sieves, J. Phys. Chem. 88 (1984) 6135–6139.
[33] F.T. Greenaway, ^{27}Al NMR-Study of aluminum(III) interactions with hydroxy carboxylic acids, Inorg. Chim. Acta 116 (1986) L21–L23.
[34] F.T. Greenaway and R.J. Tepper, ^{27}Al NMR studies of hydroxycarboxylic acid complexes of Al(III). Abstracts of Papers of the American Chemical Society 192nd National Meeting, Anaheim, California (1986) 124-INOR.
[35] S.J.A. Fatemi, D.J. Williamson, G.R. Moore, A ^{27}Al NMR investigation of Al^{3+} binding to small carboxylic acids and the proteins albumin and transferrin, J. Inorg. Biochem. 46 (1992) 35–40.
[36] S.J. Karlik, E. Tarien, G.A. Elgavish, G.L. Eichhorn, ^{27}Al nuclear magnetic resonance study of aluminum(III) interactions with carboxylate ligands, Inorg. Chem. 22 (1983) 525–529.
[37] S.B. Vyas, L.K. Duffy, Interaction of synthetic Alzheimer β-protein-derived analogs with aqueous aluminum: a low-field ^{27}Al NMR investigation, J. Protein Chem. 14 (1995) 633–644.
[38] G.P. Babu, P. Ganguli, K. Metcalfe, J.W. Rockliffe, E.G. Smith, Structure–property relationships of some amorphous and crystalline aluminophosphates, J. Mat. Chem. 4 (1994) 331–336.
[39] P.L. Bryant, C.R. Harwell, K. Wu, F.R. Fronczek, R.W. Hall, L.G. Butler, Single-crystal ^{27}Al NMR of andalusite and calculated electric field gradients: the first complete NMR assignment for a 5-coordinate aluminum site, J. Phys. Chem. A 103 (1999) 5246–5252.