^{7}Li-Solid-State-NMR of [Li(N,N,N′,N′-Tetramethylethylenediamine)]ClO_4 and [Li(N,N,N′,N′-Tetramethylethylenediamine)$_2$]$Al(CH_3)_4$*

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The temperature dependent ^{7}Li-solid-state-NMR spectra of the two compounds [Li(N,N,N′,N′-tetramethylethylenediamine)]ClO_4 and [Li(N,N,N′,N′-tetramethylethylenediamine)$_2$]$Al(CH_3)_4$ are presented. Both compounds were investigated in the temperature range $160\ K \leqq T \leqq 360\ K$. Above room temperature, the spectra for the tetramethylaluminate show the typical line shape for a first-order quadrupolar-disturbed central transition with an axially symmetric asymmetry parameter and a slightly positive temperature dependence of the quadrupole coupling constant. The mean temperature coefficient $\bar{\alpha} = +9 \cdot 10^{-4}\ K^{-1}$. The quadrupole coupling constant is in the range of 36–39 kHz. In the temperature range $240\ K \leqq T \leqq 275\ K$ the quadrupolar splitting cannot be resolved. Below 240 K the quadrupole coupling constant is about 100 kHz. Contrarily, in the perchlorate the quadrupole coupling constant is 75 kHz and is temperature independent. With increasing temperature the satellites lower in intensity and the central transition undergoes motional narrowing.

Key words: ^{7}Li solid state NMR, Quadrupolar interaction.

Introduction

Lithium compounds nowadays play an important role as reagents as well as intermediates in organic and organometallic synthesis. Very often nitrogen bases coordinating the lithium atom are added to improve reactivity and yield [1, 2]. A lot of work has been done on the investigation of these species in solution, but as there are complicated equilibria of different aggregation states depending on the nature of the solvent [3, 4], these results cannot be transferred to the solid state. As only very few data are available in this field [5–7], we have tried to generate a set of model compounds with nitrogen coordination at the lithium atom and investigate the solid state structure by the means of temperature dependent ^{7}Li-solid-state NMR.

Results and Discussion

Above room temperature, the ^{7}Li powder spectra of the aluminate show the typical line shape for a first-order quadrupolar-disturbed central transition with an axially symmetric asymmetry parameter (Figure 1). Below room temperature the satellites flatten, so that the quadrupolar splitting cannot be determined anymore. Below 240 K, edges can be resolved again that most probably represent the satellites of a quadrupole coupling constant of about 100 kHz. In the temperature range $240\ K \leqq T \leqq 275\ K$ no quadrupole splitting can be determined.

Above room temperature there is a slightly positive temperature dependence of the quadrupole splitting. The quadrupole coupling constant increases from 36 kHz to 39 kHz, which implies a positive mean temperature coefficient $\bar{\alpha} = +9 \cdot 10^{-4}\ K^{-1}$.

The spectra of the perchlorate compound [Li(N,N,N′,N′-tetramethylethylenediamine)]ClO_4 are depicted in Figure 2. In the whole temperature range the spectra have the line shape of a resonance with first-order quadrupole splitting and a vanishing asymmetry parameter. The satellites are very strong in intensity and increase with decreasing temperature. Even the edges can be resolved. With increasing temperature the central transition becomes narrower and the intensity of the satellites lowers. The line width at half maximum height decreases from 5000 Hz at 150 K to 1100 Hz at 360 K. The quadrupole coupling constant is in the range of 75 kHz and is independent on temperature.

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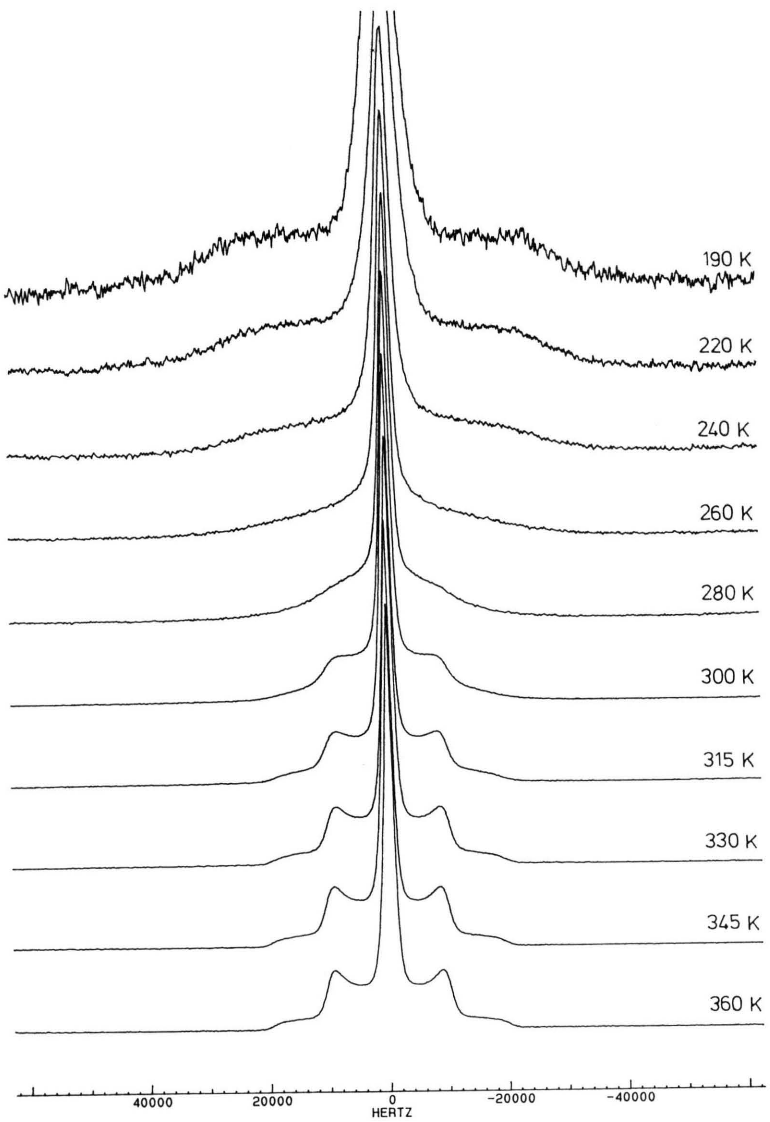

Fig. 1. ^{7}Li powder spectra of [Li(N,N,N',N'-tetramethylethylenediamine)$_2$]-Al(CH$_3$)$_4$; spectrometer frequency: 116.64 MHz, sweep width: 125 kHz, number of scans: 1024, recycle delay: 2 s, pulse programme: quadecho, τ-delay: 4 μs.

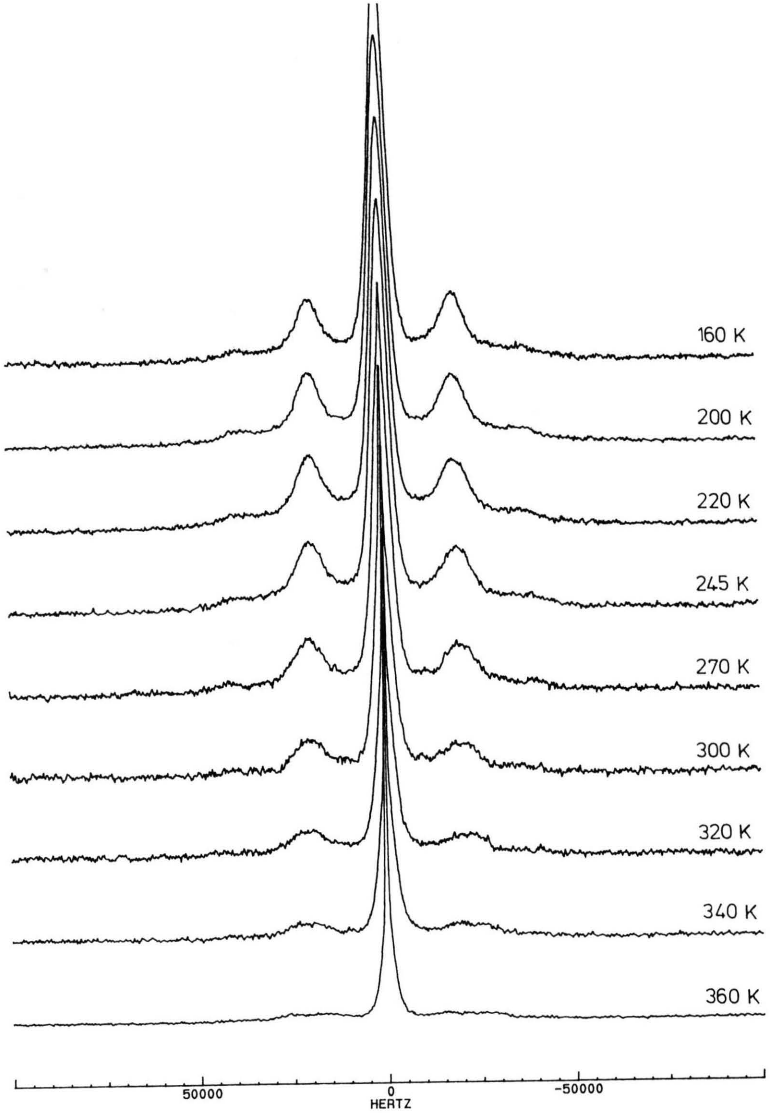

Fig. 2. ^{7}Li powder spectra of [Li(N,N,N',N'-tetramethylethylenediamine)]-ClO$_4$; spectrometer frequency: 116.64 MHz, sweep width: 200 kHz, number of scans: 96, recycle delay: 4 s, pulse programme: quadecho, τ-delay: 3 μs.

Conclusions

1. From the small quadrupole coupling constant, an almost tetrahedral environment by the four nitrogen atoms of the two (N,N,N′,N′-tetramethylethylenediamine ligands can be assumed for the lithium aluminate. Contrarily, in the perchlorate the coordination number four for the lithium atom cannot be reached by the nitrogen atoms of the ligands. So there must be some interaction with the oxygen atoms of the perchlorate anion, too. Thus the lower symmetry is manifested in the higher quadrupole coupling constant.

2. A positive mean temperature coefficient of ^{7}Li has already been observed in $LiNbO_3$ and $LiTaO_3$ [8]. In the case of $LiNbO_3$, the positive temperature dependence is attributed to anisotropical vibrations of the lithium atoms about their equilibrium positions. The average value of the electric field gradient sampled by the moving nucleus was calculated assuming the Einstein oscillator model. This simple model predicts a linear temperature dependence of the quadrupole coupling constant. But in the case of the lithium aluminate the assertion of anisotropic motion is questionable as the lithium atom is surrounded almost symmetrically by the four nitrogen atoms.

Experimental

The spectra were recorded on a Bruker spectrometer MSL 300 in a solenoid coil with an inner diameter of 5 mm. Temperature control was maintained by a Bruker Eurotherm unit with a stability of 0.1 K.

The perchlorate compound was synthesized in a nitrogen atmosphere by dropwise addition of a N,N,N′,N′-tetramethylethylenediamine solution in THF to a solution of dehydrated lithium perchlorate in THF and crystallization upon cooling (elemental analysis: C 31.95 (32.38), H 7.27 (7.24), Cl 15.24 (15.93), Li 3.10 (3.12) N 12.43 (12.58), O 29.58 (28.75)).

The aluminate was prepared according to [9].

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[1] W. A. Butte, J. Org. Chem. **29**, 2928 (1964).
[2] C. J. Screttas and J. F. Eastham, J. Amer. Soc. **87**, 3276 (1965).
[3] W. Bauer, W. R. Winchester, and P. v. R. Schleyer, Organomet. **6**, 2371 (1987).
[4] G. Fraenkel, A. Chow, and W. R. Winchester, J. Amer. Chem. Soc. **112**, 6190 (1990).
[5] S. G. Bishop, P. J. Ring, and P. J. Bray, J. Chem. Phys. **45**, 1525 (1966).
[6] J. F. Hon and P. J. Bray, Phys. Rev. **110**, 624 (1958).
[7] L. Baiqin, W. Yening, and X. Ziran, J. Phys. C: Solid State Phys. **21**, L251 (1988).
[8] T. K. Halstead, J. Chem. Phys. **53**, 3427 (1970).
[9] H. H. Karsch, A. Appelt, and G. Müller, Organomet. **4**, 1624 (1985).