⁷Li Solid State NMR Study of a TMEDA Complex of Trimethylsilylcyclopentadienyllithium

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⁷Li solid state NMR spectroscopy of N,N,N',N'-tetramethylethylenediamine-trimethylsilylcyclopentadienyllithium yielded an unusually large quadrupole coupling constant, that decreases with increasing temperature (188–165 kHz in the temperature range 210–335 K). Structural features, known from the X-ray analysis, are compared with the NMR results.

Introduction

Organolithium compounds are widely used as reagents in organic and organometallic synthesis. Since organolithium compounds usually form aggregates in solution, their reactivity is drastically reduced. Therefore, donor reagents are added to the reaction mixture, which coordinate to the lithium atoms and thus break up the aggregates. The result is a considerable enhancement in reactivity (and yield) [1, 2]. N,N,N',N'-Tetramethylethylenediamine (TMEDA) is one of the most common donors used. We studied structural and dynamic features of one of its adducts by means of ⁷Li solid state NMR spectroscopy. ⁷Li has a nuclear spin $I = 3/2$ and a quadrupole moment [3] of $-40.1 \cdot 10^{-3} \text{ m}^2$. The quadrupole effect on the solid state NMR spectra is a sensitive probe and provides valuable structural information.

Experimental

The title compound was prepared by slowly adding a solution of TMEDA in dry pentane to a suspension of trimethylsilylcyclopentadienyllithium [4] in dry pentane at 0 °C followed by filtration and crystallization (*cf.* Lappert *et al.* [5]).

⁷Li NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer operating at a resonance frequency of 116.64 MHz for ⁷Li. The 90°

pulse length used for the broadband probe with a solenoid coil was 2.5 μ . Temperature control was maintained by a Bruker Eurotherm unit with a stability of $\pm 0.1 \text{ K}$. The sample was packed under argon in a sample tube of 5 mm outer diameter.

Results

The X-ray structure of the title compound is known [5] so that NMR results can be directly related to structural features. The crystal lattice consists of monomeric units. The lithium atom in each unit is located above the center of the cyclopentadienyl ring indicating η^5 -coordination. The remaining coordination sites are occupied by the nitrogen atoms of one TMEDA ligand. The silicon atom is located in the plane of the cyclopentadienyl ring.

Fig. 1. Temperature dependent ⁷Li solid state NMR spectra of N,N,N',N'-Tetramethylethylenediamine-trimethylsilylcyclopentadienyllithium.

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The X-ray structure provided also evidence for a high thermal mobility of the ligands.

Some of the temperature dependent ^7Li solid state NMR spectra are shown in Fig. 1. At low temperatures, the satellites characteristic for a first order quadrupolar interaction [6] with zero asymmetry parameter are resolved very clearly. As the melting point of the sample (347 K) is approached, the central transition narrows considerably and the intensity of the satellites decreases. The quadrupole coupling constant e^2qQ/h was estimated from the spectra assuming axial symmetry of the electric field gradients. The values are plotted *versus* temperature in Fig. 2. They reveal a continuous decrease in the quadrupole coupling constant with increasing temperature.

Fig. 2. Temperature dependence of the quadrupole coupling constant e^2qQ/h ; $\Delta(e^2qQ/h) = \pm 2$ kHz.

Discussion

1. Theory

The temperature dependence of the quadrupole coupling constant is caused by a change in the electric field gradient (i) due to changes in the atomic coordinates, (ii) due to a change in the electron density distribution or (iii) a change in the time average of the electric field gradient sampled by the moving nucleus [7]. Kushida, Benedek, and Bloembergen [8, 9] provided a theoretical model. They predict generally a negative temperature dependence, since the electric field gradients should decrease with increasing temperature due to the averaging effect by the increasing mobility of the atoms in the lattice. Halstead [7] predicts a de-

crease of the quadrupole coupling constant with increasing temperature if the nucleus under study is heavy or part of a covalently bound group which may rotate or librate. In this case the temperature dependence should be nonlinear, whereas light atoms in an environment allowing anisotropic vibrations should yield an increase of the quadrupole coupling constant with increasing temperature.

2. Temperature dependence of the ^7Li quadrupole interaction

The data for the title compound show an approximately linear decrease of the quadrupole coupling constant with increasing temperature for a light atom. The averaging effect of the highly mobile TMEDA ligands, as stated in the X-ray analysis [5], explains the negative temperature dependence in agreement with the Kushida, Benedek, Bloembergen theory.

The X-ray structure analysis of lithium halides coordinated with one molecule of TMEDA yielded lithium-nitrogen bond lengths [10] comparable to those of the title compound. ^7Li solid state NMR spectra of TMEDA coordinated lithium salts have been recorded for the bromide [11], nitrate [11], perchlorate [12] and, with a coordination of two TMEDA ligands per lithium unit, for the tetramethylaluminate [12]. The quadrupole coupling constants of the bromide ($e^2qQ/h = 136$ kHz), nitrate ($e^2qQ/h = 75$ kHz) and perchlorate (75 kHz) are temperature independent, whereas the tetramethylaluminate revealed a slightly positive temperature dependence¹² ($e^2qQ/h = 36$ – 39 kHz). The structure of the bromide is known to consist of dimeric units, in which each lithium ion is coordinated by one molecule of TMEDA and connected to another lithium atom by a bridging bromine atom [10]. The symmetry in this coordination type is considerably lower than in the monomeric units of the nitrate [10] and supposedly the perchlorate as manifested in the larger quadrupole coupling constant. Only the doubly TMEDA coordinated lithium tetramethylaluminate revealed a temperature dependence of the quadrupole coupling constant consistent with Halsteads [7] model for a light atom. In this case the extremely small quadrupole coupling constants can be easily explained in terms of a nearly perfect

tetrahedral surrounding of the lithium ion by the two TMEDA ligands [12].

Comparison with the title compound shows that its quadrupole coupling constant is considerably larger than that of the other salt complexes, and is, overall, one of the largest quadrupole coupling constants [13] known for ^7Li .

Interaction of the vacant coordination sites at the lithium atom with a single TMEDA ligand results in a lower symmetry compared to the doubly TMEDA coordinated species. In the monomeric units of the nitrate, perchlorate and cyclopentadienyl compound an interaction of the coordination sphere of the lithium ion with the respective anions is required. The change from a planar ni-

trate anion to a tetrahedral perchlorate anion has no effect on the electric field gradient at the lithium nucleus, indicating an equivalent coordination of the oxygen atoms in both anions to the lithium. In comparison, the change to a cyclopentadienyl group as the anion causes a dramatic increase in the quadrupole coupling constant. This indicates that the η^5 -coordination of the cyclopentadienyl group reduces the symmetry, resulting in a larger electric field gradient at the lithium site.

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