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Short Communication

^{23}Na and ^{13}C solid state NMR spectroscopy of *N,N,N′,N′*-tetramethylethylenediamine-sodiumcyclopentadienide

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Abstract

The static ^{23}Na NMR spectrum of *N,N,N′,N′*-tetramethylethylenediamine-sodiumcyclopentadienide revealed a lineshape that could not be unambiguously discussed. Nutation NMR spectroscopy combined with MAS allowed a definite assignment of the splitted signal to a second order quadrupolar interaction with vanishing asymmetry parameter. The quadrupole coupling constant is in the range of 2 MHz. The ^{13}C CP-MAS spectrum yielded the expected signals.

Introduction

Pentahapto-coordinated cyclopentadienyl–alkaline metal compounds play an important role in the transfer of cyclopentadienyl groups in metallocene chemistry [1]. In most cases the complexes can only be isolated as base adducts [2]. Our interest is to obtain structural information by examining the interaction of the quadrupolar metal nucleus with the electric field gradients generated by the lattice via solid state NMR spectroscopy. In this work the ^{23}Na and ^{13}C NMR spectra of *N,N,N′,N′*-tetramethylethylenediamine-sodiumcyclopentadienide (NaCp–TMEDA), a compound with known crystal structure [3], are discussed.

Experimental

The title compound was prepared as described in ref. 3. ^{23}Na and ^{13}C NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer at a resonance frequency of 79.39 and 75.468 MHz, respectively. For static spectra a solenoid coil probehead for sample tubes of 10 mm outer diameter was used. MAS spectra were obtained by the use of ZrO_2 spinners with Kel-F rotor caps. The sample was packed in a glovebox.

Results and discussion

In the crystal structure, NaCp–TMEDA adopts a puckered chain structure with pentahapto-coordinated C_5H_5 rings bridging Na(TMEDA) units [3]. There are two different sodium positions in the lattice caused by different Na–Na–Na angles (128 and 119°).

The static ^{23}Na NMR spectrum reveals a splitting of 6.7 kHz (84 ppm) of the signal (inset in Fig. 1) that can either be attributed to (i) a chemical shift anisotropy with axialsymmetric tensor [4], (ii) a second order quadrupolar splitting with axialsymmetric asymmetry parameter η [5] or (iii) a chemical shift due to two different sodium positions in the lattice.

However, (iii) is very unlikely as both crystallographically inequivalent sodium atoms are in a very similar chemical surrounding and the usual chemical shift range for sodium cations is 30 ppm [6].

To distinguish between the two remaining possibilities (i) and (ii), a ^{23}Na nutation [7] spectrum (inset in Fig. 1) and ^{23}Na MAS NMR spectra (Fig. 1) were recorded.

The nutation spectrum yielded two components shifted from the central transition at ω_{rf} corresponding

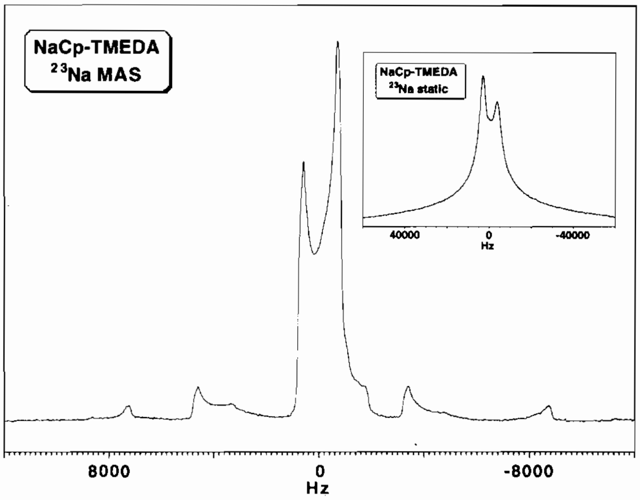

Fig. 1. ^{23}Na spectra of NaCp–TMEDA. MAS spinning frequency: 4 kHz, repetition rate: 2 s, pulse width: 4 μs, ^{1}H-high power decoupling time: 32 ms, number of scans: 200, line broadening factor: 14. Inset: projection of the static nutation spectrum in the F2 dimension. Sweep width: 125 kHz, repetition rate 2 s, number of increments: 128, number of scans: 328, line broadening factor: 500.

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to the case $\omega_Q < 0.1\omega_{rf}$ [8]. It demonstrates that a quadrupolar interaction is definitely contributing to the lineshape; but it does not rule out the contribution of a chemical shift anisotropy (i). Thus the final assignment demanded the analysis of the MAS data.

The lineshape of the MAS spectrum fits very well a second order quadrupolar interaction with vanishing asymmetry parameter [9].

Calculating the quadrupole coupling constant for a second order perturbation from the splitting $\Delta\nu = 6.7$ kHz yields in the static case [10]

$$\Delta\nu = \left(\frac{e^2qQ}{h}\right)^2 \left(\frac{3}{2I(2I-1)}\right)^2 \frac{1}{144\nu_L} \left[I(I+1) - \tfrac{3}{4}\right] f(\eta)$$

with $f(\eta) = 25$ for $\eta = 0, I = \frac{3}{2}$ and Larmor frequency ν_L

$$e^2qQ/h = \tfrac{8}{5}\sqrt{3\nu_L \Delta\nu} = 2.0 \text{ MHz}$$

For the calculation of e^2qQ/h from the MAS spectrum the method of Engelhardt and Koller [11] was applied. With $\eta = 0$, $I = \frac{3}{2}$ and a splitting $\Delta\nu_{MAS} = 1270$ Hz, the quadrupole coupling constant is given by

$$e^2qQ/h = \left(\frac{16\nu_L\,\Delta\nu_{MAS}}{0.4821}\right)^{1/2} \times 10^{-3} = 1.8 \text{ MHz}$$

The agreement of the static value of the quadrupole coupling constant with the MAS value is satisfactory considering the dipolar broadening and rough approximation of the method itself. For a more exact value, a simulation should be performed which, however, was not the aim of this work. Additionally, in the case of a chemical shift anisotropy no reduction of the splitting was observed. Thus the splitting of the signal can unambiguously be attributed to a second order quadrupolar interaction.

The ^{13}C CP-MAS spectrum (Fig. 2) recorded at a spinning frequency of 3 kHz reveals sidebands (marked with an asterisk) only for the signal of the cyclopentadienyl ring at $\delta = 103$ ppm indicating a large chemical shift anisotropy for their ring carbon atoms.

The signals for the methyl ($\delta = 47$ ppm) and methylene carbons ($\delta = 57$ ppm) show a considerable linewidth (full width half maximum 3.3 ppm and 4.6 ppm, respectively) that might be related to a relaxation phenomenon as all other interactions are averaged out by MAS. All chemical shifts agree with the expected values.

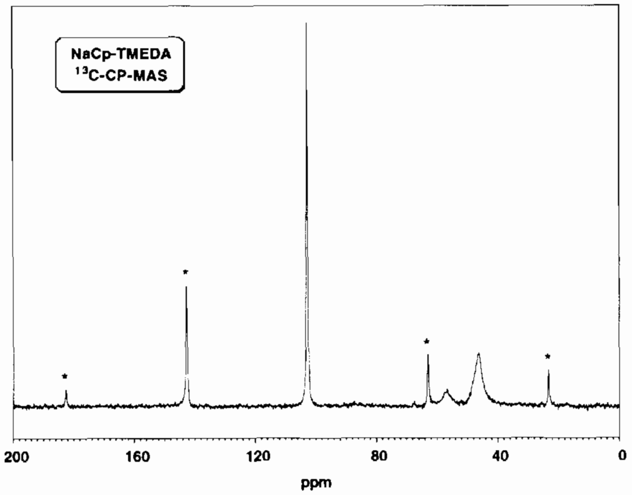

Fig. 2. ^{13}C CP-MAS spectrum of NaCp–TMEDA. MAS spinning frequency: 3 kHz, sweep width: 20 kHz, repetition rate: 4 s, pulse width: 4 μs, contact time: 5 ms, decoupling time: 100 ms, number of scans: 168, line broadening factor: 4.

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