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Concentration dependence of the ^{1}H- and ^{29}Si-NMR chemical shifts of tetramethyldisiloxanediol in deuterated chloroform

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Abstract

In literature, NMR chemical shifts of protons and silicon atoms in silanols have always been discussed with respect to the polarity of the solvents used. In this paper, chemical shift values of tetramethyldisiloxanediol M_2^{OH} are presented with regard to their change in dependence on concentration in deuterated chloroform and on temperature. These values are compared to values found in solid state NMR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NMR spectroscopy; Organosilicon chemistry; Silanol

1. Introduction

Tetramethyldisiloxanediol $HOSi(CH_3)_2OSi(CH_3)_2$-OH, described in the following as M_2^{OH} according to the generally accepted siloxane ordering system [1], is an important precursor for polysiloxane materials. It can be considered as the shortest member of the class of OH-endblocked oligo- and poly(dimethyl)siloxanes (PDMS). In the early 1990s, two research groups independently published the results of the X-ray single crystal structure determination of M_2^{OH}. Polishuk et al. [2] and Lickiss et al. [3] have shown that the siloxane molecules are intermolecularly linked by hydrogen bonds forming a double chain framework, which is also known from several other 1,3-dihydroxytetraalkyldisiloxanes $HOSiR_2OSiR_2OH$ (R = Et [4], *n*-Pr [5] and Ph [6]). The strong effect of the hydrogen bonding in M_2^{OH} can be observed even in solution. In this case, not only hydrogen bonding between the disiloxanediol molecules, but also intermolecular bonding to, preferentially polar, solvent molecules have to be taken into account. Therefore, the type of solvent, the concentration of the disiloxanediol solution and the temperature influence the bond strength. Using infrared spectroscopy, Bogunovic et al. [7] have demonstrated the influence of the solvent polarity on the O–H stretching frequency (ν), which is a widely accepted sensor for this intermolecular interaction. Dobos et al. [8] have shown the dependence of ν on the M_2^{OH} concentration. The influence of the donor ability of different solvents on the ^{29}Si-NMR chemical shift in M_2^{OH} was investigated by Williams et al. [9]. The authors observed a low frequency shift of the ^{29}Si resonance corresponding to an increase of the Lewis basicity of the used solvents. The shift range has been from $\delta = -10.5$ ppm in deuterated chloroform ($CDCl_3$) to $\delta = -16.9$ ppm in hexamethylphosphorustriamide (HMPA). However, as far as we know, no investigation has been published up to now reflecting the influence of sample concentration of siloxanes containing silanol groups, like M_2^{OH}, on NMR chemical shift parameters.

In this publication, the ^{29}Si-, ^{13}C- and ^{1}H-NMR spectra of M_2^{OH} are discussed with respect to concentration dependence using deuterated chloroform as solvent. Spectra recorded at different temperatures are also described. Finally, the results obtained in solution are compared with solid state NMR investigations.

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2. Experimental

Tetramethyldisiloxanediol can be generated by the hydrolysis reaction of the corresponding 1,3-dichloro-1,1,3,3-tetramethyldisiloxane in Et_2O in the presence of trialkylamine according to the procedure of Cella and Carpenter [10]. Long white needles (m.p. 61°C) of the title compound are yielded by crystallisation from Et_2O–pentane.

Liquid state NMR spectra were obtained using a JEOL Lambda 400 MHz spectrometer operating at the frequencies 399.65 (^{1}H), 100.40 (^{13}C), and 79.30 (^{29}Si) MHz. The samples were prepared with concentrations of 1, 2.5, 5, 10, 20, 40, 60, 80 and 100 mg of M_2^{OH} in 0.8 ml $CDCl_3$. These concentrations correspond to the following molarities, M (wt. in mg): 0.0075 (1), 0.0188 (2.5), 0.0376 (5), 0.0753 (10), 0.1506 (20), 0.3012 (40), 0.4518 (60), 0.6024 (80) and 0.7530 (100). At higher concentrations, crystallisation of the title compound started during the NMR experiments. Therefore, and because of the minor changes of the chemical shifts compared to the values found at the concentrations of 100 mg, the results of those experiments are not discussed in this context. The $CDCl_3$ (99.8% deuterated) was dried over molsieve A4 prior to use. The shifts were calibrated to the signals of deuterated $CHCl_3$ $\delta = 7.24$ (^{1}H) and $\delta = 77.00$ ppm (^{13}C) correlated to Me_4Si (TMS, $\delta = 0.0$ ppm). For the ^{29}Si chemical shift measurements, one drop of Me_4Si was added as an internal standard at $\delta = 0.00$ ppm. The NMR acquisition parameters for the three nuclei were set in the following manner: (i) ^{1}H–90° pulse length 5.1 µs, sweep width 10 kHz, number of scans 32, relaxation delay 7 s; (ii) ^{29}Si inverse gated {^{1}H} decoupling–90° pulse length 5.45 µs, sweep width 20 kHz, number of scans due to the signal-to-noise ratio, relaxation delay 20 s; (iii) ^{13}C-{^{1}H} decoupling–90° pulse length 4.50 µs, sweep width 24 kHz, number of scans due to the signal-to-noise ratio, relaxation delay 3.4 s. The measurements of the concentration dependence were carried out at 21.5°C. For the measurement of temperature dependence, a sample concentration of 100 mg of M_2^{OH} in 0.8 ml $CDCl_3$ was used.

Solid state NMR spectra were obtained using a JEOL Lambda 400 MHz spectrometer equipped with a JEOL 6 mm probe and tuned according to the resonance frequencies of the ^{1}H (400.05 MHz), ^{13}C (100.50 MHz) and ^{29}Si (79.38 MHz) nuclei. Magic angle spinning was applied and the rotation frequency was set to 5.8 kHz. ^{13}C and ^{29}Si spectra were acquired using cross-polarisation (CP/MAS). The contact time was 5 ms, and the ^{1}H–90° pulse length was set to 5 µs. The used sweep widths and number of data points were as follows: 20 kHz and 4k points for ^{1}H, 30 kHz and 16k points for both ^{13}C and ^{29}Si. The ^{1}H and ^{13}C spectra were referenced to TMS using adamantane as secondary standard [11] (δ(^{1}H): 1.85, δ(^{13}C): 38.53 and 29.47 ppm). The ^{29}Si spectrum was referenced to TMS using Q_8M_8 as secondary standard [12]. Here, the high frequency component of the Q 'quartet' was taken $\delta = -108.34$ ppm.

3. Results and discussion

3.1. ^{1}H-NMR concentration dependence

The solid state ^{1}H-NMR spectrum of M_2^{OH} shows signals at $\delta = 0.14$ ppm for the protons of the methyl groups and at $\delta = 5.82$ ppm for the protons of the hydroxyl end-groups (Fig. 1). There is a broad background signal visible under the CH_3 signal showing maybe more associated OH groups. At $\delta = 14.47$ and -14.34 ppm, small rotation sidebands of the methyl proton signal are detected.

The liquid state spectrum of M_2^{OH} at the highest concentration used (100 mg in 0.8 ml $CDCl_3$) is shown in Fig. 2. The peak assignment is analogous to the solid state spectrum: methyl protons at $\delta = 0.15$ ppm, and silanol protons at $\delta = 5.09$ ppm (thereafter named as OH (A)). The narrow signal at $\delta = 7.24$ ppm represents the residual $CHCl_3$ in the deuterated solvent $CDCl_3$ and was used as reference signal.

The correlation of sample concentration and ^{1}H chemical shift of the OH and the CH_3 protons is shown in Table 1 and Fig. 3. For the OH signal (A), a higher sample concentration leads, as expected, to a higher frequency shifted value. This reflects the increase of hydrogen bonding strength with higher concentration. The proton obviously loses electron density by hydrogen bond formation and, therefore, it is more deshielded [13]. Fig. 3 shows the quasi-exponential nature of the curve. Interestingly, at concentrations lower than 80 mg in 0.8 ml $CDCl_3$, an additional OH peak (B) appears, which grows in intensity towards lower concentrations. This additional peak always has a lower shift value than the 'original' OH peak, indicating less hydrogen bonding effects. At the lowest measured concentration (1 mg of M_2^{OH} in 0.8 ml) this OH (B) peak is even greater in intensity than the original peak (see Table 1).

Of course, it has to be considered that, despite careful drying, $CDCl_3$ still contains residual water (30 ppm). In the spectrum of the pure dried solvent, the residual water appears at $\delta = 1.55$ ppm with an intensity of 13% of the signal of residual non-deuterated $CHCl_3$ in $CDCl_3$. Therefore, in the M_2^{OH} spectra, OH (B) could represent residual water from the solvent. Taking the intensity of the $CHCl_3$ peak at $\delta = 7.24$ ppm in each spectrum as a comparable value, the known intensity ratio of $CHCl_3$/residual H_2O from the pure solvent spectrum can be used to correct the intensity of the OH (B) peak in the following manner: $I_{\mathrm{corr}}^{\mathrm{OH(B)}} = I_{\mathrm{exp}}^{\mathrm{OH(B)}} - 0.13I^{\mathrm{CHC13}}$. If OH (B) were to represent only the residual water from dried $CDCl_3$, the value for $I_{\mathrm{corr}}^{\mathrm{OH\,(B)}}$ would be zero. But this is not the case, $I_{\mathrm{corr}}^{\mathrm{OH\,(B)}}$ grows with reducing M_2^{OH} concentration. The original and corrected intensity values for OH (B) are listed in Table 1. It is quite obvious that the OH (B) peak cannot be explained only by residual water of the dried $CDCl_3$. If one assumes that M_2^{OH} itself might contain adsorbed water and thus cause a contribution to OH (B), there should be no corresponding concentration dependence on M_2^{OH}. If OH (B) does not represent

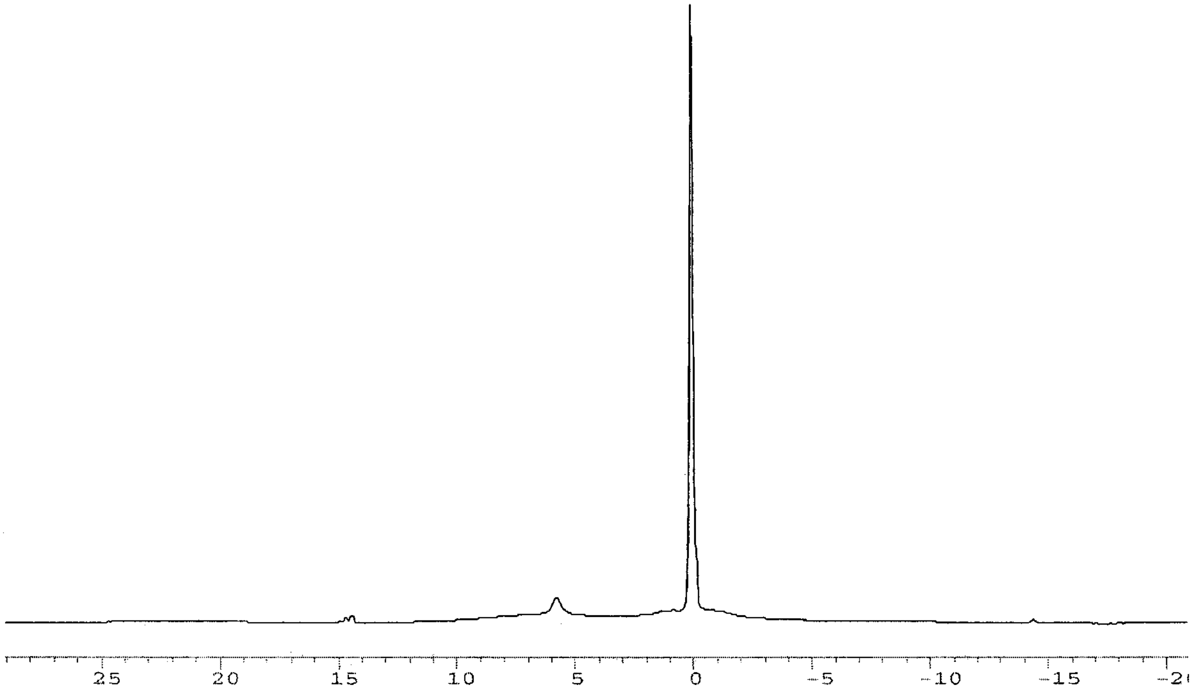

Fig. 1. ^{1}H solid state NMR spectrum of M_2^{OH}.

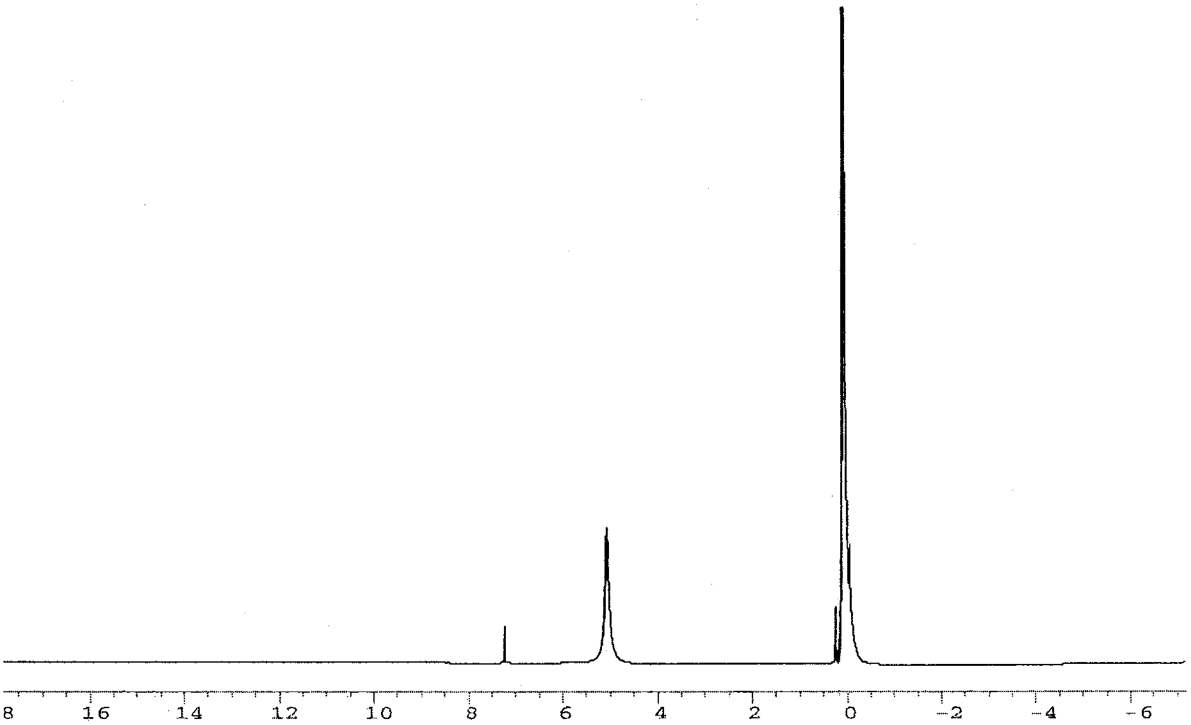

Fig. 2. ^{1}H-NMR spectrum of M_2^{OH} at a concentration of 100 mg in 0.8 ml $CDCl_3$.

Table 1
Chemical shift and intensity data in ^{1}H-NMR spectra of M_2^{OH} in $CDCl_3$ solution related to concentration

Concentration (mg M_2^{OH} in 0.8 ml $CDCl_3$)	Chemical shift δ (ppm)			Relative integrals			
	OH (A)	OH (B)	CH_3	OH (A)	OH (B), spectrum	OH (B), corrected	CH_3
100	5.09		0.10	0.94			6.00
80	5.05	3.32	0.10	0.93	<0.01	<0.01	6.00
60	4.94	3.24	0.10	0.93	<0.01	<0.01	6.00
40	4.73	2.94	0.11	0.90	<0.01	<0.01	6.00
20	4.28	2.33	0.12	0.92	0.11	0.11	6.00
10	3.66	1.90	0.13	0.90	0.22	0.20	6.00
5	3.04	1.69	0.14	0.87	0.27	0.23	6.00
2.5	2.61	1.60	0.14	0.87	0.39	0.33	6.00
1	2.27	1.55	0.14	0.88	0.90	0.74	6.00

water, but a different sort of OH group from M_2^{OH} (e.g. monomers which are more flexible than the other sort and which, therefore, experience weaker hydrogen bonding), the sum of OH (A) and OH (B) should be constant — however, this is also not the case (T_1 effects can be excluded). The most likely hypothesis for the questionable peak representing OH (B) is water that was taken from the environment while preparing and running the sample. This water amount was higher, the smaller the M_2^{OH} concentration. This could be caused by the fact that at higher M_2^{OH} concentration, there is relatively strong hydrogen bonding between the M_2^{OH} molecules themselves, while with lower M_2^{OH} concentration, less and less M_2^{OH} molecules are available for the formation of hydrogen bonds. As a result, the affinity to water seems to increase.

In one additional experiment, the sample of the lowest M_2^{OH} concentration (1 mg in 0.8 ml $CDCl_3$) was treated with a small amount of water. The corresponding ^{1}H spectrum showed a much higher intensity of the OH (B) peak at constant intensity ratios for all other peaks. As for OH (A), the chemical shift of OH (B) shows an exponential behaviour (see Fig. 3)

In contrast to the tremendous chemical shift change of the silanol protons, the chemical shift of the protons of the methyl groups differs through the whole concentration range by only 0.04 ppm because the CH_3 groups are positioned far away from the silanol end-groups, the location for the hydrogen bonding.

With regard to the chemical shift values, the signal for OH (A) shows up at $\delta = 5.08$ ppm in the spectrum of the most concentrated solution (100 mg in 0.8 ml $CDCl_3$) in comparison to $\delta = 5.89$ ppm in the solid state spectrum. This could indicate a stronger hydrogen bonding in the solid crystals than in the highly concentrated solutions; thus the chemical shift values in the solid state spectrum could be approximately considered as the limitation of the reachable shift range for the highest possible concentration in solution. However, it is difficult to compare shifts from solution and solid state because of additional solvent effects and/or crystal packing effects.

3.2. ^{29}Si-NMR concentration dependence

The ^{29}Si solid state CP/MAS NMR spectrum of tetramethylsiloxandiol M_2^{OH} is shown in Fig. 4. The two signals at $\delta = -9.93$ and -10.56 ppm with intensity ratio 1:1 represent the isotropic chemical shift values of the two different Si sites in the molecule seen in the crystal structure of the compound. The main values of the anisotropy of the chemical shift tensor have also been determined (signal at $\delta_{iso} = -9.93$ ppm: $\delta_{11} = 8.2$, $\delta_{22} = 0.4$, $\delta_{33} = -38.4$ ppm; signal at $\delta_{iso} = -10.56$ ppm: $\delta_{11} = 5.9$, $\delta_{22} = 0.0$, $\delta_{33} = -37.6$ ppm) but will be discussed elsewhere [14].

In solution only one ^{29}Si signal is to be expected because of the Brownian motion of the molecules. Fig. 5 shows the ^{29}Si spectrum of the solution with the highest used concentration (100 mg in 0.8 ml $CDCl_3$). The chemical shift is $\delta = -10.38$ ppm. The peak at $\delta = 0.00$ ppm represents the TMS reference.

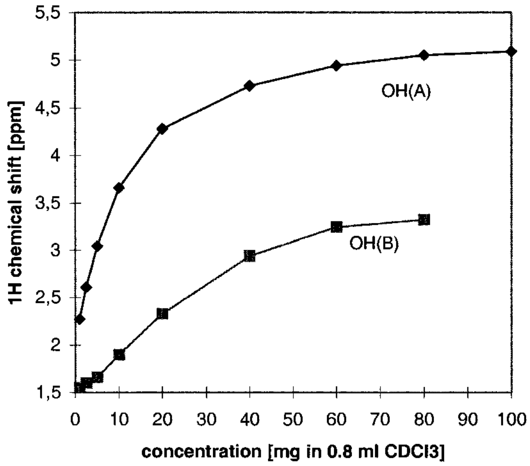

Fig. 3. Correlation between ^{1}H chemical shift of silanol protons (OH (A)) and water protons (OH (B)) and sample concentration of M_2^{OH} in $CDCl_3$.

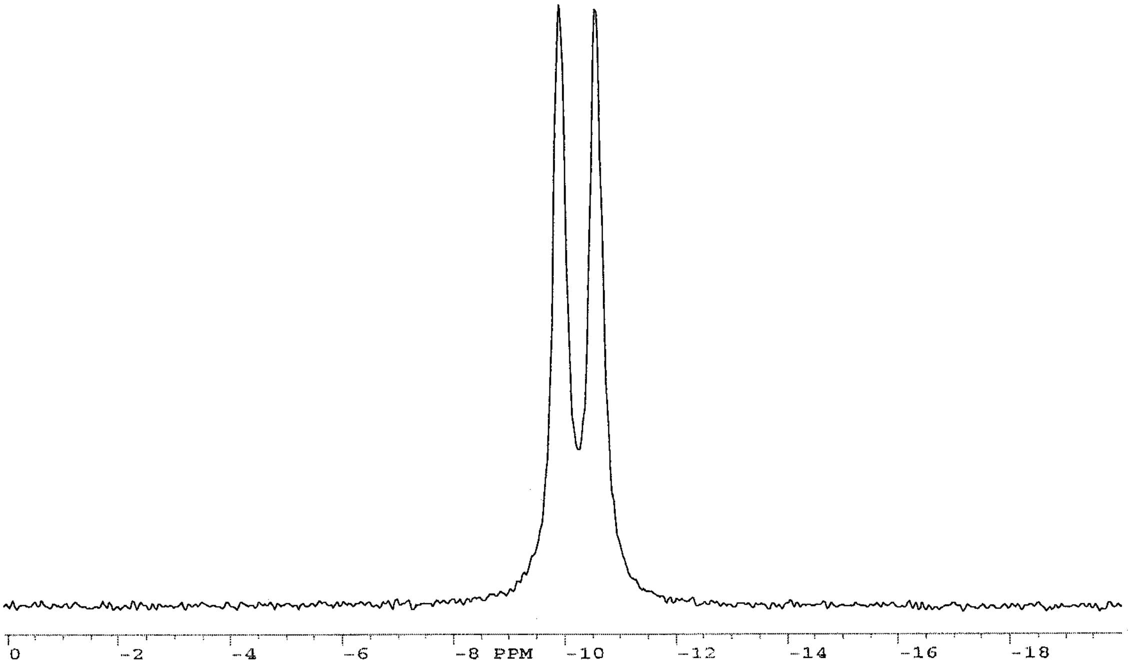

Fig. 4. ^{29}Si solid state CP/MAS NMR spectrum of M_2^{OH}.

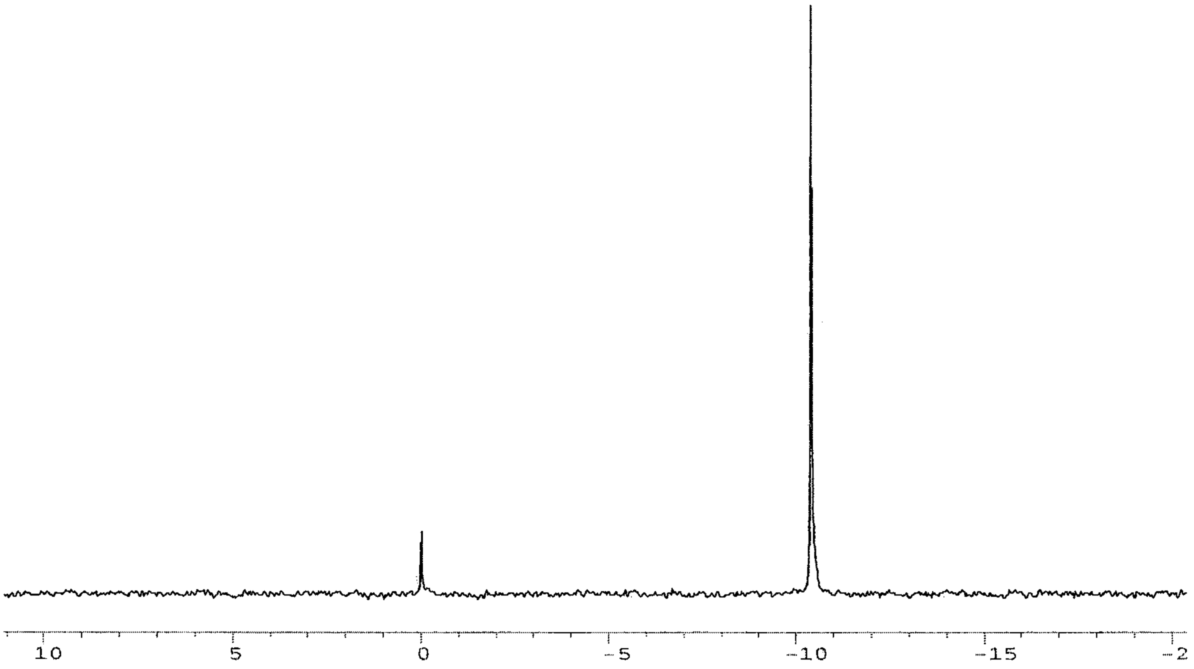

Fig. 5. ^{29}Si-NMR spectrum of 100 mg M_2^{OH} in 0.8 ml $CDCl_3$.

The dependence of the ^{29}Si chemical shift on sample concentration is shown in Table 2 and Fig. 6. There the obvious correlation can be observed that the higher the concentration of M_2^{OH} is in $CDCl_3$, the more the chemical shift towards low frequency. Therefore, in ^{29}Si spectra we observe the opposite direction of chemical shift changes as a function of concentration in comparison to the ^{1}H spectra. The concentration dependence of the silicon shift is much smaller than the proton shift in the silanol end-group. At the highest measured concentration, the ^{29}Si chemical shift is at $\delta = -10.38$ ppm and is found between the two shifts at $\delta = -9.93$ and -10.56 ppm found in the solid state spectrum. However, in both cases the hydrogen bonding shows a clearly detectable effect. At a low concentration of 1 mg in 0.8 ml $CDCl_3$ the ^{29}Si chemical shift of $\delta = -9.41$ ppm is considerably shifted, because hydrogen bonding has been minimised.

Table 2
Chemical shift data of ^{29}Si spectra of M_2^{OH} in $CDCl_3$ solution related to concentration

Concentration (mg M_2^{OH} in 0.8 ml $CDCl_3$)	Chemical shift, δ (ppm)
100	−10.38
80	−10.34
60	−10.29
40	−10.18
20	−9.98
10	−9.77
5	−9.58
2.5	−9.47
1	−9.41

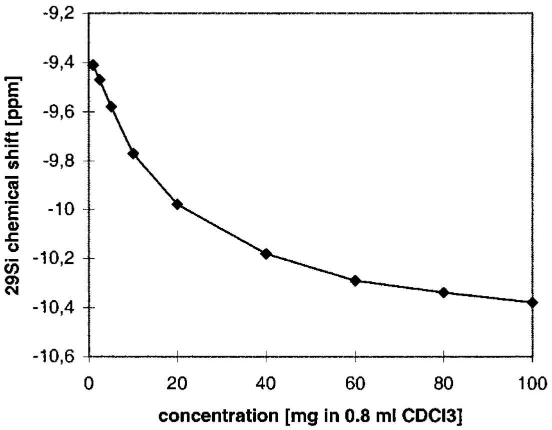

Fig. 6. Correlation between ^{29}Si chemical shift and sample concentration of M_2^{OH} in $CDCl_3$.

^{1}H- and ^{29}Si-NMR spectra show an exponential chemical shift dependence on concentration. The stronger dependence in ^{1}H-NMR spectroscopy is not surprising because the OH protons reflect directly the hydrogen bonding effect whereas the ^{29}Si nuclei are one bond away from the hydroxyl group. The low frequency shift of the ^{29}Si signals at higher concentration is in agreement with Williams' observation that δ values are shifted to low frequency if the solvent is more polar and, therefore, the hydrogen bonding is stronger [8].

3.3. ^{13}C-NMR concentration dependence

The ^{13}C solid state spectrum is shown in Fig. 7. From the crystal structure determination there are four different ^{13}C sites in the molecule reflected by the four signals at $\delta = 0.52$, 0.83, 1.59 and 1.70 ppm with an intensity ratio of 1:1:1:1. However, as observed for ^{29}Si-NMR spectroscopy, the liquid state spectrum of the sample with the highest used concentration (100 mg in 0.8 ml $CDCl_3$) shows only a single signal at $\delta = 0.45$ ppm (see Fig. 8).

A second ^{13}C-NMR spectrum was recorded at a concentration of 20 mg M_2^{OH} in 0.8 ml $CDCl_3$. This second spectrum showed only a minor shift difference of 0.02 ppm compared to the spectrum of the higher concentrated solution: $\delta = 0.43$ versus 0.45 ppm. The methyl groups are far away from the location of the hydrogen bonding; thus, like the protons of the methyl groups they are not highly affected in their chemical shift values.

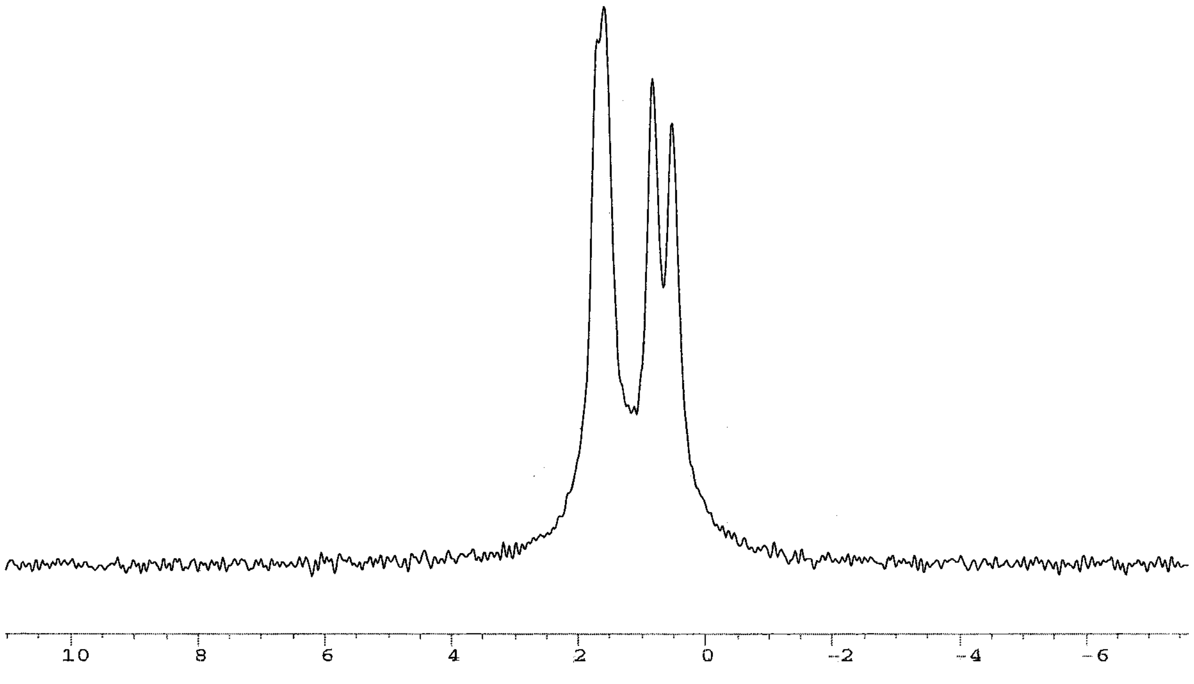

Fig. 7. ^{13}C solid state CP/MAS NMR spectrum of M_2^{OH}.

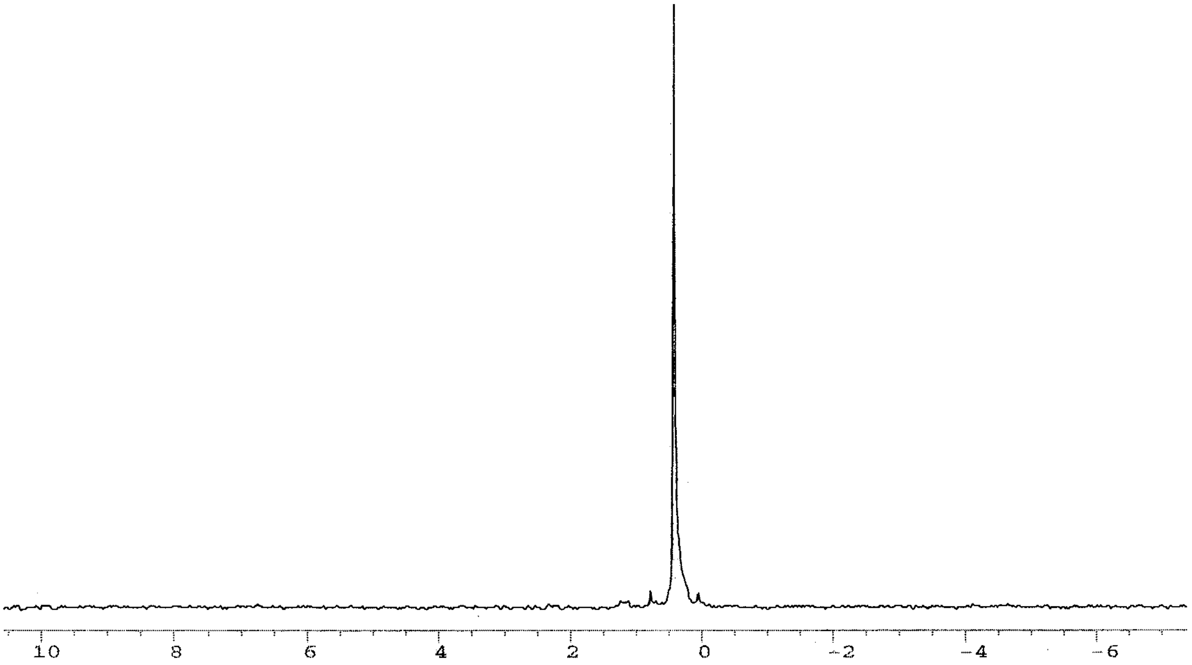

Fig. 8. ^{13}C-NMR spectrum of 100 mg M_2^{OH} in 0.8 ml $CDCl_3$.

3.4. *^{1}H and ^{29}Si-NMR temperature dependence*

Another possibility for monitoring the impact of hydrogen bonding effects on NMR chemical shift data is by varying the temperature. The most concentrated sample, 100 mg M_2^{OH} in 0.8 ml $CDCl_3$, was used to record the ^{1}H and ^{29}Si chemical shift dependence on the temperature. Because of the solvent properties, the temperature range was selected to be between 20 and 60°C. Figs. 9 and 10 show the results. The values are listed in Table 3. In ^{1}H- and ^{29}Si-NMR spectra, the chemical shift shows a linear correlation with the temperature in the chosen range. In the proton spectra the chemical shift goes to low frequency at higher temperatures. At the concentration used, only the OH (A) peak is detectable. Higher temperatures weaken the hydrogen bonding and, therefore, show the same effect on chemical shift as lower concentration. The difference between both effects is the correlation function (exponential curve for the concentration dependence and linearity for the temperature dependence). In ^{29}Si spectroscopy the temperature dependence is reversed, at higher temperatures the shift is going to high frequency (as at lower concentrations) with a linear correlation, which is also different from the exponential correlation for the concentration dependence.

4. Conclusions

^{1}H and ^{29}Si chemical shift values reflect the hydrogen bonding strength in M_2^{OH} in liquid and in solid states. In $CDCl_3$ solution, there is an exponential concentration dependence and a linear temperature dependence visible. The dependence in ^{1}H-NMR spectroscopy is much stronger because of the direct observation of the silanol protons involved in the hydrogen bonding. Nevertheless, ^{29}Si chemical shifts also reflect the hydrogen bonding strength of M_2^{OH} significantly. The concentration dependence shows that the hydrogen bonding between the M_2^{OH} molecules is an intermolecular and not an intramolecular effect. Further investigation, e.g. the usage of different solvents, can show the effect of solvent polarity on the concentration dependence. These experiments are currently being carried out.

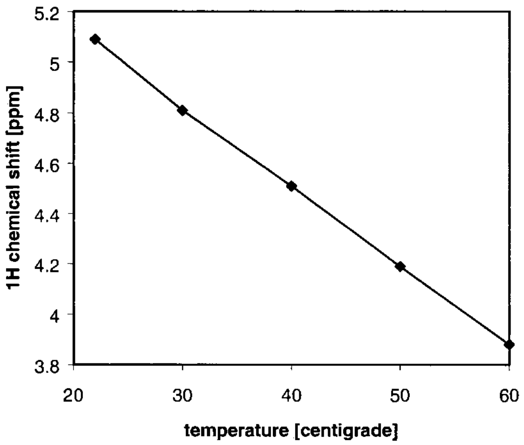

Fig. 9. Correlation between ^{1}H chemical shift of M_2^{OH} (100 mg in 0.8 ml $CDCl_3$) and temperature.

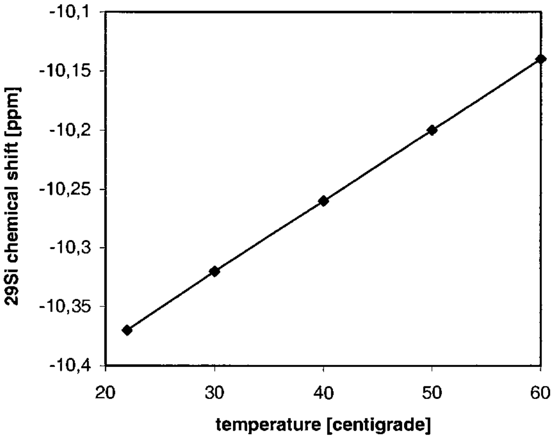

Fig. 10. Correlation between ^{29}Si chemical shift of M_2^{OH} (100 mg in 0.8 ml $CDCl_3$) and temperature.

Table 3
Chemical shift data of ^{1}H and ^{29}Si solution spectra of 100 mg M_2^{OH} in 0.8 ml $CDCl_3$ dependent on temperature

Temperature (°C)	^{1}H chemical shift, δ (ppm)	^{29}Si chemical shift, δ (ppm)
22	5.09	−10.37
30	4.81	−10.32
40	4.51	−10.26
50	4.19	−10.20
60	3.88	−10.14

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