

Intermolecular and intramolecular coordination interactions in solutions of *N*-(dimethylchlorosilylmethyl)acetamides

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Abstract

The coordinate structure of *N*-methyl- and *N*-phenyl-*N*-(dimethylchlorosilylmethyl)acetamide in solutions is investigated by multinuclear ^1H , ^{13}C , ^{17}O , and ^{29}Si NMR spectroscopy. At low temperatures (up to -90°C), two pentacoordinated silicon species are detected for the first time as an example of compounds including the coordinative OSiC_3Cl unit. At higher temperatures their fast (on the NMR time scale) interconversions are observed. On the basis of concentration, solvent and temperature dependence we assume that one species contains the intramolecular coordination $\text{O} \rightarrow \text{Si}$ bond, while the other includes the intermolecular coordination $\text{O} \rightarrow \text{Si}$ bond.

Keywords: Silicon; Hypervalence; Dynamics; Intermolecular coordination; Intramolecular coordination; Multinuclear NMR

1. Introduction

Among pentacoordinated organosilicon compounds, the derivatives of amides and lactams containing an $\text{SiCH}_2\text{NC}(\text{O})$ fragment which in turn contain a coordinative OSiC_3X unit (where X is an electron-deficient group), have been comparatively well studied [1]. The X-ray structural data show that in crystals these compounds have slightly to considerably distorted trigonal bipyramidal structure corresponding to the character of the substituent X [2–4]. The formation of the $\text{O} \rightarrow \text{Si}$ intramolecular coordination bond is accompanied by an upfield shift in the ^{29}Si NMR spectra and also a low-frequency shift in the $\nu(\text{C}=\text{O})$ band in IR spectra relative to that expected for structures without an $\text{O} \rightarrow \text{Si}$ bond [1,5].

The known data for the intermolecular coordination interactions in solutions of hypervalent silicon compounds are rather contrary. In particular, the intramolecular character of coordination in (aroyloxymethyl)trifluorosilanes has been confirmed by the fact that their IR

and ^{13}C , ^{19}F and ^{29}Si NMR spectral parameters in solution are independent of the concentration. Moreover, these compounds are monomeric in crystals [6]. Alternatively, the absence of any concentration dependence of $\nu(\text{C}=\text{O})$ frequency in solutions of *N*-(dimethylchlorosilylmethyl)-2-pyrrolidone suggests the intramolecular character of coordination in liquid phase [5].

However, the detection of the concentration dependence of the spectral parameters can be difficult owing to a fast exchange between the species which include the intramolecular and intermolecular coordination $\text{O} \rightarrow \text{Si}$ bond. This assumption is supported by molecular weight measurements of (O–Si)-chelate *N,N*-bis(dimethylchlorosilylmethyl)acetamide in C_6H_6 , which revealed that the compound is monomeric in dilute solution but is somewhat associated at higher concentrations [7]. So, at present the possibility for the formation of the intermolecular coordination $\text{O} \rightarrow \text{Si}$ bond in solutions of pentacoordinated silicon compounds is not supported by factual evidence.

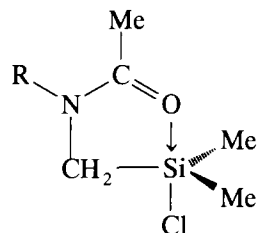
We have studied the structure and dynamic behavior of *N*-(dimethylchlorosilylmethyl)acetamides in solutions by NMR spectroscopy.

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2. Results and discussion

2.1. ^1H , ^{13}C , ^{17}O and ^{29}Si NMR spectra

N-Methyl-*N*-(dimethylchlorosilylmethyl)acetamide (**Ia**) and *N*-phenyl-*N*-(dimethylchlorosilylmethyl)acetamide (**Ib**) were selected for the detail investigation of coordinate structure of hypervalent silicon compounds:



(A, **Ia**, **b**)

R = Me(a), Ph(b)

It has been suggested that the form A can be used for their structures in solutions [7–12]. The solvent- and temperature-dependent parameters of the NMR spectra of **Ia** and **Ib** are shown in Tables 1–3.

At room temperature in different solvents the NMR spectra of **Ia** and **Ib** are characterized by a single set of signals. The high ^{17}O and ^{29}Si screening constants together with a slight downfield shift of the ^{13}C resonance provide evidence of Si atom pentacoordination [1]. Decreasing the temperature leads to the broadening of the ^1H , ^{13}C and ^{29}Si NMR signals which results in two sets of signals (species A and B) with different

intensities at temperatures less than -70°C (Fig. 1 and Tables 1–3). In both cases, the upfield ^{29}Si shifts (-35 ppm or more) are consistent with a pentacoordinated species in solution [1], and are temperature dependent (Fig. 2 and Table 3). At -90°C the A to B ratios are 64 to 36 and 43 to 57 for 0.5 M solutions of **Ia** and **Ib** respectively. Increasing the temperature results in broadening and coalescence of the signals of the two species, i.e. the process is reversible.

Within the temperature range from -30 to -50°C we also detected the weak intensive (about 5%) signals of a tetracoordinated silicon species ($\delta(^{29}\text{Si}) \approx 4\text{--}5$ ppm) in the ^1H , ^{13}C and ^{29}Si NMR spectra of **Ia** and **Ib** in addition to the two above-mentioned signals of the pentacoordinated silicon. These signals were found to belong to the corresponding disiloxanes which are the products of a plausible hydrolysis of chlorides **Ia** and **Ib**. At room temperature, only the averaged signals have been observed in NMR spectra as a result of a fast exchange between the chlorides **Ia** and **Ib** and the corresponding disiloxanes. A temperature decrease up to -20°C gives rise to the two sets of the signals.

2.2. The structure of the pentacoordinated species of *N*-(dimethylchlorosilylmethyl)acetamides

The detection of the two pentacoordinated silicon signals in the NMR spectra of **Ia** and **Ib** at low temperatures could be explained by the availability of the two topomers with the intramolecular coordination $\text{O} \rightarrow \text{Si}$

Table 1
 ^1H and ^{13}C NMR chemical shifts of **Ia** in different solvents at variable temperatures

Solvent	NMR	T ($^\circ\text{C}$)	δ (ppm)						
			MeC	MeN	CH_2	SiMe_2	C=O		
C_6D_6	^1H	20	1.02	1.77	2.51	0.96			
	^{13}C	20	16.45	35.92	44.21	7.88	172.40		
	^a	^1H	25	2.16	3.15	2.73	0.56		
		^{13}C	25	17.78	37.60	43.57	6.68	174.40	
$\text{C}_6\text{H}_5\text{Cl}$	^1H	^c	1.52	2.40	2.57	0.76			
CD_3CN	^1H	^c	2.08	3.05	2.74	0.46			
CH_2Cl_2	^1H	^c	2.11	3.07	2.77	0.48			
CD_2Cl_2	^1H	20	2.14	3.11	2.80	0.49			
		^{13}C	20	17.57	37.70	44.10	6.29	173.87	
		^{13}C	-60	17.57	37.47	44.49	7.50	173.95	
				$\text{Si}_{\text{intra}}^{\text{V}}$	17.57	37.47	44.84	3.99	173.95
			-90	$\text{Si}_{\text{intra}}^{\text{V}}$	17.88	37.48	44.54	7.60	174.02
				$\text{Si}_{\text{inter}}^{\text{V}}$	17.87	37.47	43.92	2.64	174.15
$(\text{CD}_3)_2\text{C}(\text{O})$	^1H	20	2.17	3.18	2.73	0.47			
	^{13}C	20	17.22	37.30	44.61	7.77	174.69		
CD_3OD	^1H	20	2.22	3.23	2.82	0.32			
	^{13}C	20	17.30	38.27	40.98	0.79	175.91		

^a 1 : 1 mixture of CDCl_3 : CH_2Cl_2 ; data from [12].

^b Data from [8].

^c At room temperature.

^d Data from [15].

^e Data from [9].

Table 2
 ^1H and ^{13}C NMR chemical shifts of **1b** in different solvents at variable temperatures

Solvent	NMR	T (°C)	δ (ppm)				
			MeC	CH ₂	SiMe ₂	C=O	
C ₆ D ₆	^1H ^{13}C	20	1.27	3.08	0.99		
		20 ^b	18.08	46.10	7.27	172.96	
C ₆ H ₅ Cl ^a	^1H ^{13}C	20	1.56	3.07	0.86		
		20	1.97	3.13	0.49		
CD ₂ Cl ₂	^1H ^{13}C	20	19.03	46.16	6.73	173.91	
		-60	18.07	45.72	7.10	174.06	
		-90	Si ^v _{intra}	18.07	41.84	2.16	174.06
			Si ^v _{inter}	17.99	45.07	6.95	174.04
(CD ₃) ₂ C(O)	^1H ^{13}C	20	1.99	3.09	0.56		
		20	18.71	46.59	7.40	174.69	
CD ₃ OD	^1H ^{13}C	20	1.98	3.16	0.32		
		20	19.67	43.37	0.45	174.98	

^a Data from [8].

^b At room temperature.

bond which are distinguished by the ligands at the trigonal bipyramidal silicon atom [13] (which is unlikely from our point of view) or by an increase in the number of the pentacoordinated species with intramolecular and intermolecular coordinate interactions.

For the purpose of determining the detected pentacoordinated species structure we have studied the dependence of the signals intensity in the ^1H NMR spectra as a function of the compound concentration of **1a** (Table

Table 3
 ^{17}O and ^{29}Si NMR chemical shifts of **1a** and **1b** in different solvents at variable temperatures

Compound	Solvent	T (°C)	δ (ppm)	
			^{29}Si	^{17}O ^a
1a	C ₆ D ₆	20	-38.3	
		20	-37.8	259
	CD ₂ Cl ₂	-60	-41.9 ^b	
		-90	-45.0; -41.0	
		-90	-44.4 ^b	
	(CD ₃) ₂ C(O)	20	-41.0	
		-60	-44.4 ^b	
-90		-45.8; -43.6		
CD ₃ OD	20	-29.0		
	-60	-46.2		
	-90	-49.1		
	^c	25	-40.3	
1b	C ₆ D ₆	20	-31.8	
		20	-36.8 ^b	281
	CD ₂ Cl ₂	-60	-43.3; -39.3	
		-90	-45.0; -40.0	
		-90	-43.1; -45.9	
	(CD ₃) ₂ C(O)	20	-37.1 ^b	278
		-60	-42.4; -44.8	
		-90	-43.1; -45.9	
CD ₃ OD	20	-22.7 ^b		
	-60	-41.0		
	-90	-42.5		

^a At 50°C.

^b A broadening signal.

^c 1:1 mixture of CDCl₃:CH₂Cl₂; data from [12].

4). The data show that the signals intensity of species B (the upfield shift of the ^{13}C and ^{29}Si NMR signals) increases with increasing concentration of **1a** in CD₂Cl₂ solution together with decreasing signal intensity of species A.

The type of the concentration dependence obtained is evidence of the intramolecular character of the coordinate bond in species A (Si^v_{intra}) and for the intermolecu-

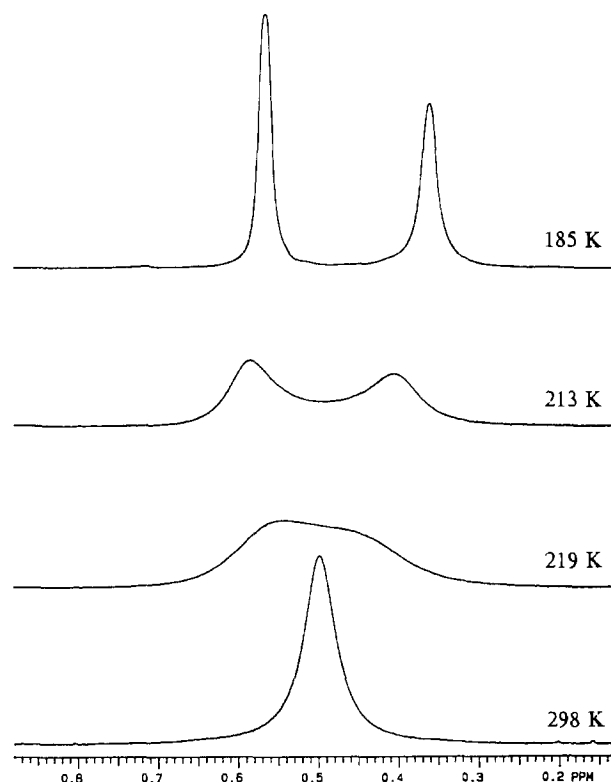


Fig. 1. ^1H DNMR (400 MHz, CD₂Cl₂) spectra of **1b** for Si(Me)₂ resonances.

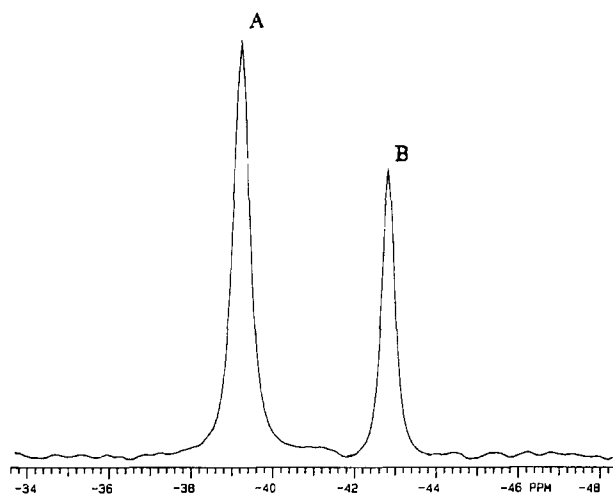


Fig. 2. ^{29}Si NMR (79.5 MHz, CD_2Cl_2) spectra of **Ib** at -63°C .

lar character in the species B ($\text{Si}_{\text{inter}}^{\text{V}}$). The latter can be described as the dimeric (B') or n -meric (B'') species:

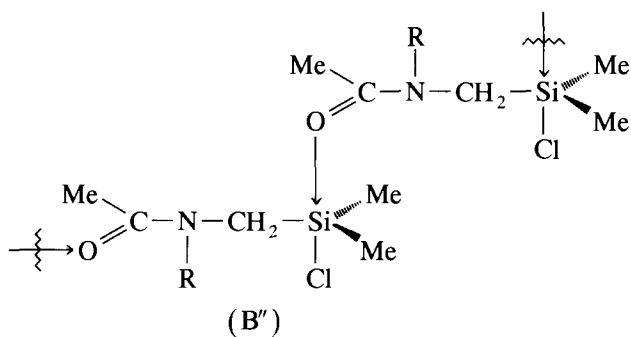
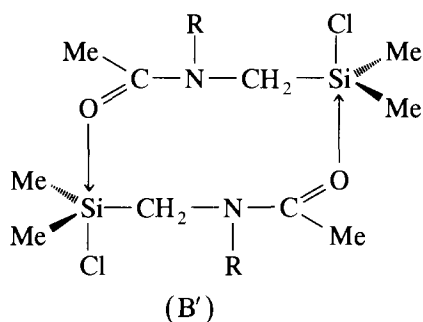
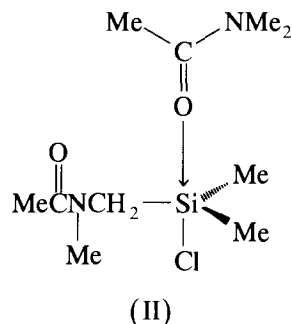


Table 4
Relative amounts of the pentacoordinated species of **Ia** in CD_2Cl_2 at -90°C

c_0 (M)	$\text{Si}_{\text{intra}}^{\text{V}}$ (%) (A)	$\text{Si}_{\text{inter}}^{\text{V}}$ (%) (B)
0.05	97	3
0.30	77	23
0.45	68	32
0.50	64	36
0.60	54	46
0.80	47	53

The tendency of N -(dimethylchlorosilylmethyl)acetamides (**Ia** and **Ib**) involved in the formation of intermolecular coordination $\text{O} \rightarrow \text{Si}$ bonds in solution leads to the specific interaction with N,N -dimethylacetamide. Thus, on the addition of an excess of N,N -dimethylacetamide to **Ia** and **Ib** in CD_2Cl_2 solution the ^{29}Si NMR spectrum at -90°C contained only a new high field peak (at -24.7 ppm for **Ia** and at -22.1 ppm for **Ib**). It seems likely that this signal belongs to the heteroassociate **II** containing a pentacoordinated silicon as a result of the intermolecular coordination:



There appears to be an enhancement in the electron-donating ability of N,N -dimethylacetamide in comparison with **Ia** and **Ib** [14].

At room temperature the ^{29}Si NMR spectrum contains a very broad peak at about -32 ± 2 ppm ($1/2\Delta\nu \approx 100\text{--}200$ Hz). It is apparent that such broadening results from the complicated intermolecular interactions between the different pentacoordinated species in solution.

2.3. Solvent effects

As is evident from the data outlined in Table 3 the higher field signals in the ^{29}Si NMR spectra of **Ia** and **Ib** at room temperature are observed in acetone solutions (-41.0 and -37.1 ppm respectively). It seems likely that this is due to $\text{O} \rightarrow \text{Si}$ bond strengthening in polar solvents [1]. Decreasing the temperature of solutions to -90°C causes a high field shift in the ^{29}Si NMR signals (at 2–6 ppm) and leads to the recording of two signals (species A and B).

The analogous high field shifts of the ^{29}Si NMR signals and their splitting into two peaks are also observed in CD_2Cl_2 solutions of **Ia** and **Ib** at low temperatures (Table 3). According to the criteria developed previously [1], the temperature dependence obtained for the shifts in the ^{29}Si NMR signals is characteristic of compounds with the weakest $\text{O}-\text{Si}$ ("coordinative") component of hypervalent $\text{O}-\text{Si}-\text{Cl}$ fragment.

The ^{29}Si NMR spectra of **Ia** and **Ib** in CD_3OD solution at room temperature contain considerably more downfield peaks in comparison with those in the other solvents (-29.0 and -22.7 ppm respectively) (Table

3)). Decreasing the temperature results in a dramatic high field shift in the signals (up to 20 ppm) without their splitting. Also the ^{13}C NMR spectra of **Ia** and **Ib** in CD_3OD contain the most downfield signals of the $\text{C}(=\text{O})$ atoms (Table 1 and 2). It seems likely that these are effects of efficient solvation of carbonyl group by CD_3OD molecules that leads to weakening of the $\text{O} \rightarrow \text{Si}$ coordinate bond.

Thus as a result of our investigation it was found that in solutions of *N*-methyl-*N*-(dimethylchlorosilylmethyl)acetamide (**Ia**) and *N*-phenyl-*N*-(dimethylchlorosilylmethyl)acetamide (**Ib**) a fast dynamic equilibrium exists between the pentacoordinate species with the intramolecular and intermolecular coordination.

3. Experimental details

The ^1H , ^{13}C , ^{17}O and ^{29}Si NMR spectra were recorded on a Varian XL-400 spectrometer at 400.0, 100.6, 54.2 and 79.5 MHz respectively. Chemical shifts were measured using tetramethylsilane (^1H , ^{13}C and ^{29}Si NMR) as internal reference for 0.5 M solutions of the samples in 5 mm ampoules, and H_2O (^{17}O) as external reference for saturated solutions in 10 mm ampoules. Negative values indicate a high field. The compounds **Ia** and **Ib** were prepared by one-bulb synthesis from amide, dimethylchloromethylchlorosilane and hexamethyldisilazane [15].

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