

# Infrared and $^{29}\text{Si}$ NMR spectroscopic investigations on metallasiloxanes derived from organosilanetriols <sup>1</sup>

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## Abstract

Silanols containing one or more Si–OH groups are useful synthons for the preparation of metallasiloxanes with novel Si–O–M frameworks. Recent reports from our laboratory in this area were centred on the synthesis of stable organosilanetriols and their use as building-blocks for the preparation of a wide range of metallasiloxanes soluble in organic solvents and incorporating various transition metals and main group elements in the siloxane framework. In addition to single crystal X-ray structural investigations, infrared and  $^{29}\text{Si}$  NMR spectral techniques provide useful information for elucidating the structures and type of metallasiloxanes formed in these reactions. This article summarizes the results of studies of the IR and  $^{29}\text{Si}$  NMR spectra of these compounds.

**Keywords:** Silicon;  $^{29}\text{Si}$  NMR spectra; IR spectra; Silanetriols; Metallasiloxanes; Group 14

## 1. Introduction

In recent years there has been considerable activity in the chemistry of silanols because of the possible applications of metallasiloxanes in many areas of chemistry and materials science [1–8]. Metallasiloxanes are compounds with M–O–Si frameworks which are formally derived from silanolates with  $\text{R}_3\text{SiO}$ ,  $\text{R}_2\text{SiO}_2$  or  $\text{RSiO}_3$  functionalities. The presence of a metal in the siloxane framework improves the thermal and conducting properties of these compounds. Metallasiloxanes can, moreover, be considered as precursors for silicone polymers with metals in the polymer backbone [9,10]. The transition metal complexes immobilized on silica surfaces are known to catalyze a variety of organic transformations [11,12]. However, the exact reactions occurring at such surfaces are poorly understood owing to difficulties in detection and analysis of the transient surface species. Metallasiloxanes are structurally similar to the modified silica surfaces and have been found to mimic the role of these catalysts, hence they are useful in unravelling the reaction mechanisms of such catalytic conversions. To gain an insight into the mechanisms involved in these

processes, a thorough systematic study of metallasiloxane chemistry is essential.

We have recently initiated research in the area of organosilanetriols aimed at obtaining soluble analogues of many naturally occurring minerals and modified silica surfaces [3]. Earlier research in this area involved the use of silanols containing one or two Si–OH groups for building metallasiloxanes [7,8]. This route normally results in metallasiloxanes with acyclic or cyclic structures. However, the naturally occurring metallasilicates contain three-dimensional cage structures [13]. Suitable soluble model compounds for these cage structures can be prepared by using silanols possessing three –OH groups which are nearly perpendicular to each other. Towards this end, we synthesized a series of silanetriols in which the silicon atom is bonded to an alkyl, amino or aryloxy group (Scheme 1) [14–17]. In recent years, there have also been several reports on the synthesis of a variety of other types of silanetriol [18–26]. All the silanetriols depicted in Scheme 1 are obtained in good yields from readily available starting materials under carefully chosen experimental conditions. These silanetriols do not undergo self-condensation under normal conditions, and are also freely soluble in a variety of organic solvents. Reactions of these silanetriols with suitable precursors, such as metal alkyls, metal alkoxides or metal chlorides, under appropriate reaction conditions, yield organometallasiloxanes with novel three-

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<sup>1</sup> Dedicated to Professor R.J.P. Corriu in recognition of his outstanding contributions to organosilicon chemistry.

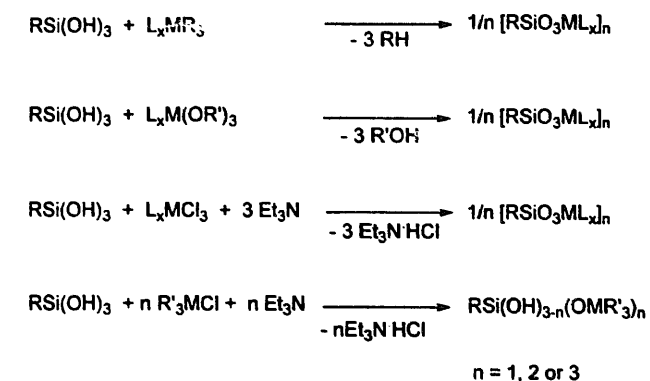
dimensional structural frameworks. A few representative reaction pathways, such as alkane/alcohol elimination and hydrogen chloride elimination, are shown in Scheme 2. A schematic structural representation of each type of compound obtained in these reactions is shown in Scheme 3. The detailed synthetic methodologies and reaction conditions used to produce these metallasiloxanes have been reported elsewhere, along with their characterization data [14–17,27–34].

All the metallasiloxanes thus prepared are highly soluble in common organic solvents such as aliphatic hydrocarbons, ether, toluene and tetrahydrofuran. Single crystal X-ray diffraction studies have been most useful in unravelling the three-dimensional structures of these complex molecules. However, obtaining suitable single crystals of these compounds for X-ray diffraction studies in all the cases is often difficult due to (1) their high solubility even in solvents such as pentane, and (2) the amorphous nature of the resultant products. Hence, it becomes necessary to use spectral techniques for elucidating the rather complex structures. Our extensive spectroscopic investigations have shown that IR and  $^{29}\text{Si}$  NMR spectroscopy are valuable tools for this purpose. In particular, on the basis of extensive  $^{29}\text{Si}$  chemical shift data obtained for a variety of these structures, it is now possible to predict the structures of the products in many of these reactions. In this article we summarize the use of these techniques in the structural elucidation of the metallasiloxanes.

## 2. IR spectral studies

### 2.1. Silanetriols

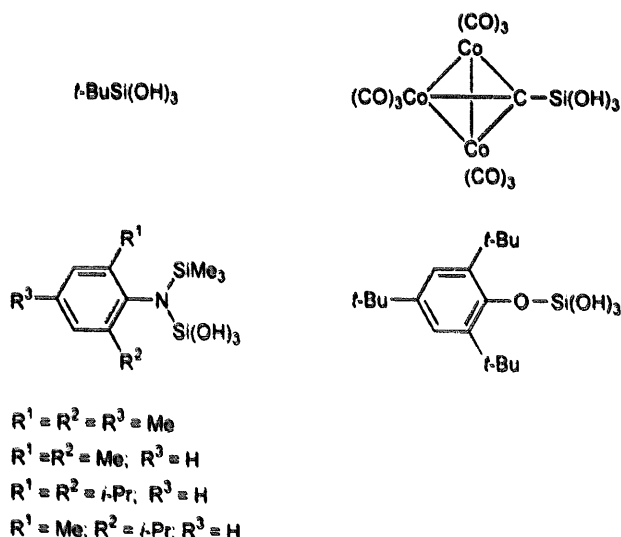
Two characteristic  $-\text{OH}$  absorptions are observed for most of the silanetriols in the region between 3400 and



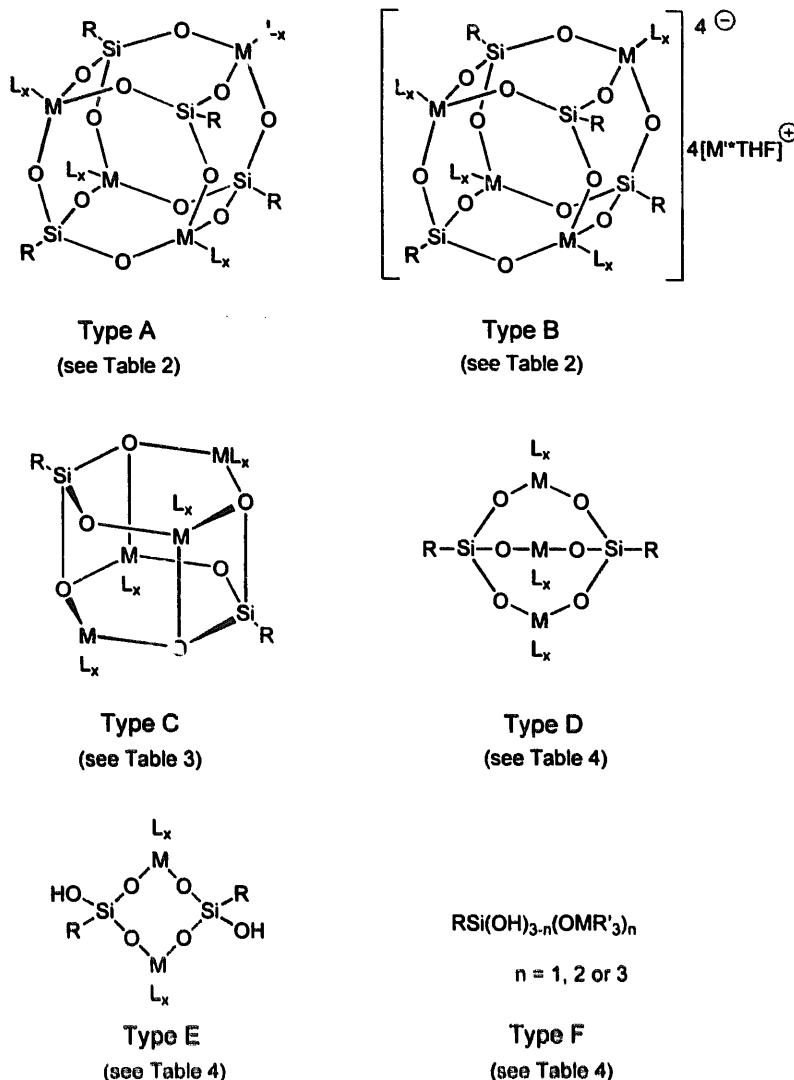
Scheme 2.

$3700\text{ cm}^{-1}$  (see Table 1). The strong and broad absorption appearing around  $3360\text{ cm}^{-1}$  is attributable to the OH groups involved in hydrogen bonding. Another, somewhat less intense but sharp, absorption is observed at around  $3600\text{ cm}^{-1}$  (Table 1), and comes from the free hydroxy groups [35]. The relative intensity of these two absorptions is an easy indication of the extent of the hydrogen bonding present in these molecules. Thus it is consistent with the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding interactions found in the X-ray crystal structure of the silanetriol  $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OH)}_3$  (1), where the molecules are arranged in a tubular form resulting from extensive intermolecular hydrogen bonds with a hydrophilic interior and a hydrophobic exterior [16]. In the case of a related silanetriol  $\text{Os}(\text{Si(OH)}_3)_3\text{-Cl}(\text{CO})(\text{PPh}_3)_2$ , only one band is observed, at  $3616\text{ cm}^{-1}$ , due to the OH groups, suggesting the absence of  $\text{O}-\text{H}\cdots\text{O}$  interactions in this compound. The single crystal X-ray study of this compound revealed that it is indeed devoid of any intra- or intermolecular hydrogen bonds [18].

Moreover, the observed spectral pattern for the (arylamino)silanetriols 1–4 does not vary significantly on changing the medium of the spectral measurement. For example, the relative intensity of these two absorptions in the OH region of the silanetriol  $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OH)}_3$  (1) obtained as a KBr pellet, Nujol mull, or as a carbon tetrachloride solution ( $1.8 \times 10^{-4}\text{ mol L}^{-1}$ ) (Fig. 1) remains almost unchanged. This observation testifies to the fact that the solid-state structural arrangement is more or less retained even in solution. In order to provide a further assessment of the concentration effects, the IR spectra of this triol were recorded at two different concentrations in  $\text{CCl}_4$ . Thus, even in a very dilute  $\text{CCl}_4$  solution ( $3.5 \times 10^{-5}\text{ mol L}^{-1}$ ), there is no significant change in the relative intensity of these two peaks. In contrast, in the case of oligomeric diorganosiloxy- $\alpha,\omega$ -diols, effects of dilution are clearly seen.



Scheme 1.



Scheme 3.

## 2.2. Metallasiloxanes

The course of the reaction of silanetriols with various metal precursors can be monitored by IR spectroscopy. As the reaction proceeds, the intensity of the bands due

to OH absorption falls, with new band(s) appearing between 950 and 1050  $cm^{-1}$ . This new absorption is assignable to an Si–O–M vibration, and this is the most intense absorption observed in the infrared spectra of all the metallasiloxanes synthesized during this study (Ta-

Table 1  
 $^{29}Si$  NMR data for silanetriols

No.	Compound	$\nu(OH)$ ( $cm^{-1}$ )	$\delta(Si(OH)_3)$ (ppm)	$\delta(SiMe_3)$ (ppm)	Ref.
1	(2,4,6- $Me_3C_6H_2$ )N(SiMe <sub>3</sub> )Si(OH) <sub>3</sub>	3592, 3400	-65.8 <sup>a</sup>	7.3	[16]
2	(2,6- $Me_2C_6H_3$ )N(SiMe <sub>3</sub> )Si(OH) <sub>3</sub>	3628, 3339	-66.2 <sup>a</sup>	7.7	[16]
3	(2,6- $^iPr_2C_6H_3$ )N(SiMe <sub>3</sub> )Si(OH) <sub>3</sub>	3574, 3344	-67.3 <sup>b</sup>	3.8	[16]
4	(2- $^iPr$ -6- $MeC_6H_3$ )N(SiMe <sub>3</sub> )Si(OH) <sub>3</sub>	3590, 3361	-65.3 <sup>a</sup>	7.5	[16]
5	(2,4,6- $^iBu_3C_6H_2$ )OSi(OH) <sub>3</sub>	3500	-83.7 <sup>b</sup>	—	[17]
6	$^iBuSi(OH)_3$	3100	-36.8 <sup>b</sup>	—	[14]
7	Co <sub>3</sub> (CO) <sub>9</sub> CSi(OH) <sub>3</sub>	3640, 3390	-56.0 <sup>a</sup>	—	[15a]

<sup>a</sup> Recorded in CDCl<sub>3</sub>.

<sup>b</sup> Recorded in DMSO-*d*<sub>6</sub>.

Table 2  
IR and  $^{29}\text{Si}$  NMR data for cubic neutral and ionic metallasiloxanes

No.	Compound	Structure (type)	$\nu(\text{SiOM})$ ( $\text{cm}^{-1}$ )	$\delta(\text{SiO}_3)$ (ppm)	$\delta(\text{SiMe}_3)$ (ppm)	$\Delta\delta(\text{SiO}_3)$ (ppm)	Ref.
8	$[\text{}^1\text{BuSiO}_3\text{Ti}(\text{C}_2\text{H}_4\text{Me})_4]$	cube (A)	974	-68.6 <sup>a</sup>	—	31.8	[17]
9	$[\text{}^1\text{SiO}_3\text{Ti}(\text{O}^i\text{Pr})_4]$	cube (A)	968	-96.9 <sup>b</sup>	6.3	31.1	[27]
10	$[\text{}^1\text{SiO}_3\text{Ti}(\text{OEt})_4]$	cube (A)	969	-97.9 <sup>b</sup>	5.2	32.1	[27]
11	$[\text{}^2\text{SiO}_3\text{Ti}(\text{O}^i\text{Pr})_4]$	cube (A)	970	-97.4 <sup>b</sup>	6.6	31.2	[27]
12	$[\text{}^2\text{SiO}_3\text{Ti}(\text{OEt})_4]$	cube (A)	970	-98.4 <sup>b</sup>	5.7	32.2	[27]
13	$[\text{}^3\text{SiO}_3\text{Ti}(\text{O}^i\text{Pr})_4]$	cube (A)	968	-96.5 <sup>b</sup>	6.0	29.2	[27]
14	$[\text{}^3\text{SiO}_3\text{Ti}(\text{OEt})_4]$	cube (A)	968	-96.6 <sup>b</sup>	6.4	29.3	[27]
15	$[\text{}^4\text{SiO}_3\text{Ti}(\text{O}^i\text{Pr})_4]$	cube (A)	973	-116.4 <sup>b</sup>	—	32.7	[17]
16	$[\text{}^1\text{SiO}_3\text{Al} \cdot \text{dioxane}]_4$	cube (A)	1049	-79.7 <sup>a</sup>	0.8	13.9	[28]
17	$[\text{}^2\text{SiO}_3\text{Al} \cdot \text{dioxane}]_4$	cube (A)	1046	-79.8 <sup>a</sup>	0.8	13.6	[29]
18	$[\text{}^3\text{SiO}_3\text{Al} \cdot \text{dioxane}]_4$	cube (A)	—	-80.3 <sup>a</sup>	2.0	13.0	[29]
19	$[\text{}^3\text{SiO}_3\text{Al} \cdot \text{THF}]_4$	cube (A)	1049	-80.4 <sup>a</sup>	0.9	13.1	[28]
20	$[\text{}^2\text{SiO}_3\text{Al} \cdot \text{THF}]_4$	cube (A)	1018	-73.6 <sup>a</sup>	—	17.6	[15b]
21	$[\text{}^1\text{SiO}_3\text{Ga} \cdot \text{dioxane}]_4$	cube (A)	1049	-76.8 <sup>a</sup>	5.0	11.0	[31]
22	$[\text{}^3\text{SiO}_3\text{Ga} \cdot \text{dioxane}]_4$	cube (A)	1052	-77.9 <sup>a</sup>	3.5	10.6	[31]
23	$[\text{}^1\text{SiO}_3\text{In} \cdot \text{dioxane}]_4$	cube (A)	1010	-77.5 <sup>b</sup>	4.7	11.7	[32]
24	$[\text{}^3\text{SiO}_3\text{In} \cdot \text{dioxane}]_4$	cube (A)	1046	-77.9 <sup>b</sup>	6.4	10.6	[32]
25	$[\text{}^3\text{SiO}_3\text{AlEt}_4][\text{Na} \cdot \text{THF}]_4$	cube (B)	—	-112.0 <sup>c</sup>	-1.0	44.7	[28]

$\text{R}^1 = (2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^2 = (2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^3 = (2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^4 = (2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)\text{O}$ ;  $\text{R}^5 = \text{Co}_3(\text{CO})_9\text{C}$ .

<sup>a</sup> Recorded in  $\text{C}_6\text{D}_6$ .

<sup>b</sup> Recorded in  $\text{CDCl}_3$ .

<sup>c</sup> Recorded in  $\text{THF-}d_8$ .

Table 3  
IR and  $^{29}\text{Si}$  NMR data for metallasiloxanes with drum structures

No.	Compound	Structure (type)	$\nu(\text{SiOM})$ ( $\text{cm}^{-1}$ )	$\delta(\text{SiO}_3)$ (ppm)	$\delta(\text{SiMe}_3)$ (ppm)	$\Delta\delta(\text{SiO}_3)$ (ppm)	Ref.
26	$[\text{}^1\text{Si}(\text{OAl}^i\text{Bu}_2)(\text{OAl}^i\text{Bu})_2]$	drum (C)	1066	-65.5 <sup>a</sup>	11.5	-0.3	[29]
27	$[\text{}^2\text{Si}(\text{OAl}^i\text{Bu}_2)(\text{OAl}^i\text{Bu})_2]$	drum (C)	1047	-65.6 <sup>a</sup>	11.8	-0.6	[29]
28	$[\text{}^3\text{Si}(\text{OAl}^i\text{Bu}_2)(\text{OAl}^i\text{Bu})_2]$	drum (C)	1053	-65.3 <sup>a</sup>	12.5	-2.0	[30]
29	$[\text{}^1\text{Si}(\text{OGaMe}_2)(\text{OGaMe})_2]$	drum (C)	1014	-66.9 <sup>a</sup>	8.7	1.1	[31]
30	$[\text{}^1\text{Si}(\text{OGaMe}_2)(\text{OGaMe})_2]$	drum (C)	1025	-65.4 <sup>a</sup>	6.7	-1.9	[31]
31	$[\text{}^1\text{Si}(\text{OInMe}_2)(\text{OInMe})_2]$	drum (C)	1011	—	—	—	[32]
32	$[\text{}^1\text{Si}(\text{OInMe}_2)(\text{OInMe})_2]$	drum (C)	1014	-65.9 <sup>b</sup>	6.4	-1.4	[32]

$\text{R}^1 = (2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^2 = (2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^3 = (2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ .

<sup>a</sup> Recorded in  $\text{C}_6\text{D}_6$ .

<sup>b</sup> Recorded in  $\text{CDCl}_3$ .

Table 4  
IR and  $^{29}\text{Si}$  NMR data for metallasiloxanes with other structures

No.	Compound	Structure (type)	$\nu(\text{SiOM})$ ( $\text{cm}^{-1}$ )	$\delta(\text{SiO}_3)$ (ppm)	$\delta(\text{SiMe}_3)$ (ppm)	$\Delta\delta(\text{SiO}_3)$ (ppm)	Ref.
33	$[\text{}^2\text{Si}(\text{OSnMe}_2\text{O})_2\text{SiR}^2]$	bicyclic (D)	964	-68.9 <sup>a</sup>	3.6	2.7	[34]
34	$[\text{}^1\text{Si}(\text{OSnPh}_2\text{O})_2\text{SiR}^1]$	bicyclic (D)	960	-67.9 <sup>a</sup>	4.9	0.6	[34]
35	$[\text{}^1\text{Si}(\text{OH})(\text{OAl}^i\text{Bu} \cdot \text{THF})_2]$	cyclic (E)	963	-77.0 <sup>b</sup>	1.3	9.7	[30]
36	$[\text{}^1\text{Si}(\text{OH})(\text{OZrCp}_2)_2]$	cyclic (E)	968	-71.8 <sup>a</sup>	5.8	4.5	[34]
37	$\text{R}^1\text{Si}(\text{OH})_2(\text{OTiCp}_2\text{Cl})$	acyclic (F)	973	-71.8 <sup>a</sup>	5.8	4.5	[34]
38	$\text{R}^1\text{Si}(\text{OH})_2(\text{OSiMe}_3)$	acyclic (F)	971	-72.9 <sup>a</sup>	6.5, 10.3	7.1	[33]
39	$\text{R}^2\text{Si}(\text{OH})_2(\text{OSiMe}_3)$	acyclic (F)	973	-72.8 <sup>a</sup>	6.3, 10.2	6.6	[33]
40	$\text{R}^3\text{Si}(\text{OH})_2(\text{OSiMe}_3)$	acyclic (F)	974	-72.9 <sup>a</sup>	6.4, 10.3	5.6	[33]
41	$\text{R}^3\text{Si}(\text{OH})(\text{OGaMe}_2)_2$	acyclic (F)	955	-74.8 <sup>a</sup>	4.1	7.5	[34]
42	$\text{R}^2\text{Si}(\text{OSnMe}_3)_3$	acyclic (F)	—	-71.9 <sup>a</sup>	2.9	5.7	[34]
43	$\text{R}^3\text{Si}(\text{OSnMe}_3)_3$	acyclic (F)	965	-71.8 <sup>a</sup>	1.5	4.5	[34]
44	$^i\text{BuSi}(\text{OSnMe}_3)_3$	acyclic (F)	—	-46.4 <sup>b</sup>	—	9.6	[17]

$\text{R}^1 = (2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^2 = (2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ ;  $\text{R}^3 = (2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ .

<sup>a</sup> Recorded in  $\text{CDCl}_3$ .

<sup>b</sup> Recorded in  $\text{DMSO-}d_6$ .

bles 2 to 4). The shift in frequency of this vibration for various metallasiloxanes seems to depend on the nature of the Si–O–M unit. Thus, for Si–O–Al compounds it is observed at ca.  $1050\text{ cm}^{-1}$ , while it appears at ca.  $960\text{ cm}^{-1}$  for the compounds containing an Si–O–Ti unit. Therefore, this absorption is very useful in revealing whether an Si–O–M unit is formed in these reactions, leading to metallasiloxanes. However, at present it is not possible to correlate the frequency of this vibration arising from various metallasiloxanes to the reduced masses of the corresponding Si–O–M units. The IR spectrum of the aluminosiloxane **20** (in the region  $900\text{--}1200\text{ cm}^{-1}$ ), showing this strong absorption at  $1049\text{ cm}^{-1}$ , is depicted in Fig. 2.

While we have not recorded the infrared spectra of all the metallasiloxanes in solution, on the basis of  $^1\text{H}$  and  $^{29}\text{Si}$  NMR studies we believe that the solid-state structures are retained in the solution.

The knowledge gained from studying the IR spectra of the molecular metallasiloxanes can also be used in assigning some characteristic vibrations found in synthetic zeolites. For example, there have been different assignments for a vibration appearing around  $960\text{ cm}^{-1}$  in Ti containing silicalites such as TS-1 and TS-2. This absorption has been attributed to the Ti=O stretch by some authors [36–38], but by others to an Si–O<sup>−</sup> species or an Si–O<sup>−</sup>–Ti<sup>+</sup> unit. It has also been suggested that the intensity of this absorption is directly related to the Ti content in the modified silicalites. For

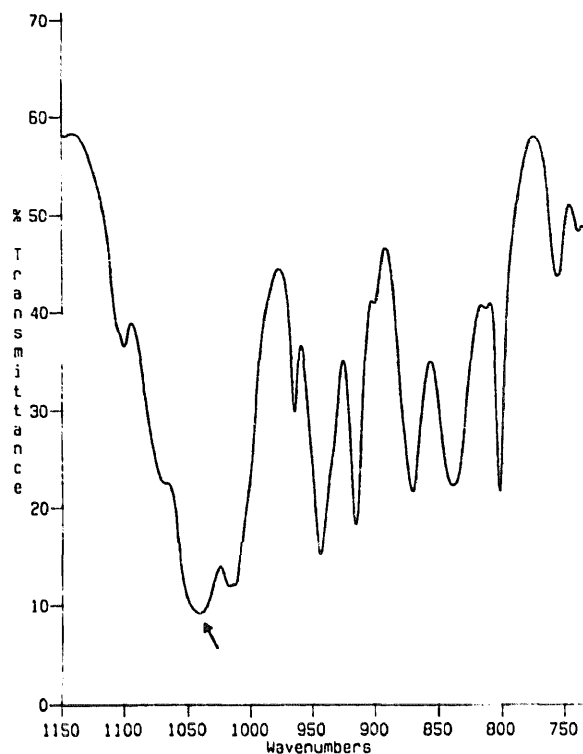


Fig. 2. The IR spectrum (in Nujol) of the cubic aluminosiloxane  $[(2,6\text{-}^1\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{SiO}_3\text{Al}\cdot\text{THF}]_4$  (**19**) showing the Si–O–Al vibration at  $1049\text{ cm}^{-1}$ .

all the molecular titanasiloxanes that we have synthesized there is a very strong absorption in the range  $960\text{--}970\text{ cm}^{-1}$ . We assign this absorption to an Si–O–Ti stretching vibration, since our compounds do not contain a Ti=O or an Si–O<sup>−</sup> unit. In order to further confirm this assignment the labelled titanasiloxane  $[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si}^{(18)}\text{O}_3\text{Ti}(\text{O}^i\text{Pr})_4]$  (**11**) was prepared from a 10%  $^{18}\text{O}$  enriched sample of the silanetriol  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$  (**2**). We observed that the stretching frequency around  $960\text{ cm}^{-1}$  undergoes considerable broadening on  $^{18}\text{O}$  enrichment, with a new shoulder appearing at a lower frequency (Fig. 3). In view of the unambiguous nature of the structural assignment of the titanasiloxanes by X-ray diffraction studies and  $^{18}\text{O}$  labelling studies, it is now possible to assign this absorption definitively to an Si–O–Ti stretching frequency. The high intensities of the  $960\text{--}970\text{ cm}^{-1}$  peak in these compounds are certainly due to the high Ti to Si ratio of 1 : 1, whereas in the modified zeolites this peak is observed with varying intensity, depending on the extent of Ti incorporation in the silicalite structure.

### 3. $^{29}\text{Si}$ NMR studies

#### 3.1. Silanetriols

The  $^{29}\text{Si}$  NMR chemical shifts for the silanetriols depicted in Scheme 1 are summarized in Table 1. As is

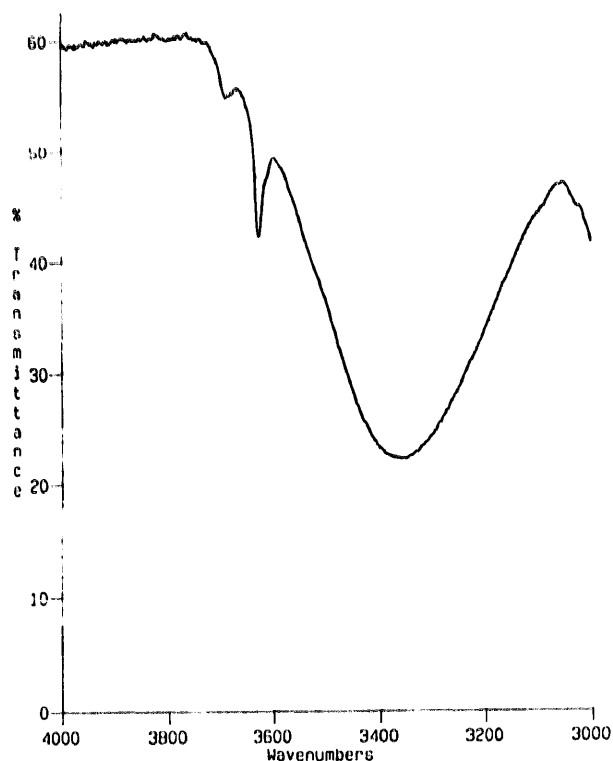


Fig. 1. The IR spectrum (in the OH region) of the silanetriol  $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$  (**1**) in  $\text{CCl}_4$  solution at  $1.8 \times 10^{-4}\text{ mol L}^{-1}$ .

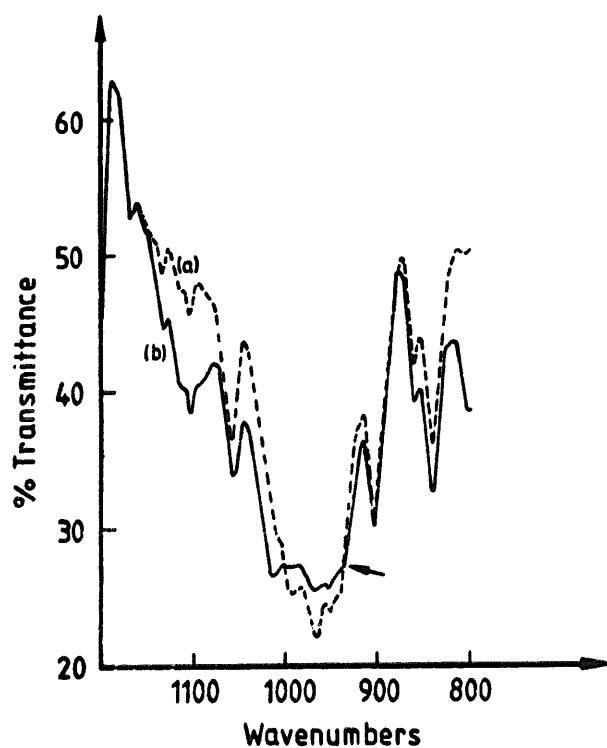


Fig. 3. The IR spectra (in Nujol) of the (a) normal and (b) 10%  $^{18}\text{O}$  enriched samples of the titanasiloxane 11 in the region 800–1200  $\text{cm}^{-1}$ . The new shoulder appearing in (b) on  $^{18}\text{O}$  enrichment is labelled with an arrow.

evident from Table 1, the resonances for the  $\text{SiO}_3$  unit of all the silanetriols are shifted to higher field. This observation is consistent with the presence of three electron-withdrawing oxygen atoms on silicon. There are also significant variations observed for this resonance depending upon the nature and magnetic shielding effect of the fourth substituent on silicon (e.g. Si, C, N or O). Thus, for example, the values of  $\delta(\text{SiO}_3)$  for C-bonded silanetriols  $^t\text{BuSi}(\text{OH})_3$  and  $\text{Co}_3(\text{CO})_9\text{CSi}(\text{OH})_3$  are  $-36.8$  and  $-56.0$  respectively. The same resonance for the N-bonded silanetriols is shifted further upfield and appears at ca.  $-65$  ppm. In the case of the O-bonded silanetriol  $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2)\text{-OSi}(\text{OH})_3$ , which contains an  $\text{SiO}_4$  tetrahedron, this resonance is observed at  $-83.7$  ppm. For the only Si-bonded silanetriol,  $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{OH})_3$ , reported in the literature, it appears at  $-25.8$  ppm. Thus, the high-field shifts for the silanetriols increase in the following order:  $\text{Si-SiO}_3 < \text{C-SiO}_3 < \text{N-SiO}_3 < \text{O-SiO}_3$ . It should also be noted that the electronegativities of these elements vary in the same order.

There have been reports on the synthesis and crystal structures of the silanetriols of type  $\text{ML}_n\text{Si}(\text{OH})_3$  containing a metal-silicon bond [18–20]. However, the absence of  $^{29}\text{Si}$  NMR data for these compounds rules out a discussion on the effect of a transition metal on  $\delta_{\text{Si}}$  or a comparison with the systems discussed above.

### 3.2. Metallasiloxanes

The silicon chemical shifts for the metallasiloxanes synthesized in the present study seem to depend heavily on both the nature of the metal and the structure of the product. The structures of the metallasiloxanes can be broadly classified into six types (Scheme 2): type A, the neutral cubic metallasiloxanes; type B, the ionic cubic metallasiloxanes; type C, metallasiloxanes with drum-like structures; type D, bicyclic metallasiloxanes; type E, cyclic metallasiloxanes; and type F, acyclic metallasiloxanes. The  $^{29}\text{Si}$  NMR chemical shifts for these types are listed in Tables 2–4, along with the coordination shifts observed [ $\Delta\delta(\text{SiO}_3)$ ]. A common observation in the case of all metallasiloxanes derived from (amino)silanetriols is that the resonance due to the  $\text{SiMe}_3$  groups in these molecules remains more or less unchanged upon formation of the metal derivatives.

In the case of all cubic titanasiloxanes of type A, the value  $\delta(\text{SiO}_3\text{Ti})$  is shifted upfield by ca. 30 ppm relative to those for the corresponding silanetriols (Table 2). For the titanasiloxane  $[^t\text{BuSiO}_3\text{Ti}(\text{C}_5\text{H}_4\text{Me})]_4$  (8), having a  $\text{CSiO}_3$  coordination environment, this resonance is observed at  $-68.6$  ppm. For the titanasiloxanes  $[\text{RSiO}_3\text{Ti}(\text{OR}') ]_4$  (9–14), derived from (arylamino)silanetriols containing silicon atoms in an  $\text{NSiO}_3$  coordination geometry, it is observed at ca.  $-97$  ppm. For the titanasiloxane 15, which contains  $\text{SiO}_4$  tetrahedra, it is shifted further upfield to  $-116.4$  ppm. Thus, among the cubic titanasiloxanes, on going from  $\text{C-SiO}_3 \rightarrow \text{N-SiO}_3$ , the resonances are shifted upfield by approximately 30 ppm. Similarly, on going from  $\text{N-SiO}_3$  to an  $\text{SiO}_4$  tetrahedral arrangement an additional shift of 20 ppm is observed.

In contrast, all the cubic metallasiloxanes of type A containing Group 13 elements 16–24 (aluminum, gallium and indium) show very similar chemical shifts. For example, in the case of aluminosiloxanes 16–19, derived from (arylamino)silanetriols, this resonance is observed at ca.  $-80$  ppm. In the case of the corresponding gallium and indium analogues, it is shifted downfield by less than 5 ppm. Furthermore, the coordination shifts accompanying the formation of these metallasiloxanes are much smaller (approximately 10–13 ppm) than in the case of titanasiloxanes.

The most significant coordination shift of 44.7 ppm is observed for the anionic cubic aluminosiloxane 25 of type B (Table 2), for which the  $\text{NSiO}_3$  signal appears at  $\delta -112.0$  ppm. The crystal structure of this anionic aluminosiloxane shows many similarities to the structure of sodium zeolite A. It should also be mentioned that the silicon chemical shift observed for this compound is very similar to that of the solid-state NMR chemical shifts for a variety of aluminosilicate glasses [39].

In the case of the metallasiloxanes **26–32**, which have a drum-like polyhedral structure, almost no coordination shift is observed. The  $^{29}\text{Si}$  NMR chemical shifts listed in Table 3 for the aluminum-, gallium- and indium-containing metallasiloxanes of type C indicate that the coordination shifts are often close to zero. The bicyclic stannasiloxanes **33** and **34** of type D also show similar behaviour. Although the exact reason for this anomalous behaviour is not readily understood, it can be partly attributed to the large ring strain associated with the Si–O–M frameworks in these molecules.

The  $^{29}\text{Si}$  NMR characteristics of the aluminosiloxane **35** (of type E), which contains an  $\text{Al}_2\text{Si}_2\text{O}_4$  cyclic eight-membered structure, is similar to that of all the cubic aluminosiloxanes of type A discussed above. This behaviour is easily attributed to the presence of  $\text{Al}_2\text{Si}_2\text{O}_4$  structural units in both types of compound. The zirconasiloxane **36** of type E is also no exception to

this observation. In the case of all acyclic metallasiloxanes **37–44** of type F listed in Table 4, a small coordination shift of 5 to 10 ppm is observed.

As mentioned earlier, the dependence of the  $^{29}\text{Si}$  NMR chemical shifts on the resulting Si–O–M framework is very great. Starting from the same silanetriol **3** and appropriate aluminum alkyl precursors, by carefully altering the stoichiometry and reaction conditions, it has been possible to obtain aluminosiloxanes with various Si–O–Al polyhedral structures. The change in the structure of the Si–O–Al framework in these compounds has a pronounced effect on their silicon chemical shifts, and this observation is depicted in Fig. 4.

In summary, the observed silicon NMR shifts for a metal containing siloxane are very useful in identifying the Si–O–M framework present in these molecules. While a coordination shift of around 10 ppm is normally associated with the eight-membered cyclic and

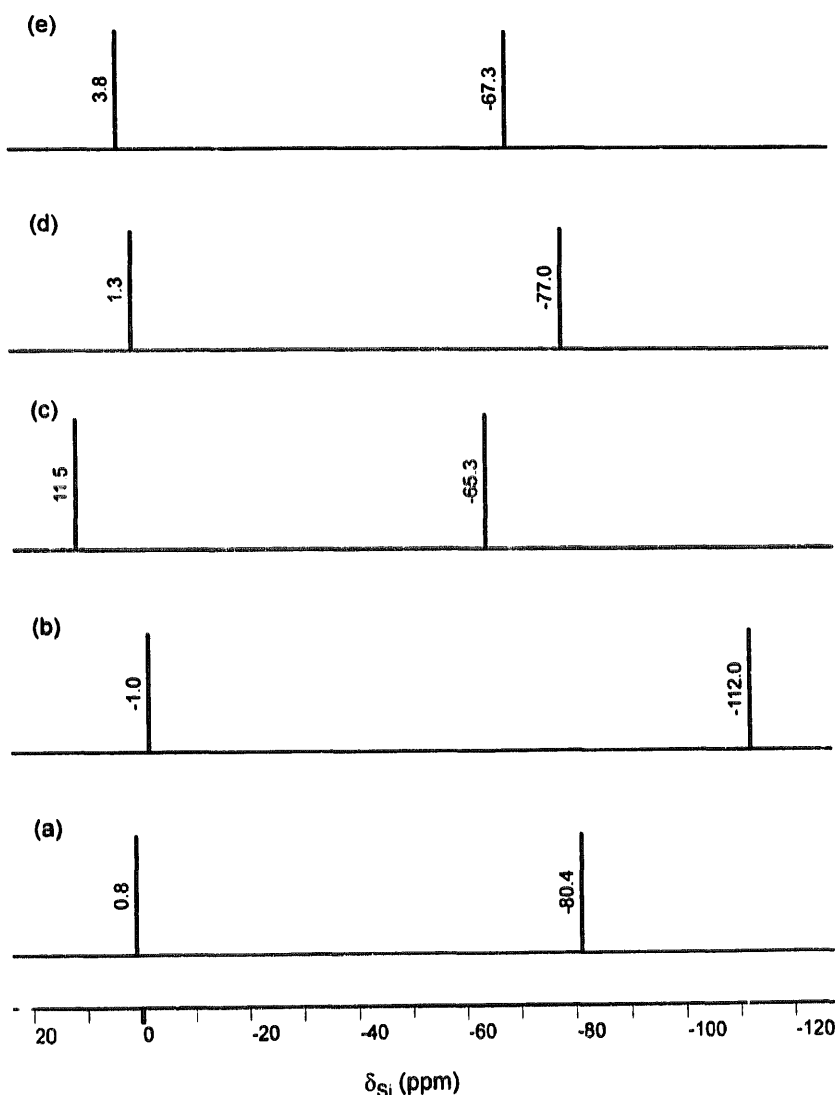


Fig. 4. The schematic representation of the  $^{29}\text{Si}$  NMR spectra of the silanetriol **3** and the derived aluminosiloxanes with different Si–O–Al frameworks: (a) cubic aluminosiloxane **19**; (b) anionic cubic aluminosiloxane **25**; (c) drum-shaped aluminosiloxane **28**; (d) cyclic aluminosiloxane **35**; and (e) the silanetriol **3**.

cubic Group 13 siloxanes, the transition metals containing cubic siloxanes (e.g. cubic titanasiloxanes) show upfield shifts as large as 30 ppm. When anionic siloxanes are formed the upfield shifts are as high as 45 ppm.

#### 4. Experimental

The synthesis of the silanetriols 1–7 [14–17] and the metallasiloxanes derived from them 8–44 have been described previously [14,15,17,27–34]. The  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument using  $\text{C}_6\text{D}_6$ ,  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$  or  $\text{THF}-d_8$  as solvents [40]. The chemical shifts are reported in ppm relative to external  $\text{SiMe}_4$ . The IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer for KBr pellets, Nujol mulls or  $\text{CCl}_4$  solutions. The solution IR studies were carried out in KBr or NaCl cells with a path length of 0.1 cm.

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