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Anion recognition by 1,3-disiloxane-1,1,3,3-tetraols in organic solvents

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ABSTRACT

Anion recognition by 1,3-disiloxane-1,1,3,3-tetraols has been elucidated by ^{1}H NMR titrations and ESI-MS in organic solvents. The association constants of the receptors for halide anions are larger than those of silanediol and 1,3-disiloxane-1,3-diol due to the cooperative hydrogen bonds by four silanol hydroxy groups of 1,3-disiloxane-1,1,3,3-tetraols.

Anion recognition has attracted growing attention due to important roles of anions in chemical and biological processes.[1] The design and synthesis of artificial anion receptors have been developed in the last two decades. Although, a number of neutral receptors bearing N–H groups, such as amide, sulfonamide, urea, thiourea, and pyrrole have been reported, there are limited examples of receptors incorporating O–H groups as an anion recognition site.[2,3] We have focused on the OH-based anion receptors to explore the efficiency of recognition ability of hydroxy groups on anion recognition chemistry.[4,5] More recently, we have reported the anion recognition by novel artificial receptors bearing two silanol groups in a molecule,[6] such as *gem*-silanediol (**1**) and 1,3-disiloxane-1,3-diol (**2**) in organic solvents. These receptors have sufficient recognition ability for anions by the cooperative hydrogen bonds of two silanol hydroxy groups to an anion. It should be noted that the carbon analogs of *gem*-silanediol and 1,3-disiloxane-1,3-diol are not effective anion receptors because of the instability to form the corresponding ketone and intramolecular hydrogen bonds, respectively. Increasing numbers of recognition sites should lead to more effective recognition for anions. Then we designed 1,3-disiloxane-1,1,3,3-tetraol, which consists of the structural combination of *gem*-silanediol and 1,3-disiloxane-1,3-diol, and four hydroxy groups of the receptor expect to cooperatively associate one anion in organic solvents. Nevertheless silanepolyols are generally unstable to self-condensation to form oligo- or polysiloxanes, the stability against condensation of silanepolyols can be improved by introduction of sterically bulky substituents on the silicon atoms. Therefore, bulky aryl (Tip: 2,4,6-triisopropylphenyl) and alkyl (Tx: 1,1,3-trimethylpropyl) groups are introduced in 1,3-disiloxane-1,1,3,3-tetraols **3a** and **3b**, respectively (see Scheme 1).

Receptors **3a** and **3b** were prepared by the previously reported procedures by us from $TipSiCl_3$[7] and $TxSiCl_3$,[8] respectively. The structure of receptors was characterized by NMR and MS. It is well known that silanol derivatives form dimer, oligomer, or polymer networks by intermolecular hydrogen bonds in the solid states.[9] Indeed, the X-ray crystal structures of two 1,3-disiloxane-1,1,3,3-tetraols, 1,3-di-*t*-butyldisiloxane-1,1,3,3-tetraol, and 1,3-diphenyldisiloxane-1,1,3,3-tetraol were reported by Lickiss et al.[10] and Abe and co-workers,[11] respectively and both disiloxanetetraols form intermolecular hydrogen bond networks. However, there is no intramolecular hydrogen bond in the solid state. Intermolecular hydrogen bonds to form dimer or oligomer diminish the recognition ability for anions because the intermolecular hydrogen bond must be broken during the course of complexation with anions.[6c,12]

The chemical shift of the silanol OH group of **3a** and **3b** was found at 4.37 and 3.79 ppm by ^{1}H NMR spectroscopy in MeCN-d_3, respectively. To confirm no dimerization or oligomerization in solution, concentration dependence of the chemical shifts of **3** was evaluated by ^{1}H NMR in MeCN-d_3. As shown in Figure 1, the silanol OH signal of receptor **3a** showed no shift over a concentration range from 4.94×10^{-3} to 6.2×10^{-4} mol dm^{-3}, and the result clearly indicates no or negligible dimerization or higher order aggregation of receptors **3** at least in our experimental conditions.

ESI-MS of **3a** in MeCN showed ion peaks corresponding to 1:1 complex with Cl^- in good agreement with isotope patterns

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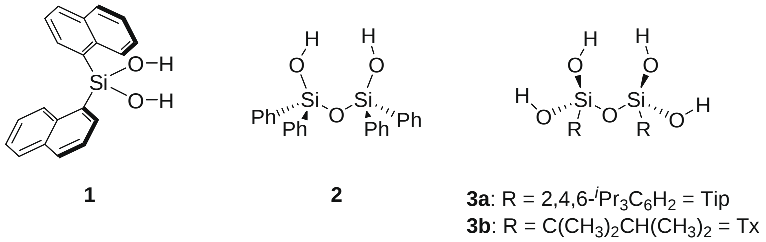


3a: R = 2,4,6-$^{i}Pr_3C_6H_2$ = Tip
3b: R = $C(CH_3)_2CH(CH_3)_2$ = Tx

Scheme 1.

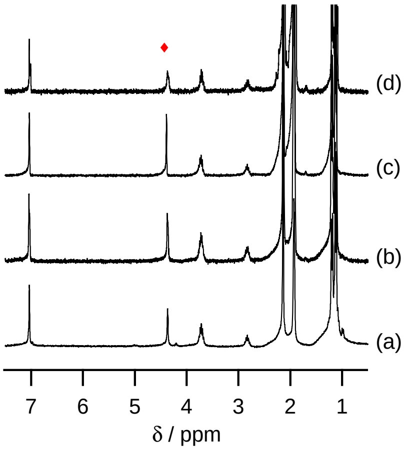


Figure 1. ^1H NMR dilution experiment of **3a** MeCN-d_3. [**3a**] = 4.94 × 10^{-3} (a), 2.47 × 10^{-3} (b), 1.23 × 10^{-3} (c), 6.2 × 10^{-4} (d) mol dm^{-3}.

(Fig. S1). The results suggest that receptor **3a** recognizes the anionic species such as Cl^- in MeCN. Receptor **3b** showed similar results.

The ^1H NMR spectrum of **3a** showed considerable changes in the chemical shift upon the addition of tetrabutylammonium bromide in MeCN-d_3 as shown in Figure 2. A large downfield shift of the OH signal indicates hydrogen bonds of SiOH and Br^-. The methine protons of 2,6-^{i}Pr and 4-^{i}Pr groups of **3a** showed small downfield and upfield shifts, respectively, and aryl C–H showed small upfield shift. The chemical shift changes can be fitted with a theoretical isotherm for a 1:1 complexation and the association constant (K_{11}) was calculated to be 128 ± 5 mol^{-1} dm^3 by non-linear curve fitting analysis.[13] Titration with tetrabutylammonium iodide shows similar but smaller changes (Fig. S2).

The addition of tetrabutylammonium chloride into solution of receptor **3a** caused a significant downfield shift of SiOH and smaller downfield and upfield shifts of the methine proton of 2,6-^{i}Pr and the aryl C–H of Tip groups, respectively, as shown in Figure 3. The titration curve can be fitted with host/guest = 1:2 curves rather than 1:1 and the association constants, K_{11} and K_{12} can be calculated to be 2480 ± 100 and 7.2 ± 0.7 mol^{-1} dm^3, respectively.[14] The K_{12} was significantly smaller than the K_{11} suggesting the electrostatic repulsion of bound chloride anions.

The SiOH signal was broadening upon the addition of tetrabutylammonium acetate and new peaks were evolved during the course of titration suggesting that the condensation of **3a** to form siloxane derivatives may be due to catalytic reaction by strong base, AcO^-. Receptor **3b** showed similar spectral changes (see Supplementary data). Calculated association constants of **3a** and **3b** are summarized in Table 1.

The association constants of **3b** are comparable to those of **3a** for all halide anions. The results indicate no difference between alkyl and aryl substituents on silicon atom for anion recognition by silanol. It is noteworthy that receptor **3b** is the first example of a silanol-based receptor bearing an alkyl substituent on silicon atoms. It is clear that receptors **3a** and **3b** associate Cl^- most strongly, followed by Br^- and I^-. This order can be explained by both the basicity and the charge density of the anions. By comparing the association constants of **3a** and **3b** with receptors bearing two silanol groups, **1** and **2**, it was found that the association constants of **3** are one or two order magnitude larger than those of **1** and **2** for all halide anions. These results strongly imply that the four silanol groups cooperatively associate one halide anion in MeCN-d_3 as shown in Scheme 2. For Cl^-, the second complexation (1:2 complex) can be detected by slightly strong hydrogen bonds between one of the silanediol moieties due to the strong basicity of Cl^- than those of Br^- and I^-.

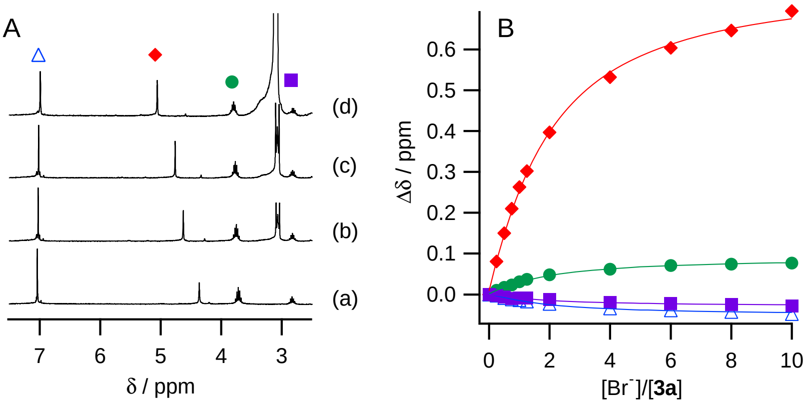


Figure 2. ^1H NMR titration of **3a** with tetrabutylammonium bromide in MeCN-d_3. [**3a**] = 4.94 × 10^{-3} mol dm^{-3}. (A) NMR spectra in the presence of 0 (a), 1.0 (b), 2.0 (c), and 10.0 (d) equiv of Br^-. (B) The chemical shift changes and the best fitting curves by a 1:1 complexation model of Ar C–H (△), Si–OH (◆), 2- and 6-CH of ^{i}Pr on Tip (●), and 4-CH of ^{i}Pr on Tip (■), respectively.

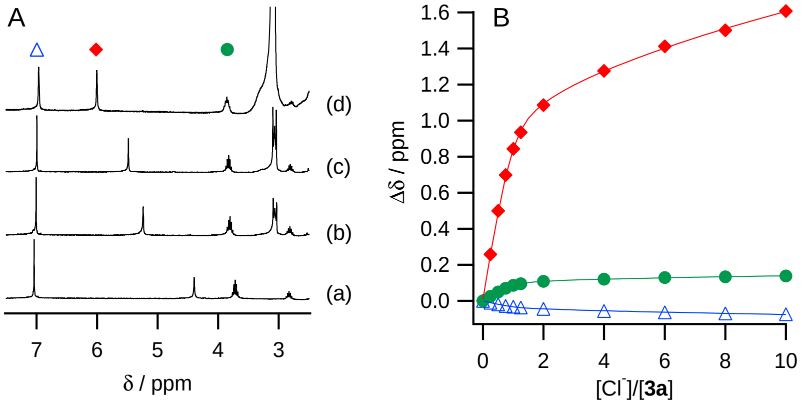


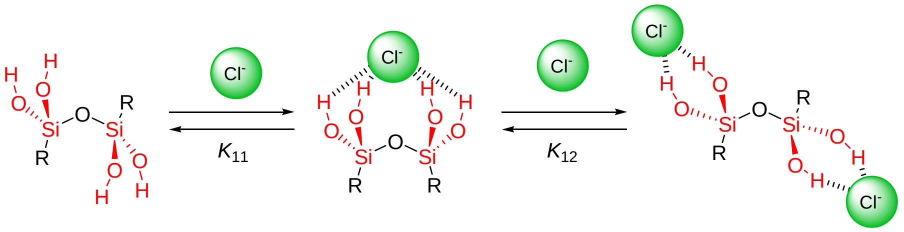
Figure 3. ^{1}H NMR titration of **3a** with tetrabutylammonium chloride in MeCN-d_3. [**3a**] = 4.94 × 10^{-3} mol dm^{-3}. (A) NMR spectra in the presence of 0 (a), 1.0 (b), 2.0 (c), and 10.0 (d) equiv of Cl$^-$. (B) The chemical shift changes and the best fitting curves by a 1:2 complexation model of Ar C–H (△), Si–OH (♦), and 2- and 6-CH of ^{i}Pr on Tip (●), respectively.

Table 1
The association constants of receptors **1**–**3** with anion

	K_{11}[a] (mol^{-1} dm^3)			
	1	**2**[b]	**3a**	**3b**
AcO$^-$	25,000 ± 500	ND[c]	ND[c]	ND[c]
Cl$^-$	46.0 ± 6.4	670 ± 44	2480 ± 100 (7.2 ± 0.7)[d]	2,760 ± 110 (11.8 ± 0.1)[d]
Br$^-$	6.4 ± 0.4	52.5 ± 1.5	128 ± 5	77.7 ± 5.4
I$^-$	0.7 ± 0.2	4.3 ± 0.3	8.6 ± 0.2	10.1 ± 1.6

[a] Determined by 300 MHz ^{1}H NMR spectroscopy at 298 K in MeCN-d_3.
[b] Ref. 5b.
[c] Not determined due to the condensation of the receptors in the presence of AcO$^-$.
[d] K_{12}/dm^3 mol^{-1}.

The solubility of receptor **3b** in $CDCl_3$ is poor, however, receptor **3a** can be easily dissolved in $CDCl_3$, then, ^{1}H NMR dilution experiment for **3a** was also performed in $CDCl_3$. As shown in Figure 4, the silanol OH peak showed downfield shift by increasing the concentration of **3a** in $CDCl_3$. The chemical shifts were plotted against the concentration of **3a** and the plot was in good agreement with the theoretical curve of a dimerization equilibrium as shown in Figure 4b. The dimerization constant for **3a** was calculated to be 407 mol^{-1} dm^3. The calculated chemical shifts of monomer **3a** and dimer **3a**$_2$ were 2.05 and 7.29 ppm, respectively, and these values are acceptable.[6c,15] The intermolecular hydrogen bond formation might be expected because this solvent is less competitive for hydrogen bond interactions than acetonitrile. Titration of receptor **3a** with Cl$^-$ was performed in $CDCl_3$ and the silanol peak



Scheme 2.

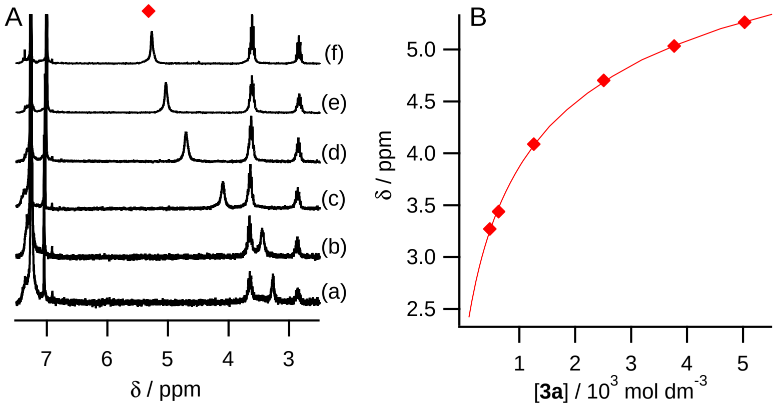


Figure 4. ^{1}H NMR dilution experiment of **3a** in $CDCl_3$. [**3a**] = 4.7 × 10^{-4} (a), 6.3 × 10^{-4} (b), 1.26 × 10^{-3} (c), 2.51 × 10^{-3} (d), 3.77 × 10^{-3} (e), and 5.03 × 10^{-3} (f) mol dm^{-3}.

showed downfield shift upon the addition of Cl^- indicating formation of hydrogen bond. However the titration curve is too complex by biphasic change (Fig. S7), therefore, we cannot determine the association constants.

In conclusion, we have reported anion recognition properties of 1,3-disiloxane-1,1,3,3-tetraols **3a** and **3b** for the first time. Both receptors recognize halide anions more effectively than silanediol **1** and 1,3-disiloxane-1,3-diol **2** due to cooperative hydrogen bonds of the four silanol OH groups. As far as we know, **3b** is the first example of anion recognition by the silanol-based receptor bearing alkyl groups on silicon atoms. Further functionalization of 1,3-disiloxane-1,1,3,3-tetraols might provide promising candidates for various applications such as ion selective electrode and a chloride transport reagent across the membrane.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.134.

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