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Anion recognition by a disiloxane-1,3-diol in organic solvents

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Abstract—To explore the anion recognition ability of silanol derivatives, ESI-MS and ^{1}H NMR titrations of a 1,3-disiloxanediol **1** with anions were studied in $CDCl_3$ and MeCN-d_3. The results indicate that **1** showed strong binding to anions such as AcO^- and halides.

Anion recognition chemistry has been attracting considerable attention because anions such as chloride and carboxylates play critical roles in a wide range of biological processes and in environmental pollutants.[1] In the design of anion receptors, the choice of binding sites for anions is one of the critical points. Typically, NH groups such as amide, urea, and pyrrole are widely used as hydrogen bond donors.[2] We and other groups have reported the anion receptors bearing less explored alcoholic[3] and phenolic[4] hydroxy groups as recognition sites to expand the variation of hydrogen bond donor sites for anion recognition chemistry. We have firstly demonstrated that a silanol hydroxy group is also an effective recognition site for anions.[5] The X-ray crystallographic analysis and ^{1}H NMR titrations in $CDCl_3$ of a silanediol, di(1-naphthyl)silanediol (**2**) revealed that two silanol groups cooperatively bind anionic species such as chloride, bromide, and acetate. Meanwhile, disiloxane-1,3-diols are fundamental siloxane skeletons bearing silanol hydroxy groups. Although the intramolecular hydrogen bond of hydroxy groups of the corresponding carbon analogue (1,3-diols) is well-known, the two silanol groups of disiloxane-1,3-diols can form intermolecular hydrogen bond rather than intramolecular one due to longer Si–O distances and obtuse Si–O–Si angles.[6,7] Therefore, effective recognition of anions by the two silanol groups of disiloxane-1,3-diols should be expected. Indeed, Hossain et al. reported the X-ray crystal structure of 1,1,3,3-tetraphenyldisiloxane-1,3-diol (**1**, Scheme 1) with pyridinium chloride, which was obtained as a side product by the reaction of **1** with $TiCl_4$ in the presence of pyridine.[8] In the solid state, two silanol groups of **1** and a pyridinium NH form hydrogen bonds with one chloride anion. However, no information on the recognition event of siloxanediols including the association constants with anions in solution has been reported previously. The understanding of anion recognition ability of disiloxane-1,3-diol is valuable not only for host–guest chemistry, but also the surface chemistry of various kinds of silicon compounds. In this Letter, we show the anion recognition properties of **1** in organic solvents.

Synthesis of 1,1,3,3-tetraphenyl-1,3-disiloxane-1,3-diol **1** was carried out according to the literature.[9] The X-ray crystal structure of **1** reported so far indicated that silanol OH groups form an intermolecular hydrogen bond network in the solid state.[7] In ^{1}H NMR measurement, the silanol OH proton of **1** ($[\mathbf{1}] = 5.0 \times 10^{-3}$ mol dm^{-3}) appeared at 2.90 ppm in $CDCl_3$, which was confirmed by H–D exchange by the addition of D_2O in the sample and the chemical shift of the silanol proton is a typical chemical shift of a silanol OH without hydrogen bonding to electronegative atoms. Dilution of **1** ($5.0–0.625 \times 10^{-3}$ mol dm^{-3}) caused virtually no shift ($\Delta\delta < 0.05$ ppm) (see Supplemental data) indicating that intermolecular dimerization or intramolecular hydrogen bond with another silanol oxygen atom of **1** are negligible at least in our experimental concentration range in $CDCl_3$. As a result, two silanol OH groups of **1** can effectively used for anion recognition in solution.

Keywords: Anion recognition; Silanol; 1,3-Disiloxanediol; Hydrogen bond.

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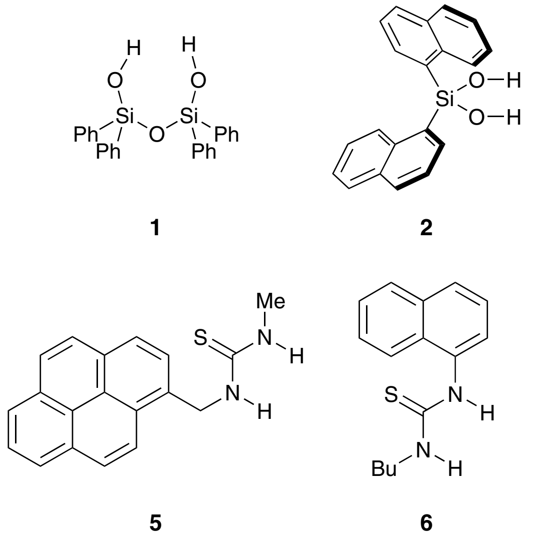


Scheme 1.

Electrospray ionization mass spectra (ESI-MS, negative mode) of **1** in the presence of tetrabutylammonium chloride, bromide, and acetate were measured in MeCN:$CHCl_3$ = 1:1 (v/v), respectively, as shown in Figure 1.[10] Ion peaks corresponding to a 1:1 complex were clearly observed in good agreement with the isotope patterns in the presence of Cl^- and Br^-. These results suggest the complex formation between **1** and Cl^- or Br^- in the solvent. In all cases, deprotonated species from **1**, $[\mathbf{1}-H]^-$ could be observed. In the ESI-MS spectra upon the addition of Br^- and AcO^-, predominant $[\mathbf{1}+Cl]^-$ peaks were also observed, even though Cl^- was not added into the solution. However, no complexation peaks of $[\mathbf{1}+AcO]^-$ were observed in the presence of AcO^-, which may be due to high basicity of AcO^- to abstract the proton from **1** in vapor phase.

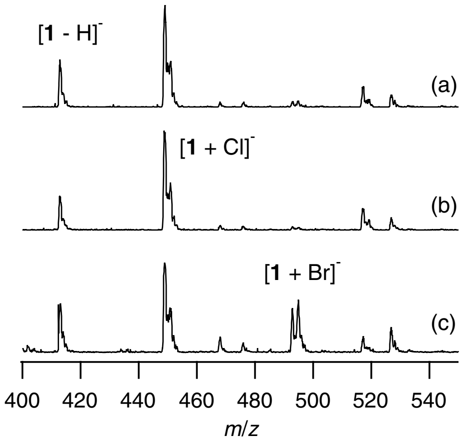


Figure 1. ESI-MS spectra (negative ion mode) of **1** in the presence of 1 equiv of AcO^- (a), Cl^- (b), and Br^- (c).

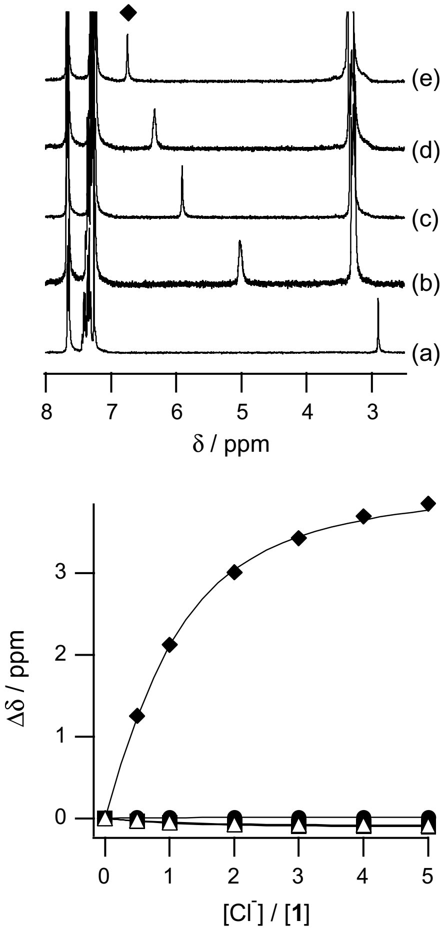


Figure 2. ^1H NMR spectra in the absence of (a) and the presence of 1.0 (b), 2.0 (c), 3.0 (d), and 5.0 (e) equiv of Cl^- in $CDCl_3$ (top) and shifts of –OH (diamonds) and *o*- (circles), *m*- (triangles), and *p*-positions (squares) of phenyl C–H protons (bottom). $[\mathbf{1}] = 5.0 \times 10^{-3}$ mol dm^{-3}.

^1H NMR titrations were conducted in $CDCl_3$ (Fig. 2). The OH signal of **1** was greatly downfield shift upon the addition of $Cl^-(\Delta\delta_\infty = 4.27 \pm 0.03$ ppm), $Br^-(\Delta\delta_\infty = 3.55 \pm 0.10$ ppm), and $I^-(\Delta\delta_\infty = 2.50 \pm 0.20$ ppm). These results strongly suggest that silanol groups of **1** act as hydrogen bond donors to form the receptor–anion complexes. In addition, *para*- and *meta*-protons of phenyl groups were shifted upfield around 0.1 ppm, however, *ortho*-protons of phenyl groups were slightly shifted downfield for Cl^- (+0.02 ppm) and upfield for Br^- (−0.01 ppm). Upon the addition of I^-, small spectral changes of the phenyl CH protons were observed. The association constants for Cl^-, Br^-, and I^- were calculated by least-square curve fitting of the chemical shift changes of all the protons with a 1:1 binding model and the values are listed in Table 1. Upon the addition of AcO^- into **1**, the OH signal of **1** was broadening and disappeared. Although *para*- and *meta*-protons of **1** showed upfield shift as mentioned above, *ortho*-protons were upfield shift until the addition of ca. 0.5 equiv and downfield shift with the addition of more than 0.5 equiv of AcO^- as shown in Figure 3. This result suggests 2:1 complex formation rather than 1:1 complex formation between **1** and AcO^- as shown in Scheme 2. The stoichiometry of the complexation was confirmed by Job's plot analysis. As shown in Figure 4a, the maximum for complexation of **1** with Cl^- at mole fraction 0.5 indicates 1:1 complex formation. However, maxima of calculated complex

Table 1. The association constants of **1** and **2** with anion

Anion	K_{11}/mol^{-1} dm^{3} [a]		
	$CDCl_3$		MeCN-d_3
	1	**2**[b]	**1**
AcO^-	3620 ± 100 (24.7 ± 3.1)[c]	5470 ± 50	ND[d]
Cl^-	377 ± 15	144 ± 11	670 ± 44
Br^-	59.8 ± 4.8	50.0 ± 1.3	52.5 ± 1.5
I^-	9.6 ± 1.1		4.3 ± 0.3

[a] Determined by 300 MHz ^{1}H NMR spectroscopy at 298 K. [Host] = 5.0×10^{-3} mol dm^{-3}.

[b] Ref. 5.

[c] K_{21}/mol^{-1} dm^3.

[d] Not determined due to condensation of receptor **1** in MeCN-d_3.

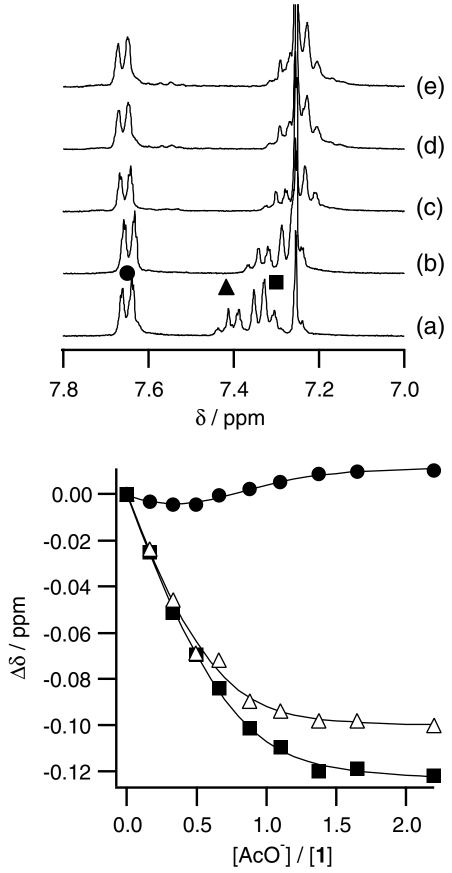
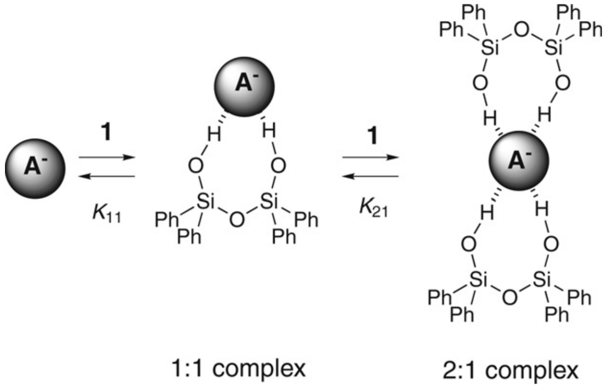


Figure 3. ^{1}H NMR spectra in the absence of (a) and the presence of 0.495 (b), 1.10 (c), 1.65 (d), and 2.2 (e) equiv of AcO^- in $CDCl_3$ (top) and shifts of *o*- (circles), *m*- (triangles), and *p*-positions (squares) of phenyl C–H protons (bottom). [**1**] = 5.0×10^{-3} mol dm^{-3}.

concentration at mole fraction ca. 0.6 for *m*-CH and *p*-CH of phenyl groups and large deviation from theoretical 1:1 curve for *o*-CH of phenyl groups for complexation of **1** with AcO^- in $CDCl_3$ were observed as shown in Figure 4b. These results strongly suggest the formation of higher order of complex such as host:guest = 2:1. The chemical shifts of phenyl C–H protons of **1** upon the addition of AcO^- could be well fitted onto the 2:1 binding isotherms and K_{11} and K_{21} were calculated to be 3620 ± 100 and 24.7 ± 3.1 mol^{-1} dm^3, respectively, by non-linear curve fitting.



Scheme 2.

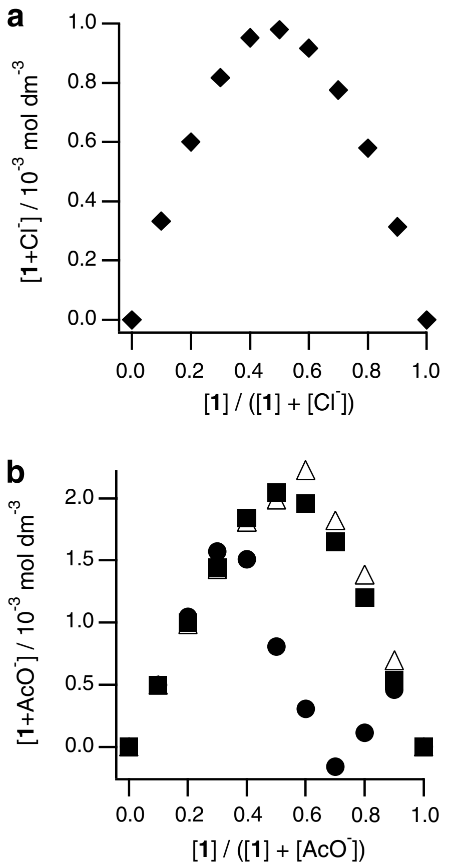
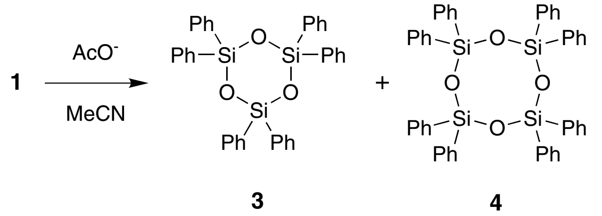


Figure 4. Job's plots for **1** with (a) Cl^- and (b) AcO^- in $CDCl_3$. [**1**]+[anion] = 5.0×10^{-3} mol dm^{-3}. Symbols: SiOH (diamonds) and *o*- (circles), *m*- (triangles), and *p*- positions (squares) of phenyl C–H protons. [**1**+anion] was calculated by assuming 1:1 complexation.

It should be noted that receptor **1** is slightly unstable in $CDCl_3$ in the presence of a basic anion such as AcO^- to form cyclic siloxanes such as hexaphenylcyclotrisiloxane (**3**) and octaphenylcyclotetrasiloxane (**4**), which were detected by HPLC analysis after a few days as shown in Scheme 3 (see Supplementary data). However, there is no problem during the course of the titration experiments in this solvent. Meanwhile, the cyclization reaction of **1** in the presence of AcO^- is faster in MeCN and octaphenylcyclotetrasiloxane is produced within



Scheme 3.

10 min due to the polar transition state of the reaction (see Supplementary data). In the presence of other anions such as Cl^-, Br^-, and I^-, these cyclic siloxanes cannot be detectable even after several days in $CHCl_3$ and MeCN. Therefore, this instability of **1** with basic anions may be one of the limitations for the application of **1** as an anion receptor.

The association constants of **1** with anions in MeCN-d_3 were also determined by ^1H NMR titration technique and the results are summarized in Table 1 with the association constants of **2** in $CDCl_3$. The association constant (K_{11}) of **1** for AcO^- is slightly smaller than that of **2**; meanwhile, K_{11} of **1** for halides are larger than those of **2** resulting in the decrease of selectivity of **1** for AcO^-. This low selectivity implies the flexibility of Si–O–Si bond of disiloxane-1,3-diol skeleton. Interestingly, small solvent effects on the association of **1** with halides are observed in $CDCl_3$ and MeCN-d_3;[11] smaller Cl^- is effectively recognized by **1**, on the contrary, the association constant of **1** for larger I^- is decreased in MeCN-d_3. The association constants of thiourea derivatives **5** in acetone[12] and **6** in MeCN[13] with Cl^- were reported to be 1000 and 640 $mol^{-1}\,dm^3$, respectively, which are comparable to the association constant of **1** for Cl^- in MeCN-d_3. These results suggest that two silanol groups cooperatively form effective hydrogen bonds with Cl^- in these solvents.

In conclusion, we have shown that a disiloxane-1,3-diol can be effectively recognize anionic species in $CDCl_3$ and acetonitrile-d_3. The disiloxane-1,3-diol as a fundamental skeleton can be widely observed in various kinds of organosilicon compounds, therefore, these compounds can also be applied to anion recognition chemistry. Investigations in this context are currently underway.

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Supplementary data

Dilution experiment of **1** in $CDCl_3$ by ^1H NMR spectroscopy and HPLC analyses of the condensation of **1** in $CHCl_3$ and MeCN are available in a PDF format. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.067.

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