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Anion Recognition by a Silanediol-Based Receptor

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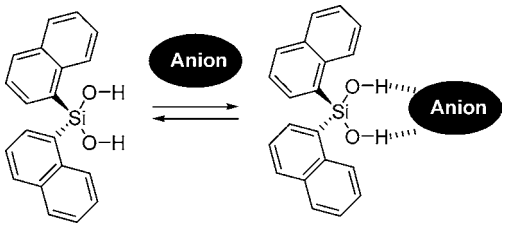
ABSTRACT



To explore the anion recognition ability of silanol hydroxy groups, a silanediol-based receptor 1 was prepared. Spectroscopic studies and X-ray crystallography revealed that the receptor exhibits the characteristic recognition of anions via two hydrogen bonds in chloroform.

The design and synthesis of neutral receptors bearing hydrogen bond donors to recognize anionic species have been one of the current challenges in the field of molecular recognition chemistry. These systems are expected to be various kinds of utilities in analytical, environmental, and medicinal chemistry.[1] In the design of artificial anion receptors, single, plural, and a combination of NH groups including amide, sulfonamide, urea, thiourea, and pyrrole have been frequently employed as hydrogen bond donors.[2] We reported the anion receptors bearing biologically important but less explored alcoholic[3] or phenolic[4] hydroxy groups. As an extension of our studies, we are interested in the molecular recognition by silanol hydroxy groups. It is well-known that terminal silanol groups on the surface of a silica gel form hydrogen bonds with various kinds of organic and inorganic substances, and the interactions are widely applied to chromatography. However, only limited examples of the anion receptors bearing silanol groups have been reported. Lee and co-workers reported that the disiloxanediol and the cyclotetrahydroxysiloxane bearing ferrocenyl moiety and ammonium group were used as carriers for anion-selective electrodes. However, participation on the recognition of anions by the silanol hydroxy group is not clear.[5] It is one of the characteristic properties of silicon compounds that silanediols are stable compounds relative to the corresponding carbon species, geminal carbon diols, which immediately transform into the corresponding ketones by elimination of H_2O. The crystal structures of silanediols and other organosilanols reveal that the silanol hydroxy groups form intermolecular hydrogen bonds to produce linear tapes and cyclic structures in the solid state.[6,7] The X-ray structures of 1,1,3,3-tetraphenyldisiloxane-1,3-diol with pyridinium

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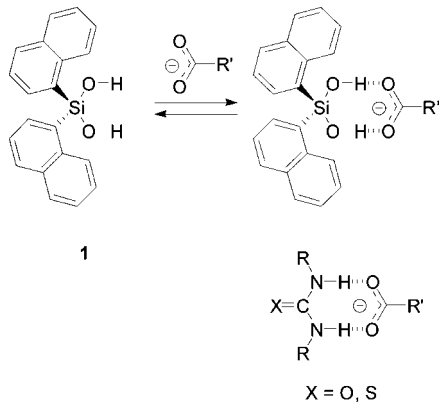
chloride[8] and 2,5-bis(di-*tert*-butylhydroxysilyl)furan with KF,[9] which were obtained as reaction products, strongly suggest the complexation ability of silanols with anions. Two silanol hydroxy groups of silanediols are expected to cooperatively form hydrogen bonds with anions in a manner similar to that with urea and thiourea NHs. In this paper, we describe the anion recognition ability of di(1-naphthyl)-silanediol (**1**)[10] in chloroform to explore silanediols as a new class of anion receptor (Scheme 1). Obvious evidence of the

Scheme 1



hydrogen bond formation of silanol hydroxy groups to anions should advance the design of anion receptors.

Dichlorodi(1-naphthyl)silane was prepared from 1-naphthyllithium and tetrachlorosilane at −78 °C in 43% yield, and the dichlorosilane was hydrolyzed by ether/water to give **1** in 91% yield. The product was characterized by melting point, NMR, and electrospray mass spectroscopy (ESI-MS).[11] To confirm no intermolecular dimerization of the silanediol **1** in solution, a dilution experiment was performed by ^{1}H NMR spectroscopy in $CDCl_3$. Only small shifts (<0.02 ppm) of the resonance for the hydroxy groups were observed at 5.0−1.25 × 10^{-3} mol dm^{-3} (Supporting Information, Figure S1), indicating that a negligible amount of intermolecular dimer is formed at least in our experimental conditions.

The negative ion mode of ESI-MS of **1** in the presence of anions such as AcO^- or Cl^- (tetrabutylammonium was used as a countercation) showed the peaks corresponding to a 1:1 complex with good agreement of isotope patterns. These results support the exclusive generation of the 1:1 complex with the anions. Proton NMR titration of **1** with chloride anion in $CDCl_3$ at 298 K is shown in Figure 1. The signal

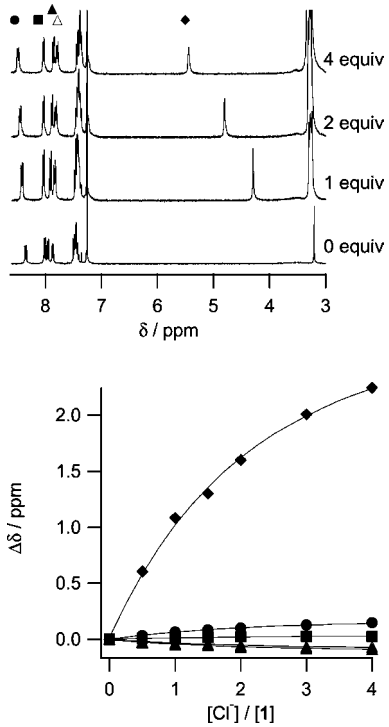


Figure 1. ^{1}H NMR titration of **1** with tetrabutylammonium chloride in $CDCl_3$ at 298 K. The symbols on the spectra correspond to the symbols of the protons in the titration plot below. [**1**] = 5.0 × 10^{-3} mol dm^{-3}, [Cl^-] = 0−2.0 × 10^{-2} mol dm^{-3}.

for the silanol hydroxy groups of **1** initially appeared at 3.21 ppm and showed a significant downfield shift over 2 ppm upon the addition of Cl^-. The resonances for the aromatic protons were also shifted. Addition of acetate anion into the solution of **1** caused a downfield shift of the signal for the hydroxy groups, but it disappeared due to broadening. The CH peaks for naphthyl groups of **1** were more significantly shifted upon the addition of AcO^- than Cl^-, as shown in Figure 2. Figure 3 shows a Job's plot of **1** with AcO^-. The maximum at mole fraction 0.5 indicates 1:1 complexation of **1** with AcO^- in $CDCl_3$. The association constants of the complexation were calculated by a nonlinear curve fitting with the 1:1 model by the data of ^{1}H NMR titrations. Those of **1** for AcO^-, Cl^-, and Br^- were determined to be 5.57 ± 0.68 × 10^3, 1.44 ± 0.11 × 10^2, and 50.0 ± 1.3 mol^{-1} dm^3, respectively, and this order is consistent with the basicity of the anions.

In studies of anion recognition, it is of primary importance to discriminate whether the process is a hydrogen bond complexation or a proton transfer of a Brønsted-type acid−base equilibrium.[12] To discriminate these two mechanisms, a ^{1}H NMR dilution experiment of a 1:1 mixture of **1** and AcO^- was performed. If the process is a hydrogen bonding interaction, the equilibrium is shifted to the dissociation

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(11) Mp 156.1−158.8 °C (lit.[10] 157−158 °C); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm) 3.16 (s, 2H), 7.45 (m, 6H), 7.87 (d, 2H, J = 7.1 Hz), 7.96 (d, 2H, J = 8.2 Hz), 8.02 (d, 2H, J = 6.8 Hz), 8.35 (d, 2H, J = 7.7 Hz); MS (EI, 70 eV) *m*/*z* (%) 316 (M^+, 100), 297 (21), 254 (29), 253 (28), 189 (22).

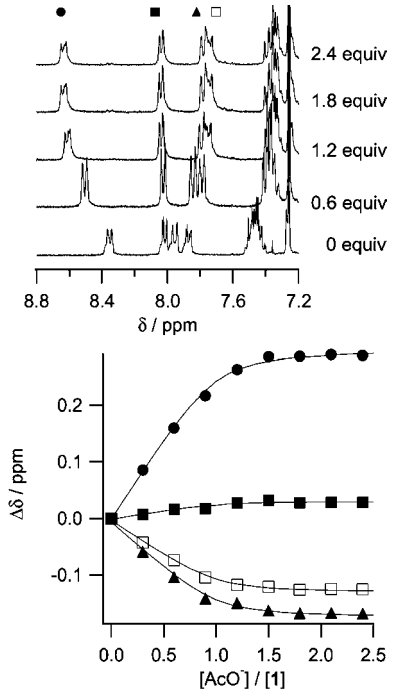

Figure 2. ^{1}H NMR spectral changes of **1** upon the addition of tetrabutylammonium acetate in $CDCl_3$ at 298 K. The symbols on the spectra correspond to the symbols of the protons in the titration plot below. [**1**] = 5.0×10^{-3} mol dm^{-3}, [AcO$^-$] = 0−1.2×10^{-2} mol dm^{-3}.

direction; therefore, spectral shifts should be observed by dilution. On the other hand, if the process is a proton transfer, the equilibrium is independent of the concentration of the host and the guest because the equilibrium constant is dimensionless.[13] The CH protons of the naphthyl groups showed a shift to the direction of dissociation by dilution (Supporting Information, Figure S2). Therefore, this process is clearly the hydrogen bond complexation rather than the proton transfer.

More direct evidence was obtained by X-ray crystallographic study. Single crystals of **1**·Cl$^-$ were grown from a 1:1 mixture of **1** and tetrabutylammonium chloride in chloroform−hexane. The ORTEP drawing of the complex is shown in Figure 4.[14] Two hydroxy groups of the silanediol

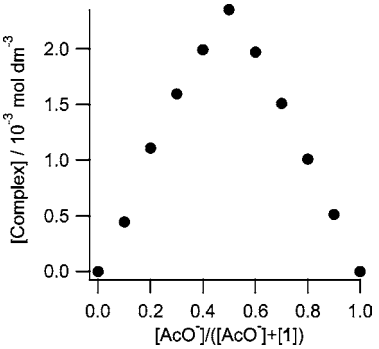

Figure 3. A Job's plot of **1** with tetrabutylammonium acetate in $CDCl_3$ at 298 K. [**1**] + [AcO$^-$] = 5.0×10^{-3} mol dm^{-3}.

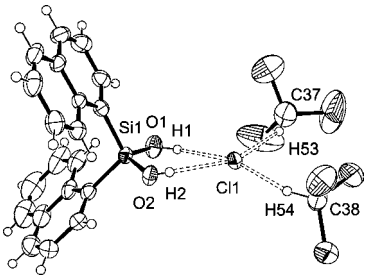

Figure 4. ORTEP view of the molecular structure of [**1**·Cl]$^-$. Displacement ellipsoids are scaled to the 50% probability level. The tetrabutylammonium ion has been removed for clarity. Dashed lines are indicative of hydrogen-bonding interactions.

cooperatively form hydrogen bonds to Cl$^-$. The distances between the chloride and the O(1)−H proton and the O(2)−H proton are 2.405 and 2.415 Å, respectively, which are significantly shorter than the sum of the van der Waals radius (3.01 Å) of hydrogen and chloride, indicating the hydrogen bond formation. Additional two chloroform molecules from solvent also hydrogen bonded to Cl$^-$.[15] The geometry of these four hydrogen bonds is a planar square. These results provide evidence that silanol hydroxy groups are possible to act as a hydrogen bond donor for anionic species.

UV−vis spectral titrations of **1** with various anions (as tetrabutylammonium salts) were performed in $CHCl_3$ at 298 K. Small but reproducible changes of the absorbance of **1** were observed upon the addition of AcO$^-$. The association constant for AcO$^-$ was calculated by nonlinear curve fitting to be $2.7 \pm 0.3 \times 10^3$ mol^{-1} dm^3, which is in fairly good agreement with that calculated from the ^{1}H NMR titration (Supporting Information, Figure S3). Receptor **1** shows fluorescence at 331 nm excited at 270 nm in chloroform. Fluorescence spectral titration of **1** with anions was also examined; however, unfortunately, only small changes were observed (Supporting Information, Figure S4). These results suggest that the electronic perturbation of the naphthyl rings of **1** is merely limited.

In summary, we demonstrate above that silanediols are possible to associate with anions such as chloride and acetate

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(14) Crystal data for **1**·$(C_4H_9)_4N^+$·Cl$^-$·2$CHCl_3$: $C_{38}H_{54}Cl_7NO_2Si$, monoclinic, space group $P2_1/c$ (#14), a = 13.328(7), b = 22.154(8), c = 15.638(6) Å, β = 108.170(6)°, V = 4387(3) Å^3, T = 173 K, Z = 4, Mo Kα radiation, 9955 total data, 9179 [$F^2 > 2\sigma(F^2)$], GOF = 1.774, R1 = 0.0793, wR2 = 0.2238.

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in chloroform. As far as we know, this is the first example of a silanediol-based anion receptor. We believe that introduction of novel functionality into the anion recognition chemistry should expand the field of this area. The study of the functionalization and application of silanediol-based receptors is in progress in our laboratory.

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Supporting Information Available: Experimental details including dilution experiments, UV−vis and fluorescence titrations, and a CIF file are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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