Dinuclear Calcium Complex with Weakly NH···O Hydrogen-Bonded Sulfonate Ligands

Akira Onoda, Yusuke Yamada, Mototsugu Doi, Taka-aki Okamura, and Norikazu Ueyama*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received March 21, 2000

The novel intramolecularly NH···O hydrogen-bonded Ca(II)−aryl sulfonate complex, $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**), sulfonate anion, $(HNEt_3)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2a**), $(PPh_4)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2b**), $(n\text{-}Bu_4N)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2c**), and sulfonic acid, $2\text{-}t\text{-}BuCONHC_6H_4SO_3H$ (**3**), were synthesized. The structures of **1**, **2a**, and **2b** depict the presence of the formation of NH···O hydrogen bonds between the amide NH and S−O oxygen for a series of compounds as determined by IR and ^{1}H NMR analyses both in the solid state and in the solution state. Thus, the NH···O hydrogen bonds with neutral amide groups are available for investigation of the electronic state of the O^- anion. The combined data from the IR and ^{1}H NMR spectra indicate that the sulfonic acid, sulfonate anion, and Ca(II) complex have a substantially weak intramolecular NH···O hydrogen bond between the SO_3 oxygen and amide NH. In the detailed comparison with the intense NH···O hydrogen bonds for the carboxylate, weak NH···O hydrogen bonds for sulfonate is due to the strong conjugation of the SO_3^- group with the lower nucleophilicity.

Introduction

Sulfonic acid derivatives are strong acids that readily form a sulfonate anion by deprotonation.[1−3] A pπ−dπ interaction between the occupied oxygen p and unoccupied sulfur d orbitals[4] is considered to cause the conjugated structure of SO_4^- or $ArSO_3^-$ to readily release the proton.

The sulfonate anion often interacts with metal ions and also hydrogen bonds[5,6] in biologically important proteins. Arylsulfatase B is supposed to contain the Ca(II) ion in the active site and catalyze the transesterification of the sulfate ester.[7] Arysulfatase A (ASA), which contains the Mg(II) ion in the active site, catalyzes analogous reactions. The crystal structure of ASA with Cl^- ion was reported by Lukatela et al. and they proposed that the sulfate exists in the same position during the reaction.[8] The crystal structure analysis of Ca-containing proteins indicates the presence of NH···O hydrogen bonds to the oxygen atoms of the oxo acids, which is coordinated to Ca(II) ions, from the neighboring peptide NHs of the main chain or side chain. In a sulfate-binding protein, the sulfate anion is tightly bound primarily by seven hydrogen bonds. Five of them are donated by the main-chain peptide NH groups.[9−11] The sulfonate anion inhibits the enzyme activity by complexation.[12,13] The crystal structure of the SO_4^{2-}-binding proteins suggests the presence of a NH···O hydrogen bond between the sulfate oxygen and protein amide NH.

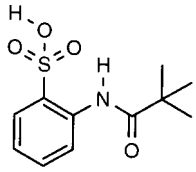
The intermolecular NH···O hydrogen bond to the sulfonate oxygen has been studied in the solid state and in solution.[14−18] The crystal structure of benzene sulfonate derivatives containing an amino substituent indicated the presence of NH···O hydrogen bonds from the ammonium NH to the sulfonate oxygen. This kind of NH···O hydrogen bond from the ammonium NH has been used in crystal engineering.[15−18] The molecular recognition between the sulfonate derivatives and the amide-containing acceptors was discussed in terms of their binding constants during the formation of intermolecular NH···O hydrogen bonds.[19,20] Although the geometry of hydrogen atoms that are hydrogen-bonded with sulfonates has been summarized[21] and these kinds of intermolecular interactions have been studied, the properties of the NH···O hydrogen bond to the sulfonate and the effect of metal coordination have not been discussed.

We aimed at clarifying the properties and the functions of the NH···O hydrogen bonds with coordinating $-SO_3^-$ groups in the Ca(II) complex. Previously, we reported that the intramolecular NH···O hydrogen bond between the carboxylate C−O$^-$

(1) Kucsman, A.; Kapovits, I. *Organic Sulfur Chemistry*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; pp 191−245.
(2) Furukawa, N.; Fujiwara, H. *Chem. Sulphonic Acids, Esters Their Deriv.* **1991**, 261−281.
(3) Massey, A. G. *Main Group Chemistry*; Ellis Horwood: New York, 1990.
(4) Kwart, H.; King, K. *D-Orbitals in the Chemistry of Silicon, Phosphorous and Sulfur*; Splinger-Verlag: Berlin, 1977.
(5) Copley, R. R.; Barton, G. J. *J. Mol. Biol.* **1994**, *242*, 321−329.
(6) Kanyo, Z. F.; Christianson, D. W. *J. Biol. Chem.* **1991**, *266*, 4264−4268.
(7) O'Brien, P.; Harshlag, D. *J. Am. Chem. Soc.* **1998**, *120*, 12369−12370.
(8) Lukatela, G.; Krauss, N.; Theis, K.; Selmer, T.; Gieselmann, V.; Figura, K. v.; Saenger, W. *Biochemistry* **1998**, *37*, 3654−3664.
(9) Pflugrath, J. W.; Quiocho, F. A. *Nature* **1985**, *314*, 257−260.
(10) Pflugrath, J. W.; Quiocho, F. A. *J. Mol. Biol.* **1988**, *200*, 163−180.
(11) Jacobson, B. L.; Quiocho, F. A. *J. Mol. Biol.* **1988**, *204*, 783−787.
(12) Huber, R.; Carrell, R. W. *Biochemistry* **1989**, *28*, 8951−8966.
(13) Lindahl, U.; Backstrom, G.; Thungerg, L. *J. Biol. Chem.* **1983**, *258*, 9826−1930.
(14) Balasubramanian, T.; Muthuah, P. T. *Acta Crystallogr.* **1996**, *C52*, 2072−2073.
(15) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941−1952.
(16) Russell, V. A.; Ward, M. D. *Acta Crystallogr. Sect. B* **1996**, *B52*, 209−214.
(17) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575−579.
(18) Ojala, W. H.; Lu, L. K.; Albers, K. E.; Gleason, W. B. *Acta Crystallogr. Sect. B* **1994**, *50*, 684−94.
(19) Kelly, T. R.; Kim, M. H. *J. Am. Chem. Soc.* **1994**, *116*, 7072−7080.
(20) Valiyaveettil, S.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 900−901.
(21) Chertanova, L.; Pascard, C. *Acta Crystallogr.* **1996**, *B52*, 677−684.

10.1021/ic0003067 CCC: $20.00
Published on Web 01/05/2001

Scheme 1 *o*-Acylaminobenzenesulfonic acid ligand



and amide NH in 2-acylaminobenzoate and 2,4-diacylaminobenzoate contributes to the prevention of the Ca−O bond from dissociation due to the lowering of the pK_a value.[22−24] The NH···O hydrogen bonds to the sulfonate oxygen, which has an even lower pK_a value, are also of interest. The location of amide NH near the SO_3H group is designed using *o*-acylaminobenzene sulfonic acid as shown in Scheme 1. The bulky amide derivatives at the ortho position prevent polymeric coordination of the sulfonate oxygen atom and locate the amide NH near the coordinate oxygen atom to reproduce the formation of the NH···O hydrogen bond and to elucidate the electrostatic effects of RSO_3^-. The NH···O hydrogen bonds with neutral amide groups allow the detailed investigation of acidity of the RSO_3H protons by structural and spectroscopic methods. This paper presents the synthesis and structure of the dinuclear Ca(II) complex with novel *o*-acylaminobenzenesulfonate ligands having NH···O hydrogen bonds. The formation of the NH···O hydrogen bond in the Ca(II) complex was examined using ^{1}H NMR, CRAMPS, and IR analyses, which results in understanding the properties of $-SO_3H$ and $-SO_3^-$ and the effect on Ca(II) coordination.

Experimental Section

Preparation of Compounds. Solvents were distilled from appropriate drying agents and degassed prior to use. Reagents were of commercial origin and were used received.

[Ca_2(SO$_3$-2-*t*-BuCONHC$_6$H$_4$)$_2$(H$_2$O)$_4$]$_n$(2-*t*-BuCONHC$_6$H$_4$SO$_3$)$_{2n}$ (1). (HNEt$_3$)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (**2a**) (300 mg, 0.85 mmol) and $Ca(OH)_2$ (31 mg, 0.42 mmol) were dissolved in 700 mL of water and concentrated. The residue was recrystallized from hot acetonitrile to give colorless crystals: Yield 63%. Anal. Calcd for $C_{22}H_{28}Ca_1N_2O_8S_2\cdot(H_2O)_3$: C, 43.55; H, 5.65; N, 4.62. Found: C, 43.52; H, 5.89; N, 5.06.

(HNEt$_3$)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (2a). 2-Aminobenzene sulfonic acid (7.7 g, 0.44 mmol) was suspended in 300 mL of THF, followed by the addition of triethylamine (12 mL, 0.88 mmol) and pivaloyl chloride (6.0 mL, 0.44 mmol). The suspension was stirred for 8 h and filtered. The filtrate was evaporated to give a yellow solid. The crude product was recrystallized from benzene solution to afford colorless crystals: Yield 81%. ^{1}H NMR (Me$_2$SO-d_6): δ 10.54 (s, 1H, NH), 8.81 (s, 1H, HNEt$_3$), 8.28 (d, 1H,3-ArH), 7.64 (d, 1H, 6-ArH), 7.26 (t,1H, 5-ArH), 6.97 (t, 1H, 4-ArH), 3.08 (q, 6H, CH_2), 1.19 (s, 9H, *t*-Bu), 1.55 (t, 9H, CH3). ^{13}C NMR (Me$_2$SO-d_6): δ 175.80, 135.46, 135.22, 129.32, 126.68, 121.79, 119.47, 45.73, 39.35, 27.10, 8.55. Anal. Calcd for $C_{17}H_{30}N_2O_4S$: C, 56.96; H, 8.43; N, 7.81. Found: C, 56.85; H, 8.46; N, 7.90.

(PPh$_4$)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (2b). Sodium 2-pivaloylaminobenzene sulfonate (200 mg, 0.71 mmol) and PPh_4Br (270 mg, 0.71 mmol) in methanol solution were mixed, concentrated, and extracted with ethanol and then the NaCl was filtered off. The filtrate was concentrated to a give white powder. It was recrystallized from THF−ether to give crystals. Yield 12%. ^{1}H NMR (Me$_2$SO-d_6): δ 10.50 (s, 1H, NH), 8.29 (d, 1H, 3-ArH), 7.95 (t, 4H, *p*-Ph), 7.80 (m, 8H, *m*-Ph), 7.72 (m, 8H, *o*-Ph), 7.63 (d, 1H, 6-ArH), 7.25 (d, 1H, 5-ArH), 6.97 (d, 1H, 4-ArH), 1.19 (s, 9H, *t*-Bu). ^{13}C NMR (Me$_2$SO-d_6): δ 176.02, 135.70, 135.49, 135.47, 134.75, 134.65, 130.66, 130.53, 129.50, 126.91, 122.00, 119.69, 118.29, 117.41, 27.33. Anal. Calcd for $C_{35}H_{34}NO_4P_1S$: C, 70.57; H, 5.75; N, 2.35. Found: C, 70.27; H, 5.72; N, 2.41.

(*n*-Bu$_4$N)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (2c). (HNEt$_3$)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (2.0 g, 0.56 mmol) was dissolved in 2 mL of ethanol and 0.56 mL of 1.0 M (*n*-Bu$_4$N)OH methanol solution was added under an Ar atmosphere. The solution was concentrated under reduced pressure to give a pale brown solid. Yield 86%. ^{1}H NMR (Me$_2$SO-d_6): δ 10.54 (s, 1H, NH), 8.28 (d, 1H, 3-ArH), 7.63 (d, 1H, 6-ArH), 7.26 (t,1H, 5-ArH), 6.97 (t, 1H, 4-ArH), 3.14 (m, 8H, CH_2), 1.55 (m, 8H, CH_2), 1.29 (m, 8H, CH_2), 1.19 (s, 9H, *t*-Bu), 0.92 (t, 12H, CH_3). ^{13}C NMR (Me$_2$SO-d_6): δ 175.78, 135.47, 135.26, 129.26, 126.26, 126.68, 121.76, 119.46, 57.48, 39.35, 27.10, 22.97, 19.10, 13.36. Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 65.02; H, 10.10; N, 5.62. Found: C, 64.37; H, 10.04; N, 5.52.

2-*t*-BuCONHC$_6$H$_4$SO$_3$H (3). (HNEt$_3$)(SO$_3$-2-*t*-BuCONHC$_6$H$_4$) (0.53 g, 1.5 mmol) was dissolved in water and 0.6 mL of 0.25 N NaOH aqueous solution was mixed, stirred for 20 min, and evaporated. The precipitated white powder, sodium 2-pivaloylaminobenenzene sulfonate, was dissolved in ethanol where HCl gas was purged until no more NaCl was precipitated. NaCl was removed by filtration under an Ar atomosphere and the filtrate was concentrated to give a white oil. MeOH and benzene were added several times to remove the water by azeotropic distillation that produced a white precipitate. The extract was distilled with acetonitrile to remove the contaminated NaCl and evaporated under reduced pressure to give a pale yellow powder in 19% yield. ^{1}H NMR (CD$_3$CN): δ 9.63 (s, 1H, NH), 8.31 (d, 1H, 3-ArH), 7.84 (d, 1H, 6-ArH), 7.53 (t,1H, 5-ArH), 7.20 (t, 1H, 4-ArH), 5.01 (s, 1H, SO_3H), 1.27 (s, 9H, *t*-Bu). ^{13}C NMR (Me$_2$SO-d_6): δ 175.82, 135.47, 135.23, 129.33, 126.69, 121.81, 119.50, 39.10, 27.12. Anal. Calcd for $C_{11}H_{15}NO_4S\cdot H_2O$: C, 47.99; H, 6.22; N, 5.09; O, 29.06; S, 11.65. Found: C, 47.56; H, 6.15; N, 4.99.

(*n*-Bu$_4$N)(SO$_3$-4-*t*-BuCONHC$_6$H$_4$) (4). Triethylamine (10.5 mL, 76.1 mmol) and pivaloyl chloride (4.7 mL, 35 mmol) were added to a suspended THF solution (200 mL) of 4-$NH_2C_6H_4SO_3H$ (2.0 g, 34.6 mmol). After the mixture was stirred for 8 h, a white precipitate was filtered from it. The filtrate was concentrated to give a mixture of (HNEt$_3$)(SO$_3$-4-*t*-BuCONHC$_6$H$_4$) and HCl·NEt$_3$. The residue (0.40 g, 0.80 mmol) was dissolved in water, and then 3.2 mL of 0.5 M NaOH solution was added. After being stirred for 20 min, the solution was evaporated to obtain a white powder, which was a mixture of sodium 4-pivaloylaminobenzene sulfonate and NaCl. This mixture and {N(*n*-Bu)$_4$}Br (0.20 g, 0.64 mmol) were dissolved in 10 mL of water and the product was extracted with ethyl acetate. The organic layer was washed with a NaCl-saturated solution, dried over sodium sulfate, and evaporated to a give white powder. The contaminated excess of {N(*n*-Bu)$_4$}Br was washed with ethyl acetate for an 18% yield. ^{1}H NMR (Me$_2$SO-d_6): δ 9.18 (s, 1H, NH), 7.54 (d, 2H,), 7.47 (d, 2H,), 3.14 (m, 8H, CH_2), 1.55 (m, 8H, CH_2), 1.29 (m, 8H, CH_2), 1.20 (s, 9H, *t*-Bu), 0.92 (t, 12H, CH_3). ^{13}C NMR (Me$_2$SO-d_6): δ 176.30, 143.44, 139.18, 125.65, 119.02, 57.47, 27.10, 22.98, 19.10, 13.38. Anal. Calcd for $C_{27}H_{50}N_2O_4S_1$: C, 65.02; H, 10.10; N, 5.62. Found: C, 63.99; H, 10.15; N, 5.52.

General Methods. ^{1}H NMR spectra were recorded on a JEOL EX 270 or JEOL EX 400 spectrometer. CRAMPS (combined rotation and multipulse spectroscopy) ^{1}H NMR in the solid state was taken on a Chemmagnetics CMX-300 with a 4 mmϕ pencil rotor cell, and the spectrum of each compound was measured at a different rotation frequency from 1 to 2.0 kHz to differentiate the signals from the sideband. The IR spectra in solution and in the solid state were taken on a Jasco FT/IR-8300 spectrometer.

X-ray Structure Determination. Single crystals of **1**, **2a**, and **2b** were sealed in glass capillaries. The X-ray data for **1** and **2b** were collected at 23 °C on a Rigaku AFC5R and AFC7R diffractometer equipped with a rotating anode X-ray generator. The radiation used was Mo Kα monochromatized with graphite (0.71069 Å). The X-ray data for **2a** were collected at −180 °C on a Raxis RAPID. No empirical absorption correction was applied. The basic crystallographic parameters for **1**, **2a**, and **2b** are listed in Table 1. The unit cell dimensions were refined by 20 reflections. These standard reflections were monitored

(22) Ueyama, N.; Hosoi, T.; Yamada, Y.; Doi, M.; Okamura, T.; Nakamura, A. *Macromolecules* **1998**, *31*, 7119−7126.
(23) Ueyama, N.; Takeda, J.; Yamada, Y.; Onoda, A.; Okamura, T.; Nakamura, A. *Inorg. Chem.* **1999**, *38*, 475−478.
(24) Yamada, Y.; Onoda, A.; Ueyama, N.; Okamura, T.; Adachi, H.; Nakamura, A., to be submitted.

Table 1. Crystal Parameters of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**)

parameter	1	2a	2b
chem formula	$C_{22}H_{36}Ca\ N_2O_{12}S$	$C_{17}H_{30}N_2O_4S$	$C_{33}H_{40}NO_5PS$
fw	624.73	358.49	665.78
color	colorless	colorless	colorless
cryst syst	triclinic	orthorhombic	prismatic
lattice params			
a, Å	11.032(3)	9.8079(4)	10.562(2)
b, Å	14.753(3)	20.791(1)	18.472(4)
c, Å	9.447(1)	9.4333(4)	9.301(1)
α, deg	96.67(1)	90	93.91(1)
β, deg	90.11(1)	90	95.87(2)
γ, deg	71.71(2)	90	85.05(1)
V, Å^3	1499.0(5)	1923.6 (1)	1795.1(5)
space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
Z	2	4	2
T (°C)	23	−180	23
λ (Å)	0.71069	0.71069	0.71069
D_{calc}, g/cm^{-1}	1.432	1.234	1.232
μ (Mo Kα), cm^{-1}	4.21	1.90	1.78
scan type	*ω*−2*θ*		*ω*−2*θ*
$2\theta_{max}$, deg	50.0		50
oscillation range		*ω* = 130.0°−190.0°	
(*φ* = 0.0°, *χ* = 45.0°)		*ω* = 0.0°−160.0°	
(*φ* =18 0.0°, *χ* = 45.0°)		with 4.0° step	
no. of reflections	4775	8319	1915
no. of observations	3349 ($I > 3\sigma(I)$)	1223 ($I > 0\sigma(I)$)	1621 ($I > 2\sigma(I)$)
no. of variables	353	218	381
R^a	0.076	0.039 (R1)	0.084
$R_w{}^b$	0.129	0.124 ($R_{w2}{}^c$)	0.099

[a] R, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $R_{w2} = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$.

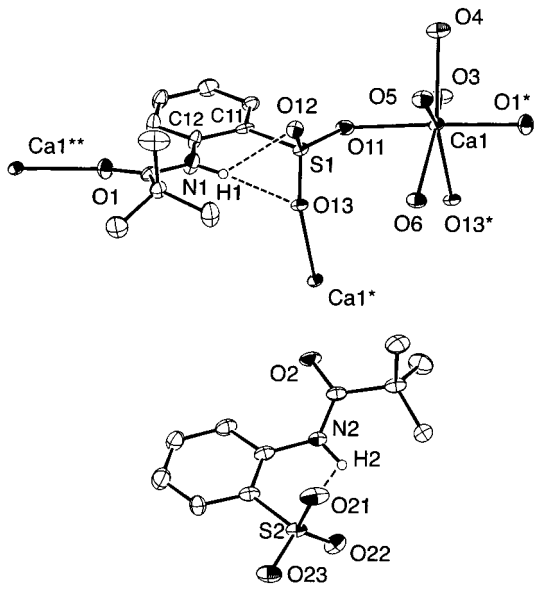


Figure 1. Cation structure portion of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**).

at every 150 reflections and did not show any significant change. The structures were solved by the direct method and expanded using Fourier techniques. Some non-hydrogen atoms were anisotropically refined, while the rest were isotropically refined. Hydrogen atoms were included but not refined.

Results and Discussion

Crystal Structures. The molecular structure of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**) is shown in Figure 1 and the selected bond lengths and angles are listed in Table 2. The cation part of **1** forms a dinuclear Ca(II) unit with two sulfonate ligands and each unit forms a one-dimensional cationic chain as represented in Figure 2. The infinite chain contains two sulfonate counteranions per one dinuclear unit. The sulfonate ligand coordinates to each Ca(II) ion in a bridging bidentate mode and each Ca(II) ion is separated by 5.308(2) Å. Both Ca(II) centers are crystallographically equivalent. The coordination geometry of the Ca(II) sphere is seven-coordinate in a pentagonal bipyramidal. The Ca(II) ion is ligated with two oxygen atoms of the sulfonate ligand, four oxygen atoms of the water molecules, and an oxygen atom of the amide carbonyl. The two oxygen atoms of sulfonate, O11 and O13, coordinate to the Ca(II) ion at the axial position and in the equatorial position, respectively. Four water molecules are coordinated in the equatorial positions within 2.36−2.47 Å. The O1 atom of the amide ligated to the Ca(II) ion in the trans position of the O11 atom by 2.341(5) Å to make the dimeric unit into a single infinite chain. This structure is different from the reported complexes.[25−29]

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for **1**

Bond Distances			
Ca1−O11	2.424(6)	Ca1*−O13	2.513(4)
Ca1**−O1	2.341(5)	Ca1−O3	2.364(4)
Ca1−O4	2.464(4)	Ca1−O5	2.442(4)
Ca1−O6	2.395(4)	S1−O11	1.463(4)
S1−O12	1.455(3)	S1−O13	1.458(4)
S2−O21	1.434(4)	S2−O22	1.438(4)
S2−O23	1.451(4)		
N1−O12	2.871(7)	N1−O13	3.135(6)
N2−O21	3.216(6)	N2−O22	2.903(5)
Ca−Ca*	5.308(2)		
Bond Angles			
Ca1−O11−S1	133.8(2)	Ca1−O13−S1	142.8(2)
Ca1**−O1−C17	165.0(4)		
O11−S1−O12	113.0(2)	O11−S1−O13	113.0(2)
O12−S1−O13	112.5(2)	O21−S1−O22	114.4(4)
O21−S1−O23	112.3(3)	O22−S1−O23	112.3(3)
Torsion Angles			
C11−C12−N1−C17	172.4(6)	O11−S1−C11−C16	−175.6(4)
O12−S1−C11−C12	−55.4(5)	O13−S1−C11−C12	64.1(5)

The distances of S1−O11, S1−O12, and S1−O13 are 1.463(4), 1.455(3), and 1.458(4) Å, respectively. These S−O distances are similar to each other in the range of the sulfonic acid and the sulfonate anion. In general, the S−O bond distances in the sulfonate anion are known to be 1.40−1.49 Å.[1] The similarity in the three S−O bond distances on SO_3^- indicates that the strong conjugation on SO_3^- is predominant in **1**. The distances of the amide N1−O12 and N1−O13 are 2.871(7) and 3.135(6) Å, respectively. The distances of the amide H1−O12 and H1−O13 are 2.20 and 2.82 Å, respectively. The amide plane is nearly coplanar with the benzene plane and the dihedral angles of C12−C11−S1−O12 and C12−C11−S1−O13 are −54.8(5) ° and 65.1(5) °, respectively. Therefore, the amide proton is not specifically directed to one of the two oxygen atoms of the sulfonate, O12 and O13. This result strongly suggests that the NH···O hydrogen bond between the amide NH and sulfonate oxygen is weak due to delocalization of the anion charge on the SO_3^- group.

The crystal structures of $(NHEt_3)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2a**) and $(PPh_4)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2b**) are represented

(25) Shakeri, V.; Haussuehl, S. *Z. Kristallogr.* **1992**, *198*, 299−301.
(26) Toffolo, P.; Rodier, N. *Acta Crystallogr.* **1988**, *C44*, 1493−1494.
(27) Shubnell, A. J.; Kosnic, E. J.; Squattrito, P. J. *Inorg. Chim. Acta* **1994**, *216*, 101.
(28) Hall, C. D.; Leineweber, A.; Tucker, J. H. R.; Williams, D. J. *J. Organomet. Chem.* **1996**, *523*, 13.
(29) Gunderman, B. J.; Squattrito, P. J. *Acta Crystallogr., Sect. C* **1996**, *52*, 1896.

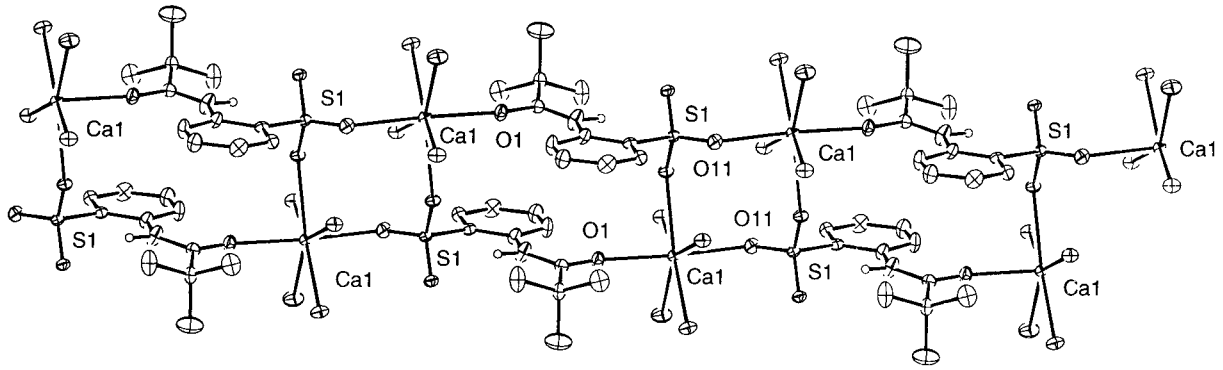


Figure 2. Polymeric structure of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**).

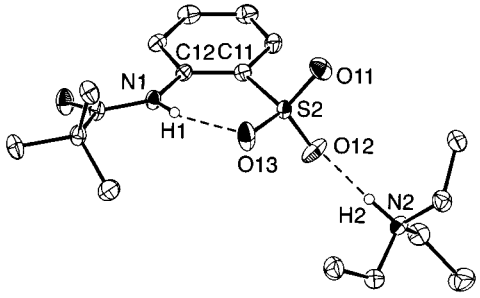


Figure 3. Molecular structure of $(NHEt_3)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2a**).

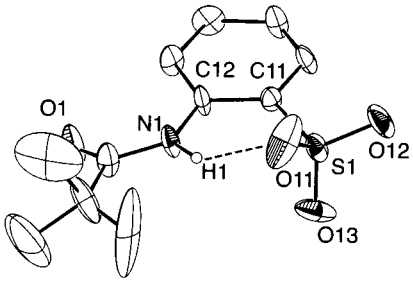


Figure 4. Molecular structure of $(PPh_4)(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2b**).

in Figures 3 and 4, respectively. The similar S−O distances, 1.444(2), 1.459(2), and 1.455(3) Å for **2a** and 1.43(1), 1.41(1), and 1.44(1) Å for **2b** are also explained by a conjugation over SO_3^- groups. The anion, **2a**, has two NH···O hydrogen bonds, an intramolecular N1H1···O13 with the N1−O13 distance of 2.668(3) Å and an intermolecular N2H2···O12 with the N2−O12 distance of 2.735(3) Å. The O13 atom in the sulfonate anion is directed toward the amide NH and the O12 atom is interacted with ammonium NH. **2b** has one intramolecular NH···O hydrogen bond between the amide NH1 and sulfonate oxygen O11 with the distance of 2.84(2) Å. The intramolecular NH···O11 hydrogen bond is not strong enough to restrict the C11−S1 rotation in the solid state. The NH···O hydrogen is thought to be formed between the amide NH and the conjugated SO_3^- group in the solid state for **2a** and **2b**.

IR Spectra. Table 3 lists the selected IR bands in the amide regions for **1**, **2a**, **2b**, **2c**, **3**, and $\{N(n\text{-}Bu)_4\}(SO_3\text{-}4\text{-}t\text{-}BuCONHC_6H_4)$ (**4**) in $CDCl_3$ solution (10 mM). **4** is employed as a standard sulfonic acid without an intramolecular NH···O hydrogen bond. The free amide NH stretching bands are known to appear in the range of 3400−3500 cm^{-1}.[30] The presence of NH···O hydrogen bonds between the amide NH and the oxygen atom of the sulfonate for the Ca(II) complex, **1**, is suggested

Table 3. Chemicals Shifts of Amide NH and Selected IR Bands of Sulfonate Complexes in the Solid State and in Solution State

	ν(NH) in the solid state	ν(NH) in CD_3Cl solution	δ(NH) in the solid state	δ(NH) in CD_3CN
1	3369	*a*	10.5	10.52
2a	3286, 3251, 3186	3315	11.3	10.30
2b	3292, 3274	3285	10.5	10.58
2c	3302	3293	11.7	10.59
3	3350	*a*	10.5	9.91
4	3291, 3258	3453	9.5	7.98

[a] The sample is not soluble in $CDCl_3$ solution.

from the slightly shifted 3369-cm^{-1} bands in the solid state. In the sulfonate anion state, more shifted bands are observed for **2a**, **2b**, and **2c**. A significantly shifted band at 3186 cm^{-1} for **2a** is due to the ammonium NH involved in intermolecular hydrogen bonds. The two shifted amide NH bands of **2b** at 3292 and 3274 cm^{-1} indicate the presence of two NH···O hydrogen bonds with the sulfonate oxygen atoms on the IR time scale. **2c** shows the ν(NH) band at 3302 cm^{-1} involved in the intramolecular NH···O hydrogen bond. **3** in the sulfonic acid state shows an NH band at 3360 cm^{-1}; thus, a weak NH···O hydrogen bond is thought to be formed in the solid state between the amide NH and S═O oxygen.

In the solution state, two sulfonate anions, **2b** and **2c**, exhibit shifted amide ν(NH) bands at 3285 and 3293 cm^{-1}, respectively. These ν(NH) bands are shifted by 168 cm^{-1} for **2b** and 160 cm^{-1} for **2c** from the free amide ν(NH) at 3453 cm^{-1} for **4**. These shifts are caused by the formation of an intramolecular NH···O hydrogen bond in the sulfonate anion state. **2a** exhibits a less shifted amide ν(NH) band at 3315 cm^{-1} because of the interaction of the NH proton of $NHEt_3^+$. The intramolecular NH···O hydrogen bonds between the amide NH and S═O oxygen of the sulfonate anion are formed in the solution state.

^{1}H NMR CRAMPS Spectra in the Solid State. CRAMPS is available to detect each proton under different circumstances in the solid state.[31] Figure 5 shows the CRAMPS spectra of **1**, the sulfonate anion, **2c**, and the sulfonic acid, **3**. The chemical shifts of ν(NH) for all the compounds are listed in Table 3. *t*-Bu of pivaloylamide or *n*-Bu of the countercation give a large signal around 1 ppm. The aromatic protons appeared broadly from 7 to 10 ppm. **1**, **2c**, and **3** gave amide NH signals at 10.5, 11.7, and 10.5 ppm, respectively. The shifted amide NH signal for **2c** is observed by the downfield shift of 1.2 ppm from that of the sulfonic acid, **3**. The sulfonate anion, **2a**, appears downshifted of the NH signal (0.8 ppm). The NH signal for **2b** is not shifted because of the deshielding effect of the PPh_4^+ cation, which is 4 Å apart from the NH proton in the solid state.

(30) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981.

(31) Shoji, A.; Kimura, H.; Ozaki, T.; Sugisawa, H.; Deguchi, K. *J. Am. Chem. Soc.* **1996**, *118*, 7604−7607.

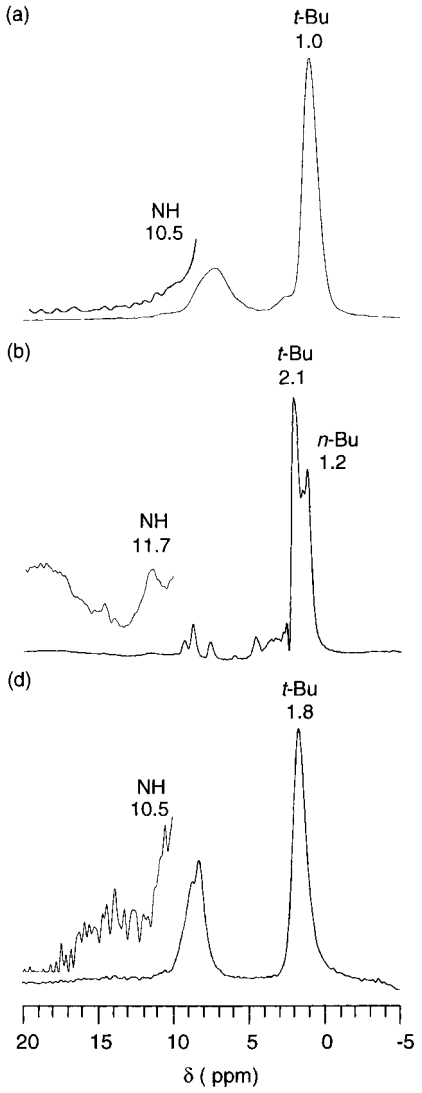


Figure 5. ^{1}H NMR CRAMPS spectra of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**), $\{N(n\text{-}Bu)_4\}(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2c**), and 2-*t*-$BuCONHC_6H_4SO_3H$ (**3**).

The shift in the amide NH ^{1}H signals in the sulfonate anion is ascribed to the increase in the activity by forming intramolecular NH···O hydrogen bonds in both the S═O and S−O$^-$ oxygen in the sulfonate anion. The amide NH signal of **1** appears at a very similar chemical shift for **3**. Thus, the strength of the NH···O hydrogen bonds between the amide NH and sulfonate oxygen in **1**, the Ca(II) complex, is as weak as that in sulfonic acid, **3**, which is compatible with the IR experiment.

^{1}H NMR Spectra in Solution State. Figure 6 shows the ^{1}H NMR spectra of **1**, **2**, and **3** in 10 mM acetonitrile-d_3. The results of the ESI-MS analysis indicated that the polymeric dimer structure in **1** becomes a smaller unit structure in the solution state. The amide NH chemical shifts of **1**, **2c**, and **3** are 10.52, 10.59, and 9.91 ppm, respectively. **1** contains a ligand sulfonate in a dimer unit and counteranion; thus, the amide NH signal of **1** is the averaged value of the two. The amide NH signal in **1** and **2c** shifts downfield by 0.61 and 0.68 ppm from that of sulfonic acid **3**, respectively. The similar values of the NH chemical shifts for **1** and **2c** indicate that both sulfonate SO_3^- groups have a similar nucleophilicity to form the NH···O hydrogen bonds due to the delocalization of the anion charge over SO_3^-. Sulfonic acid, **3**, exhibits an already-shifted amide NH signal at 9.91 ppm, which is shifted from that at 7.98 ppm

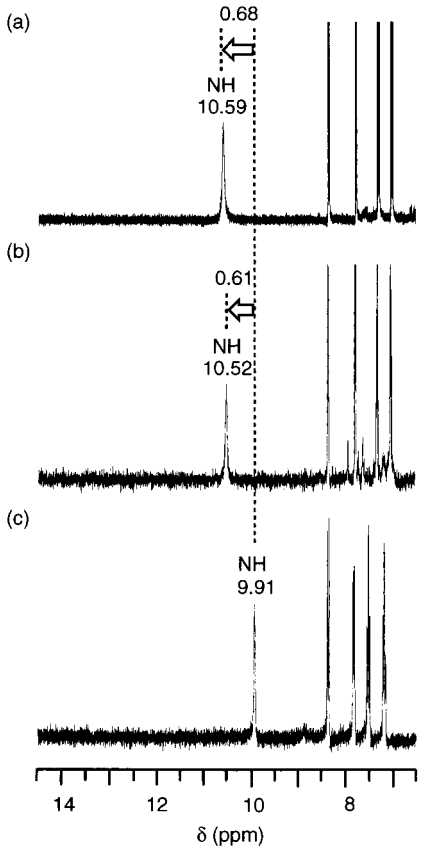


Figure 6. ^{1}H NMR spectra of $[Ca_2(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_2(H_2O)_4]_n$-$(2\text{-}t\text{-}BuCONHC_6H_4SO_3)_{2n}$ (**1**), $\{N(n\text{-}Bu)_4\}(SO_3\text{-}2\text{-}t\text{-}BuCONHC_6H_4)$ (**2**), and 2-*t*-$BuCONHC_6H_4SO_3H$ (**3**) in 10 mM acetnitrile-d_3 at 303 K.

for **4**. The shift of the amide NH is ascribed to an intramolecular NH···O hydrogen bond with S═O oxygens. Previously, we reported the large downfield shift (3.3 ppm) of the amide NH ^{1}H signal observed at 13.5 ppm in $\{N(n\text{-}Bu)_4\}\{OCO\text{-}2,6\text{-}(t\text{-}BuCONH)_2C_6H_3\}$ from that at 10.2 ppm in 2,6-(*t*-$BuCONH)_2C_6H_3$-COOH in $CDCl_3$ at 303 K. The small shift between **2c** and **3** is not due to the difference in anisotropic shielding by the tetrahedral S═O or trigonal C═O. Actually, the aromatic *o*-H signals are observed at 8.35 ppm for **2c** and at 8.31 ppm for **3** in $CDCl_3$ at 303 K. Even if the difference in the electronic effect from the SO_3^- or SO_3H group is considered, the observed shift of the aromatic *o*-H signal by the shielding is too small. Therefore, the amide NH shift is ascribed to the small change in the amide NH acidity upon formation of the weak NH···O hydrogen bond between sulfonate SO_3^- and amide NH. A ^{1}H NMR experiment revealed that the NH···O hydrogen bonds between the amide NH and oxygen is weak in the SO_3H state and a little stronger in SO_3^-.

Formation of Hydrogen Bonds with the Oxygen Atoms of the Sulfonate and Carboxylate. The formation of a NH···O hydrogen bond between the amide NH and carboxylate oxygen has already been discussed with the amide-derived benzoic acid ligand, 2,6-(*t*-$BuCONH)_2C_6H_3COOH$ (**5**), its anion $(NEt_4)\{2,6\text{-}(t\text{-}BuCONH)_2C_6H_3COO\}$ (**6**), and its Ca(II) complex $(NEt)_4[Ca^{II}\{OCO-C_6H_3\text{-}2,6\text{-}(NHCO\text{-}t\text{-}Bu)_2\}_4]$ (**7**) in chloroform-*d* by ^{1}H NMR. [24] The strength of the NH···O hydrogen bonds of **5**, **6**, and **7** in solution was investigated in acetonitrile-d_3 by ^{1}H NMR spectroscopy. **5**, **6**, and **7** give amide NH ^{1}H signals at 10.28, 13.53, and 12.08 ppm, respectively. **6** has a NH signal with a large shift of 2.25 ppm and for **7** with a very large shift of 1.88 ppm. This indicates that the NH···O hydrogen

bond between the amide NH and carboxylate oxygen in the Ca(II) complex **7** is strong but much stronger in the carboxylate state.

The behavior of amide NH signals in acid and in anion states are absolutely different between sulfonic acid and benzoic acid, which have different pK_a values. The ability to form the hydrogen bond has been thought to be correlated with the nucleophilicity of the O^-, which can be evaluated by the detection of using the NH···O hydrogen bonds from an amide group as a diagnostic tool. The downfield shift related to the deprotonation of sulfonic acid and carboxylic acid are 0.61 and 2.25 ppm, respectively. The large shift in the carboxylate anion indicates the significant ability to form a strong hydrogen bond, while the sulfonate anion is a weak hydrogen bond acceptor due to the stronger conjugation in SO_3^-. CO_2H groups have relatively high pK_a values compared to those of SO_3H groups and the charge is more localized in CO_2^- than in SO_3^-, thus making the stronger hydrogen bond acceptor.

The ability as a hydrogen bond acceptor for the O atom can be thought to change in Ca(II) coordination. The shift of the amide NH signals in the anion and in the Ca(II) complex results in a difference between the SO_3^- and CO_2^-. The downfield shift corresponding to the coordination of the Ca(II) ion in SO_3^- is 0.07 ppm, while that in CO_2^- is 1.45 ppm. This indicates that the strength of the NH···O hydrogen bonds in the carboxylate anion (**6**) is much stronger than that in the carboxylate−Ca(II) complex (**7**) and that the strengths of the NH···O hydrogen bond in the sulfonate anion (**2c**) and sulfonate−Ca(II) complex (**1**) do not show a significant difference. The decrease in O atom nucleophilicity for the carboxylate−Ca(II) complex is presumably due to a charge transfer from the coordinated oxygen atom to the Ca(II) ions, while the SO_3^- is a stable anion with strong conjugation and there are few charge-transfer O(−S) oxygens to the Ca(II) ions.

The difference of the Ca−O bond between carboxylate and sulfonate is related to the regulatory properties of NH···O hydrogen bonds. The NH···O hydrogen bonds to the coordinated oxygen atoms prevent Ca−O bonds from dissociation by ligand exchange reactions due to the lowered pK_a value of the ligands and the regulation of the Ca−O bond using NH···O hydrogen bonds was proposed.[22−24] The ^{1}H NMR results for the Ca−carboxylate complex indicate that the NH···O hydrogen bonds can decrease the nucleophilicity on the O atom, which is correlated with the charge transfer from COO^- to Ca(II) ions. In the sulfonate case, the NH···O hydrogen bonds form weakly not only in the sulfonate anion state but also in the sulfonate−Ca(II) complex. There is little difference in strength of hydrogen bonds between the two states. Therefore, the regulation of ionic Ca−O(sulfonate) bond character with the NH···O hydrogen bond is not available due to the strong delocalization on SO_3^- (Figure 7).

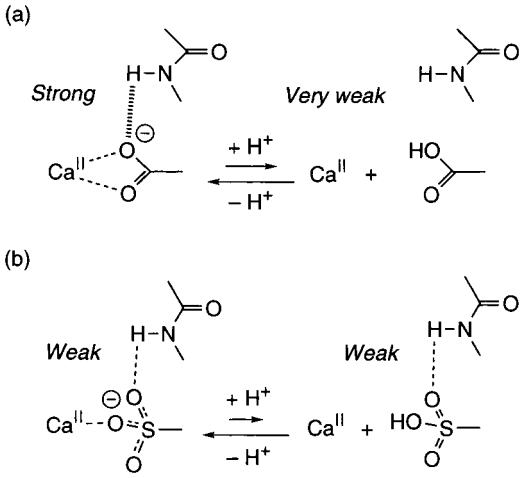


Figure 7. Schematic representation of NH···O hydrogen bond formation (a) in the Ca(II)−carboxylate and carboxylic acid state and (b) Ca(II)−sulfonate and sulfonic acid state.

Conclusion

We have synthesized and structually characterized the NH···O hydrogen-bonded Ca(II)−aryl sulfonate complex with a cationic polymer dimer. The formation of the NH···O hydrogen bonds between the amide NH and S−O oxygen of the sulfonate groups was determined by both IR and ^{1}H NMR analyses both in the solid state and in solution state. A detailed comparison of the formation of the NH···O hydrogen bonds between the sulfonate and carboxylate indicates that only a slight charge transfer is detected from the S−O oxygen to the coordinating Ca(II) ions. The analysis of the NH···O hydrogen bonds with neutral amide groups is a good diagnostic tool for the investigation of the electronic state of the O^- anion.

Acknowledgment. Support of this work by JSPS Fellowships [for A.O.; Grant 2306(1999-2002)] and a Grant-in-Aid for Scientific Research on Priority Areas (10146103) from the Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged.

Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0003067